NTNU – Trondheim
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Oil spill forensics

Identification of sources for oil spills by using data generated by GC-MS and ICP-MS combined with multivariate statistics and the COSIWeb database

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Kristine Vike

ABSTRACT

This work has been a preliminary study, aimed at investigating whether or not trace metal Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis could be a viable tool in the oil spill investigation toolbox, after having been abandoned over 20 years ago. The sample material was two previous oil spills, Full City and Server, and various heavily weathered oil samples gathered from islands off the Trøndelag coast. The islands were Kya, Sula, Vesterkalven, Storkalven, Kunna, and the bay Kjervågsundet on the larger island Frøya. The samples were prepared in a laboratory and analysed by Gas Chromatography-Flame Ionization Detector (GC-FID), Gas Chromatography-Mass Spectrometry-Selective Ion Monitoring (GC-MS-SIM) and ICP-MS.

Through integration of key elements in the oil, also known as biomarkers, by an online database called COSIWeb, the weathered samples were classified as “crude oil”, “non-NS (North Sea) crude oil”, “bunker oil”, “unknown” and “not oil”. This classification was used as a guide to assess the viability of the trace metal analysis done by ICP-MS. The database also provided correlation calculations and five of the weathered bunker oil samples were linked to oils outside the database by “probable match”.

Principal Component Analysis (PCA) was used to investigate the ability each dataset had to classify the different weathered oil types and oil spill samples Full City and Server. Subsequently, Partial Least Squares-Regression (PLS-R) was used to investigate the stability and robustness of both datasets from GC-MS-SIM and ICP-MS together, before Partial Least Squares-Discriminant Analysis (PLS-DA) was applied to investigate if the clusters seen in PCA were significant. By PLS-DA two subgroups of crude oils were identified, possibly related to terrestrial or marine source material in the oil.

Of the 46 weathered samples found on various islands, 14 samples were classified as non-NS crude oils, 9 samples were classified as crude oils, 11 samples were classified as bunker oils, 7 samples were classified as unknown oil samples, and 5 samples were classified as not oil. The last group could be oil-like material such as plastic, rubber, coal or other organic material.

The most important trace metal ratios identified in this study were ratios which have been previously been singled out as important in oil analysis. These were Ni/V, V/S, U/Pb and Mn/Fe. Other ratios were helpful as well, but these were the most influential ones. The Ni/V ratio was able to separate Full City samples from Server samples without any outliers or fuzzy classification.

SAMMENDRAG

Dette arbeidet har vært en preliminær studie med sikte på å undersøke om spormetallanalyse med Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) kan være et interessant verktøy å inkludere i oljesølsundersøkelser, etter at det ble fjernet for over 20 år siden. Prøvematerialet var olje fra to tidligere søl, Full City og Server, og diverse tungt forvitrede olje prøver som ble samlet fra øyer utenfor Trøndelagskysten. Øyene prøvene ble hentet fra var Kya, Sula, Vesterkalven, Storkalven, Kunna og bukten Kjervågsundet på Frøya. Prøvene ble opparbeidet i laboratorium og analysert med Gas Chromatography-Flame Ionization Detector (GC-FID), Gas Cromatography-Mass Spectrometry-Selective Ion Monitoring (GC-MS-SIM) og ICP-MS.

Gjennom integrasjon av nøkkelfaktorer i oljen, kjent som biomarkører, av en internettdatabase kalt COSIWeb, ble de forvitrede oljene klassifisert som “råolje”, “råolje, ikke fra Nordsjøen”, “bunkersolje”, “ukjent” og “ikke olje”. Denne klassifiseringen ble brukt som en ledetråd gjennom undersøkelsene av nytteverdien av spormetallanalyse ved ICP-MS. Databasen sammenlignet også prøvene med alle de andre prøvene i databasen, og returnerte korrelasjonsverdier. Gjennom disse verdiene ble fem av de forvitrede prøvene, klassifisert som bunkersolje, linket til oljer utenfor databasen med klassifiseringen “sannsynlig match”.

Principal Component Analysis (PCA) ble brukt til å undersøke evnen hvert datasett hadde til å klassifisere de forskjellige forvitrede oljetypene og oljesølsprøver fra Full City og Server. Deretter ble Partial Least Squares-Regression (PLS-R) brukt til å undersøke stabiliteten og robusthet når både GC-MS-SIM og ICP-MS datasettene ble kombinert, før Partial Least Squares-Discriminant Analysis (PLS-DA) ble brukt til å undersøke om gruppene sett i PCA var signifikant. Gjennom PLS-DA ble også to undergrupper i råoljene identifisert, som kanskje kan ha sammenheng med terrestrisk eller marint opphav i de forskjellige oljene.

Av de 46 forvitrede prøvene ble 14 klassifisert som råolje, ikke fra Nordsjøen, 9 prøver ble klassifisert som råoljer, 11 prøver ble klassifisert som bunkeroljer, 7 prøver ble klassifisert som ukjent og 5 prøver ble klassifisert som ikke olje. Den siste gruppen kunne være forskjellig oljelignende materiale, slik som plastikk, gummi, kull eller annet organisk materiale.

De viktigste spormetallratioene som ble identifisert i denne studien var ratioer som også tidligere har blitt pekt ut som viktige i andre studier. Disse var Ni/V, V/S, U/Pb og Mn/Fe. Flere andre ratioer var også hjelpsomme, men disse var de mest innflytelsesrike. Ni/V ratioen var i stand til å separere prøvene fra Full City og Server uten avvikere eller usikker/blandet klassifisering.

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LIST OF ACRONYMS

AAS	Atomic Adsorption Spectrometry
AC	Alternate Current
AIA	Adobe Illustrator Action file
BSH	Bundesamt für Seeschifffahrt und Hydrographie
CEN	European Committee for Standardisation
CI	Chemical Ionisation
DC	Direct Current
DCM	Dichloromethane
DR	Diagnostic Ratio
EI	Electrical Ionisation
ESI	ElectroSpray Ionization
FID	Flame Ionization detector
GC	Gas Chromatography
HFO	Heavy Fuel Oil
HREE	Heavy Rare Earth Element
ICP	Inductively Coupled Plasma
LOD	Limit Of Detection
LREE	Light Rare Earth Element
MREE	Medium Rare Earth Element
MS	Mass Spectrometry
MVA	MultiVariate Analysis
M/z	Mass to charge ratio
ND	Non Detectable values
NS	North Sea
NTNU	Norwegian University of Science and Technology
PAH	Polycyclic Aromatic Hydrocarbon
PC	Principal Component
PCA	Principal Component Analysis
PLS	Partial Least Squares
PLS-R	Partial Least Squares-Regression
REE	Rare Earth Elements
RSD	Relative Standard Deviation
RD	Relative Difference
RF	RadioFrequency
SD	Standard Deviation
SIM	Selective Ion monitoring
TLC	Thin Layer Chromatography
UCM	Unresolved Complex Mixture
Wt. %	Mass percentage

1. INTRODUCTION

1.1 OIL SPILLS

Since the 1970s, oil transportation in various forms has played a major role in the world's globalized trade economy. This invariably leads to the risk of oil spills, where measures are taken not just to avoid oil spills as much as possible, but also to make sure proper precautions are in place to reduce the impact should an oil spill occur. Oil spills have an adverse effect on local ecology in the affected area, not only through the oiling of shoreline and wildlife, but also through ingestion of oiled matter and direct toxicity of the oil itself (Couillard, 2002; Peterson et al., 2003; Whitehead et al., 2010; Zabala et al., 2011, among others).

In one sort of oil spill, ships illegally discard their waste oil "sludge" or "bilge" far at sea to avoid paying the fees some ports ask to take care of their oil waste. Several ports now accept waste oil without the fee to remedy this problem. However, as these spills are done far at sea, they mostly dissolve or evaporate before they reach any shore and are practically impossible to trace back to the source.

A second sort of oil spill are the stranded ships and accidents, often releasing large amounts of oil over a short amount of time. These spills can present an immediate threat to local birds and wildlife, persisting in the environment for years after the release, even with a thorough clean-up by the local government and volunteers. Egg and young are especially sensitive to pollution while adult individuals are generally more resilient. This means effects can take several years to show up, as the organisms mature or should have matured. This effect was observed very clearly after the Exxon Valdez spill which occurred on March 24th, 1989 where the herring population suddenly dropped 4 years later (Thorne and Thomas, 2008).

In addition to oil spills made by ships, accidents from oil platforms can also introduce pollution into the marine environment. They are not as common as ship accidents, but can be just as severe if not more so, as observed in the recent Deepwater Horizon disaster on April 20th, 2010 where 11 people died and an estimated 4.9 million barrels ± 10 % of oil was released (Deepwater Horizon Report, 2011). Investigation in this oil spill is still ongoing and after-effects are expected for many years to come.

Although the number of accidents has decreased steadily over the years, the accidents that do occur can be much larger in scale because of the generally larger ships. Today there is a trend that a few large spills are responsible for more than half of the total oil spilled over a decade (Musk, 2012).

1.2 OIL ANALYSIS

Naturally, any legal prosecution after an oil spill should be backed with sound scientific analyses linking the oil spill to the source in question. This is made possible because oil is a complex mixture made up by thousands of unique chemicals of varying concentrations.

For the past decade the revised Nordtest methodology (Faksness et al., 2002) has been the basis for the widely accepted CEN-methodology (CEN, 2012). This method implements Gas Chromatography-Flame Ionization Detector (GC-FID) for initial screening of a large number of samples before analysing a selected group of candidate samples in more detail using Gas Chromatography-Mass Spectrometry-Selective Ion Monitoring (GC-MS-SIM), further explained in chapter 2.7.

Another method which is becoming increasingly common for crude oil and petroleum oil analysis is trace metal analysis by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). This high sensitivity method is increasingly attractive to analysts, routinely detecting sub-part per trillion (ppt) levels (Thomas, 2004). Metal content in crude oil is very low (Dekkers and Daane, 1999), generally much less than 0.1 % which warrants this need for high sensitivity.

As GC-MC and ICP-MS both generate large amounts of data, it is impractical to rely on classical statistical methods which take one variable at a time into consideration. Instead, multivariate statistical analyses (MVA) are utilised to both gain an overview and more in-depth knowledge. Multivariate statistics is a powerful tool which can uncover underlying trends in a dataset, spanning multiple of the variables or samples which are impossible to detect by univariate methods (Swarbrick, 2012; Christensen and Tomasi, 2007).

1.3 PROBLEM DESCRIPTION

The main objective in this thesis has been to investigate the viability of reintroducing ICP-MS into the field of oil spill investigation, from which it was removed over 20 years ago (Faksness et al., 2002). Several labs have already started investigating the possibilities of metal analysis in crude oil by ICP-MS due to its increased sensitivity over the last years (Sánchez et al., 2013; Pereira et al., 2009), but little has been done with regards to oil spill and weathered oils.

1.3.1 THIS THESIS AIMS TO

1. Identify relevant and stable metal ratios which are viable for most oils. Ratios are preferred over raw data as they have a self-normalising effect.

2. Compare the two datasets from GC-FID/GC-MS and ICP-MS by multivariate statistics. Do they reach the same conclusion?

3. Combine the two datasets into one large, dataset and analyse it by multivariate statistics. Is this dataset more, less or equally able to identify different oils compared to GC-FID/GC-MS alone?

2. THEORY

2.1 COMPOSITION OF CRUDE OILS

Crude oil, as extracted from deep within the ground, is a complex mixture of several thousand different types of compounds. It varies widely from district to district, and even from oil well to oil well. Although the most common form of crude oil is the stereotypical black, viscous liquid, oil can be found in a wide range of colours. From thick, heavy black sludge, through a colourful range from brown to red, orange and yellow, all the way up to very light oils with no colour at all.

Image 2. 1 - An example of the wide variety of colour found in fresh crude oils.

Crude oil pockets are most often found within a porous sandstone "sponge" with a dense layer of granite above it, keeping the oil from escaping to the surface due to its lower density. Incidents where the oil did not have a granite, or similar, lid can be seen in the tar sands of Canada. Here, all the light components have evaporated, and the remaining oil is thick, heavy and asphalt-like (Tissot and Welte, 1984).

For oils which have remained sealed before discovery and exploration, a simplified summary of the major groups of compounds and their approximate distribution can be seen in image 2.2.

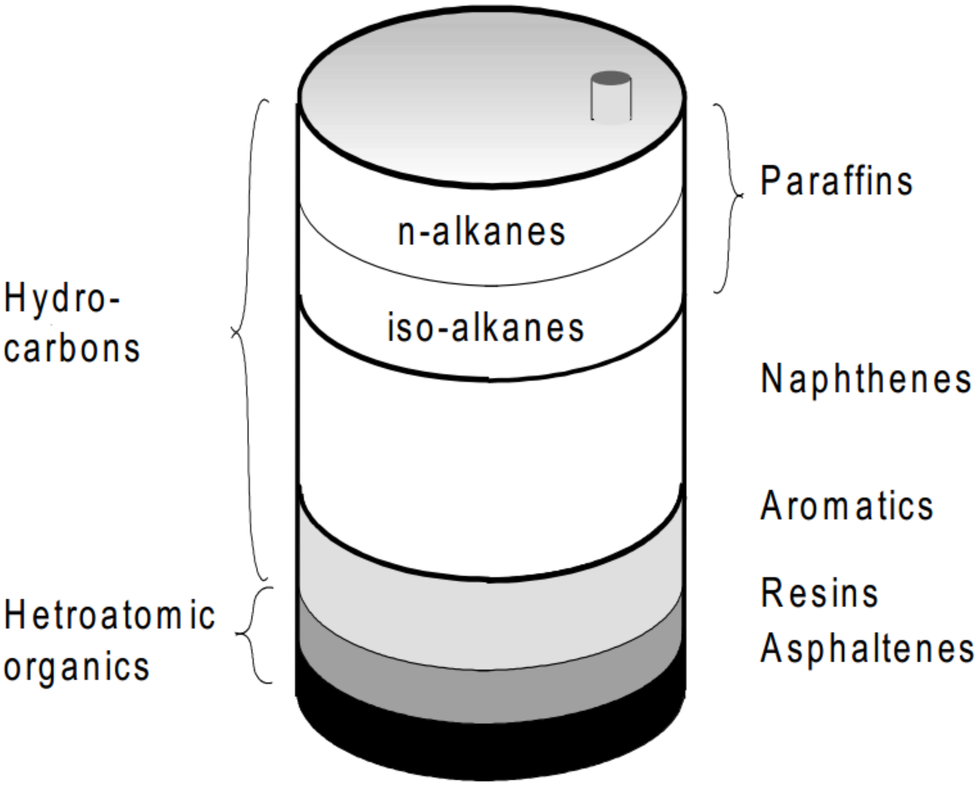


Image 2. 2 - General composition of crude oil, image courtesy of SINTEF Marine Environmental Chemistry.

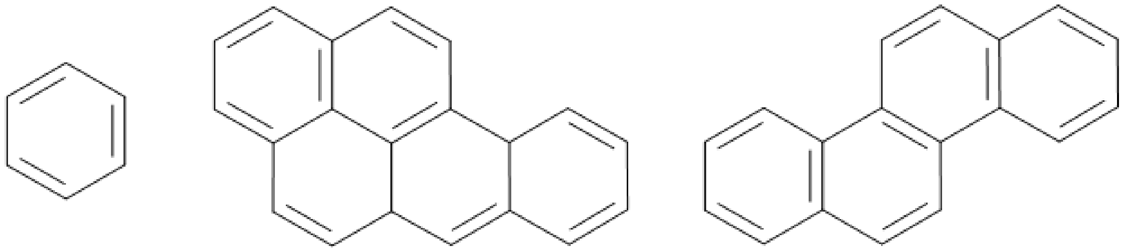
2.1.1 HYDROCARBONS

The majority of components in petroleum oil are hydrocarbons, consisting, on average of carbon (85-90 wt. %) and hydrogen (10-15 wt. %). Thousands of different combinations of straight, cyclic and branched, saturated or unsaturated carbon chains exist, from gaseous methane (CH_4) up to large, complex molecules of more than 100 carbon atoms. Hydrocarbons are divided into aromatics and aliphatics, with aliphatics' two main groups being naphthenes and paraffins (Brandvik and Daling, 2012a).

2.1.2 AROMATICS

The aromatics are, as the name implies, a group of hydrocarbons which consist of unsaturated, aromatic, cyclic molecules. Examples include benzene, benzo(a)pyrene and chrysene. Aromatic compounds are more polar compared to their paraffinic counterparts and will more readily dissolve into the water column in the event of an oil spill (Anderson et al., 1974). Large aromatics are known to persist in the environment for several years (Fuchs et al., 2011) which makes many of them viable biomarkers.

Another property which makes the aromatics worth monitoring is their toxicity. Several aromatics such as Benzo(a)pyrene (image 2.3, middle compound), naphthene, pyrene and anthracene are known carcinogens (Djomo et al., 2004). Another study by Li et al. (2010) found the toxicity of the different aromatic compounds to be strongly linked to their substituents and their ability to penetrate cell walls. Fish eggs and young are especially sensitive and often develop malformations, genetic defects and a generally higher mortality rate even at small concentrations of polycyclic aromatic hydrocarbons (PAH's), a large and highly studied subgroup of aromatic compounds (Carls et al., 1999; Heintz et al., 1999; Couillard, 2002, among others).



Benzene **Benzo(a)pyrene** **Chrysene**

Image 2. 3 - Chemical structure of benzene, benzo(a)pyrene and chrysene, respectively.

2.1.3 PARAFFINS

Paraffins are chains of saturated hydrocarbons, branched or unbranched. Waxes are an important subgroup of paraffins, recognised by their long chains and high melting temperatures. They can precipitate out of oils at low temperatures and as lighter components evaporate. Along with resins and asphaltenes, they are important for the surface properties of oil. The wax content in a crude oil can vary from 0.5 wt. % to 40 wt. % in extreme cases, although the majority of crude oil has a wax content of approximately 2-15 wt. % (Brandvik and Daling, 2012a).

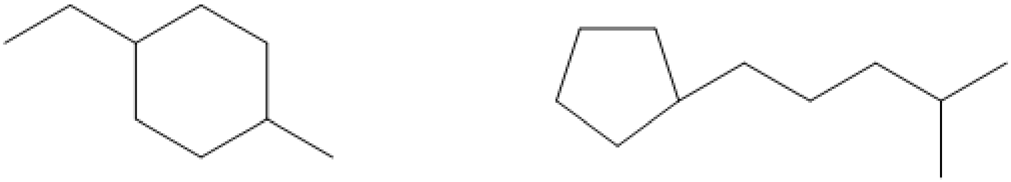
Hexane **2,4-Dimethylhexane**

Image 2. 4 - Two small paraffins, hexane and 2,4-Dimethylhexane.

Waxes are an important subgroup of paraffins, consisting of hydrocarbons with more than 20 carbon atoms. These are often dissolved in fresh oil, but might precipitate during weathering. Waxes play a key role in determining the pour point of oil (chapter 2.2.1.d). Oils with a high wax content will often be difficult to disperse by aid of chemical surfactants, as the solidified wax migrate to the surface and create a protective layer. Most oils have a wax content of 2-15 wt. %, although there have been reports of anything between 0.5-50 wt. % (Brandvik and Daling, 2012a).

2.1.4 NAPHTHENES

Naphthenes are saturated, non-aromatic cyclic hydrocarbons. They may have one or more paraffinic side chains attached and may consist of several rings, although five- and six-ring structures are most common (Brandvik and Daling, 2012a).



1-Ethyl-4-methylcyclohexane **4-Methylpentylcyclopentane**

Image 2. 5 - 2 examples of naphthenes, 1-Ethyl-4-methylcyclohexane and 4-Methylpentylcyclopentane.

2.1.5 NON-HYDROCARBONS

In addition to hydrocarbons, there are also a small fraction of molecules which contains small amounts of sulphur, oxygen, nitrogen and trace metals. These are called non-hydrocarbons, and are commonly characterized in bulk due to separation difficulties (Shi et al., 2010).

The most important sub-group of non-hydrocarbons are resins and asphaltenes. As most non-hydrocarbons are found in the heavy asphaltene fractions, it is not surprising that a higher concentration of resins and asphaltenes usually correlate with higher overall element and metal concentrations (Tissot and Welte, 1984).

2.1.6 RESINS

Resins are medium-large compounds with molecular weight ranging from 700 to 1000. They are often polar relative to hydrocarbons, and contain functional groups such as carboxylic acids, imines and thiols. They often find themselves on the surface of an oil because they are part hydrophilic and part lipophilic.

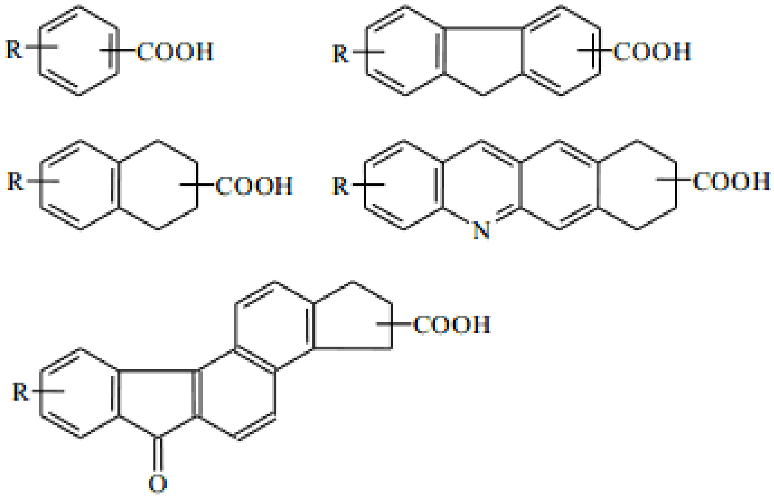
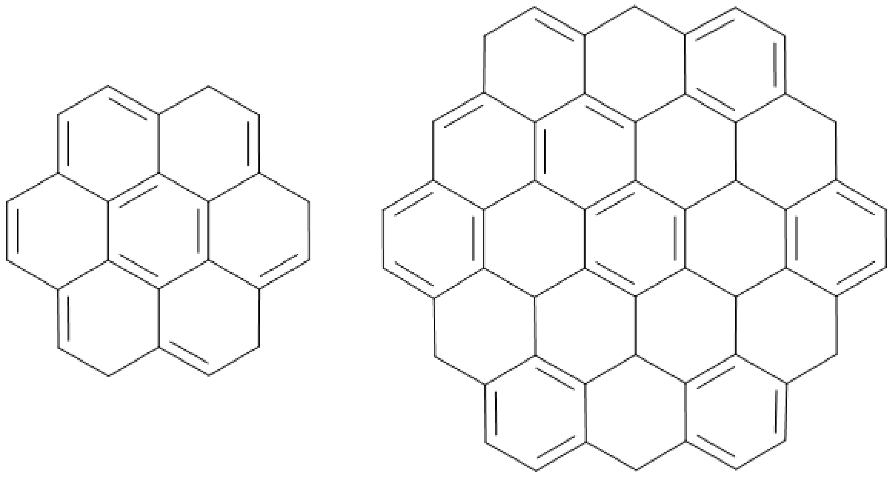


Image 2. 6 - Examples of aromatic carboxylic acids.

2.1.7 ASPHALTENES

Asphaltenes are large, poorly characterised chemical compounds, typically ranging from 6-20 carbon rings and 1000-10 000 in molecular weight (Brandvik and Daling, 2012a). They are difficult to separate and study from each other (Marcano et al., 2011).



Corone **Circicirinene**

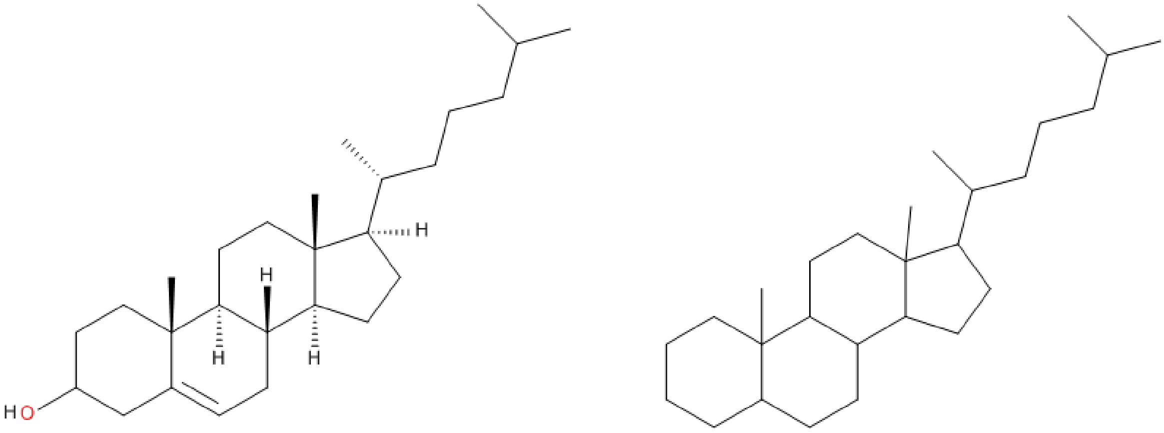
Image 2. 7 - Examples of some simple asphaltenes.

2.1.8 BIOMARKERS

In the world of petroleum oil analysis, biomarkers are ancient organic structures heavily resistant to biodegradation. They have been coined with the term “molecular fossils” as their structures are reminiscent of their biological source, and many of the can give clues to the origin of the biomass which created the oil (Tissot and Welte, 1984; Peters et al., 2005).

One of the most valuable characteristics about biomarkers after their high rate of conservation is that they differ in concentration from source to source, if they are present at all. Even two oil pockets from the same area can often be told apart because their biomarker ratios are unique.

Another factor which influences biomarkers is the refinery process, where certain tell-tale biomarkers are broken down. When it comes to oil spill identification or oil spill fingerprinting, biomarkers are of key importance in ruling out certain sources while matching others. They generally range from several hundred to less than a hundred ppm in concentration, and can be detected at sub-ppm levels. Most of them are found in the heavier fraction of oil, which makes them resilient towards evaporation and weathering, but it also means they are generally lacking from lighter oil products such as gasoline and diesel (Wang and Stout, 2007).



Cholesterol

C27-Cholestane

Image 2. 8 - Structural comparison between cholesterol and the corresponding biomarker cholestane.

Biomarkers are of biological origin, as can be seen in image 2.8. They are generally synthesized by organisms from small terpene building blocks and serve various key functions, for instance as enzymes, lignin, lipid membranes, sterols or chlorophyll. There are few pathways to break them down again once they have been formed and they are thermally stable. As seen in the example above (image 2.8), the only difference between cholesterol and cholestane is the overall reduction of the molecule. Detailed descriptions of the various biomarkers found in this study can be found in Faksness et al. (2002); Ekweozor and Udo (1988); Wang and Stout (2007); Sinninghe Damsté et al. (1995); Bastow et al. (1999); Peters et al. (2005). A simple example showing how one m/z chromatogram may separate two oils can be seen in image 2.9.

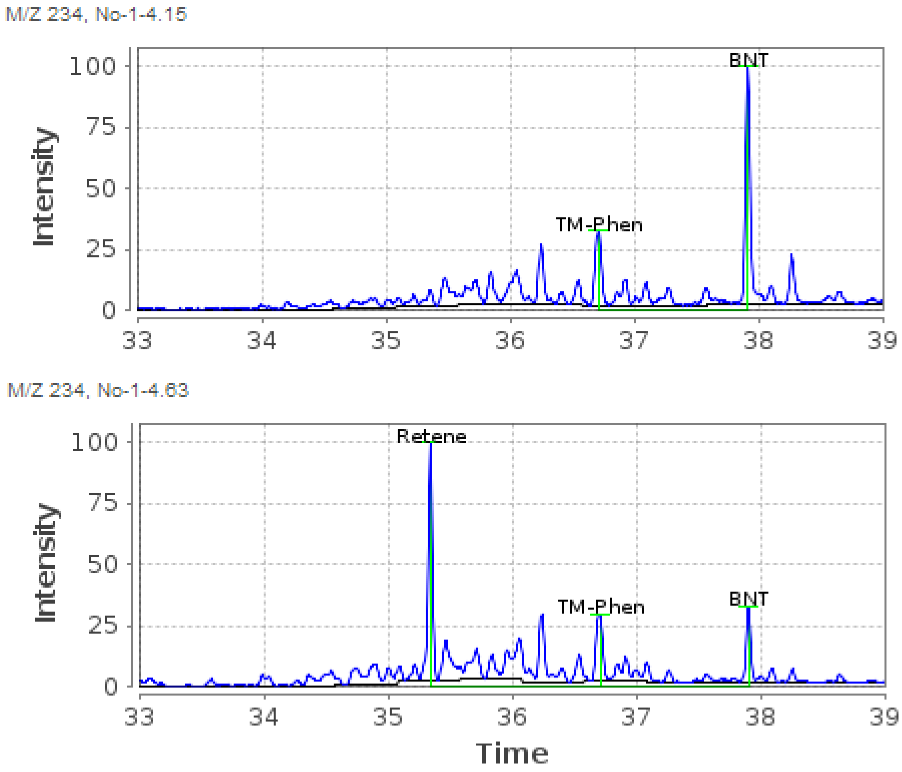


Image 2. 9 - Example showing how the biomarker retene is missing from the first chromatogram, but present in the second, making it easy to conclude that these two oils are different.

Although quantitative analysis of biomarkers can provide valuable information, it is often time-consuming. The most common way to present biomarkers is through diagnostic ratios (DR), which are calculated by dividing one biomarker by another, more weathering resistant, biomarker, as seen in equation 2.1 below. All ratios and abbreviations thereof used in this study can be found in Appendix C.

$$DR = \frac{A}{A+B} * 100 \tag{2.1}$$

Where DR is the diagnostic ratio, A is the height or area of the biomarker in question and B is the height or area of another, more weathering resistant biomarker, typically found in the same mass to charge (m/z) chromatogram which helps with the robustness of the ratios (Faksness et al., 2002). Ratios are also valuable, because small shifts in the instrument might broaden or narrow peaks slightly, but using ratios means this is not a problem.

2.1.9 METALS

Metal content in crude oils is low. Generally less than 1 % (Dreyfus et al., 2005), which makes any result susceptible to both contamination and limit of detection (LOD) issues. Metal concentrations often correlate with sulphur concentration, which in turn is related to highly reducing, marine depositional environment. Thus oils with significant terrestrial input will display low metal contents (Barwise, 1990). Other factors reducing the metal content of a crude oil include maturity and migration of the oil field (Greibrokk et al., 1994).

One study by Dekkers and Daane (1999) found that cadmium, zinc and copper levels in crude oils are mainly a product of the manufacture and handling of the oil. This is a good reminder that inside information about what is being analysed is key to a reliable result.

Important subgroups in this study are metal bearing molecules of biological origin. These are expected to be mostly among the resins. Relatives of haemoglobin and chlorophyll are important in binding metals like vanadium and nickel. Copper and iron has also been reported, but in much smaller concentrations (Tissot and Welte, 1984). Methods are emerging to separate and study these metal bearing structures (Mokhtari and Pourabdollah, 2012).

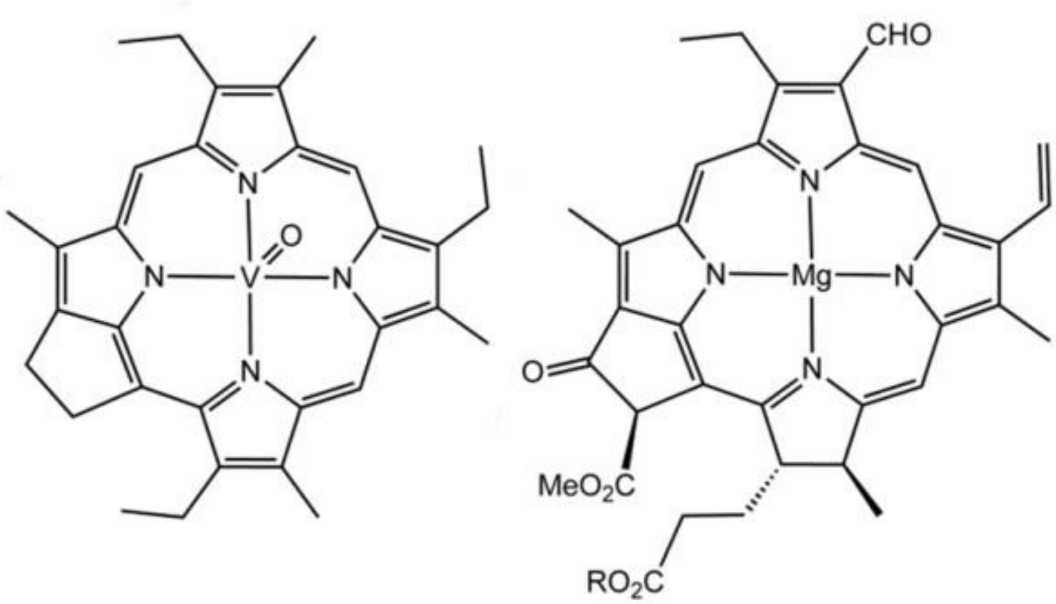


Image 2. 10 - Examples of porphyrin structures containing vanadium (left, found in oil) and manganese (right, found in chlorophyll).

Metals may also be suspended in the oil matrix as inorganic salts (mainly as chloride and sulphates of potassium, magnesium, sodium and calcium, Pereira et al., 2010), various mineral particles and introduced into the oil during processing, for instance from drilling liquid, pipelines, tanks and during refinery processes (Sánchez et al., 2013).

2.1.9.a Nickel and Vanadium

The most common metals found in petroleum oil are nickel and vanadium. These metals exists largely in complex forms with porphyrin derivatives (image 2.10), which are liable at higher temperatures (350 ˚C+). Vanadium is the more stable of the two and generally display higher concentrations compared to nickel. Exceptions have been observed in low-sulphur oils with nickel more frequently prevalent over vanadium (Tissot and Welte, 1984). Although the metals are susceptible to migration, thermal alterations, biodegradation or water washing, the ratio between nickel and vanadium itself has proven remarkably stable (Lewan, 1984) and is considered one of the most promising and easily measured ratios among possible metal biomarkers (Faksness et al., 2002).

Non-marine oils generally show low sulphur and very low metal concentrations, while marine carbonates or siliciclastics generally show moderate to high sulphur and high concentrations of nickel and vanadium, with low nickel/vanadium ratios (< 1) (Peters et al., 2005). This is thought to be attributed to how vanadium is reduced and immobilized in highly anoxic sediments, while nickel is stabilized in solution by the high sulphide concentrations (Calvert and Pedersen, 1993).

Recent studies presented by Galarraga et al. (2008) have linked the vanadium/nickel ratio to geological origin and biogenic source. This presents another potential tool in the fingerprinting toolbox of fresh crudes.

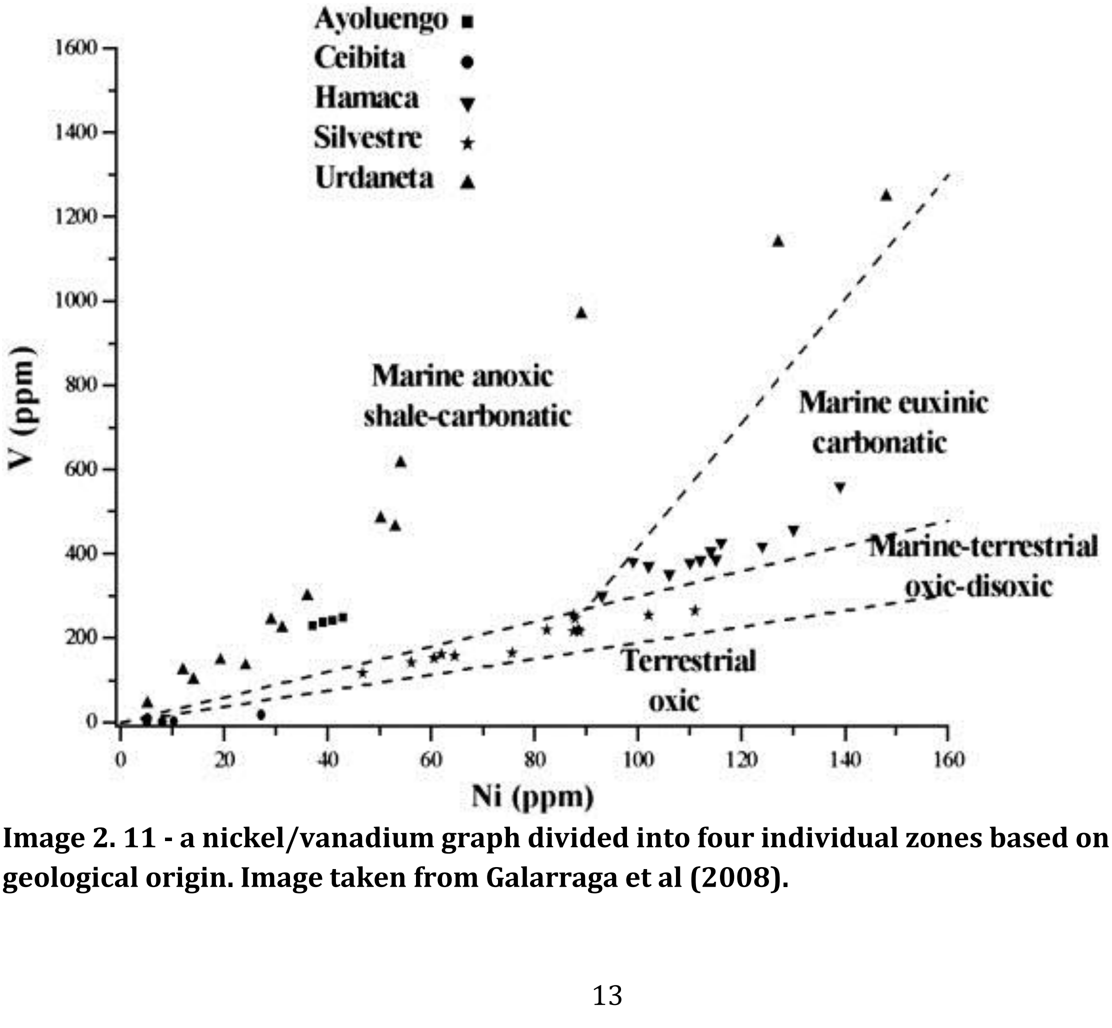


Image 2. 11 - a nickel/vanadium graph divided into four individual zones based on their geological origin. Image taken from Galarraga et al (2008).

2.1.9.b Lead isotopes

Lead is a valuable and well-known metal when it comes to identifying geochemical age in different minerals. After the introduction of uranium and the nuclear age, identifying the isotopic ratio is key to defining whether samples are naturally high in lead or if it is due to modern pollution. Although crude oils generally show very low levels of lead, it has the power to poison catalysts during refinery, and several methods have been developed for their analysis (Al-Swaidan, 1996; Hammond et al., 1998; Kowalewska et al., 1999; Dreyfus et al., 2008; Caumette et al., 2009; Damin et al., 2009, among others).

Once lead is being detected reasonably above the LOD for any specific technique, there are several interesting things which can be learned from its isotopic constitution. Three radiogenic isotopes; ^{238}U, ^{235}U and ^{232}Th decay into ^{206}Pb, ^{207}Pb and ^{208}Pb, respectively, through numerous daughter isotopes, where no daughter isotope occur in more than one decay chain. $^{238}\text{U} \rightarrow {}^{206}\text{Pb}$, for instance, has 18 unique daughter isotopes, while $^{232}\text{Th} \rightarrow {}^{208}\text{Pb}$ has only 10. Equation (2.2) illustrates the particles generated in one of the processes and the relative timespan involved. Specific details about the daughter isotopes and historical significance is illustrated in more detail in Shoene (2013).

$$^{238}U \rightarrow \ ^{206}Pb + 8\alpha + 6\beta^- + Q;\ \lambda_{238} = 1.55125e^{-10}year^{\ -1} \tag{2.2}$$

Where α is an alpha particle, β^- is a beta particle, Q is the energy released during decay and λ is the decay constant.

These three independent systems can then be summarized into three isochron equations, which allow for cross-validation and illustrates the intrinsic uncertainty of the method. The three isochron equations are as follows:

$$\left(\frac{^{206}Pb}{^{204}Pb}\right) = \left(\frac{^{206}Pb}{^{204}Pb}\right)_0 + \left(\frac{^{238}U}{^{204}Pb}\right)\left(e^{\lambda_{238}t} - 1\right) \tag{2.3}$$

$$\left(\frac{^{207}Pb}{^{204}Pb}\right) = \left(\frac{^{207}Pb}{^{204}Pb}\right)_0 + \left(\frac{^{235}U}{^{204}Pb}\right)\left(e^{\lambda_{235}t} - 1\right) \tag{2.4}$$

$$\left(\frac{^{208}Pb}{^{204}Pb}\right) = \left(\frac{^{208}Pb}{^{204}Pb}\right)_0 + \left(\frac{^{232}Th}{^{204}Pb}\right)\left(e^{\lambda_{232}t} - 1\right) \tag{2.5}$$

Where the subscript 0 follows the ratio of the isotopic composition of lead when the system is closed (e.g., crystallization of a mineral), t is the time since the system closed and λ238, λ235, and λ232 are the decay constants of ^{238}U, ^{235}U, and ^{232}Th.

^{204}Pb is used for normalisation, as it is it the only non-radiogenic isotope of lead. Normalisation brings the advantage of removing uncertainty associated with calculated moles. That is, it is easier to measure precisely the ratio ^{207}Pb/^{204}Pb, for instance, compared to measuring the concentration of ^{207}Pb alone (Shoene, 2013).

If, however, the contribution of non-radiogenic lead is considered negligible compared to radiogenic lead, the equations can be simplified to:

$$\left(\frac{^{206}Pb^*}{^{235}U}\right) = (e^{\lambda_{238}t} - 1) \tag{2.6}$$

$$\left(\frac{^{207}Pb^*}{^{235}U}\right) = (e^{\lambda_{235}t} - 1) \tag{2.7}$$

$$\left(\frac{^{208}Pb^*}{^{232}Th}\right) = (e^{\lambda_{232}t} - 1) \tag{2.8}$$

Where * indicates radiogenic material.

In image 2.12, half-lives and time span for a perfectly closed system is presented.

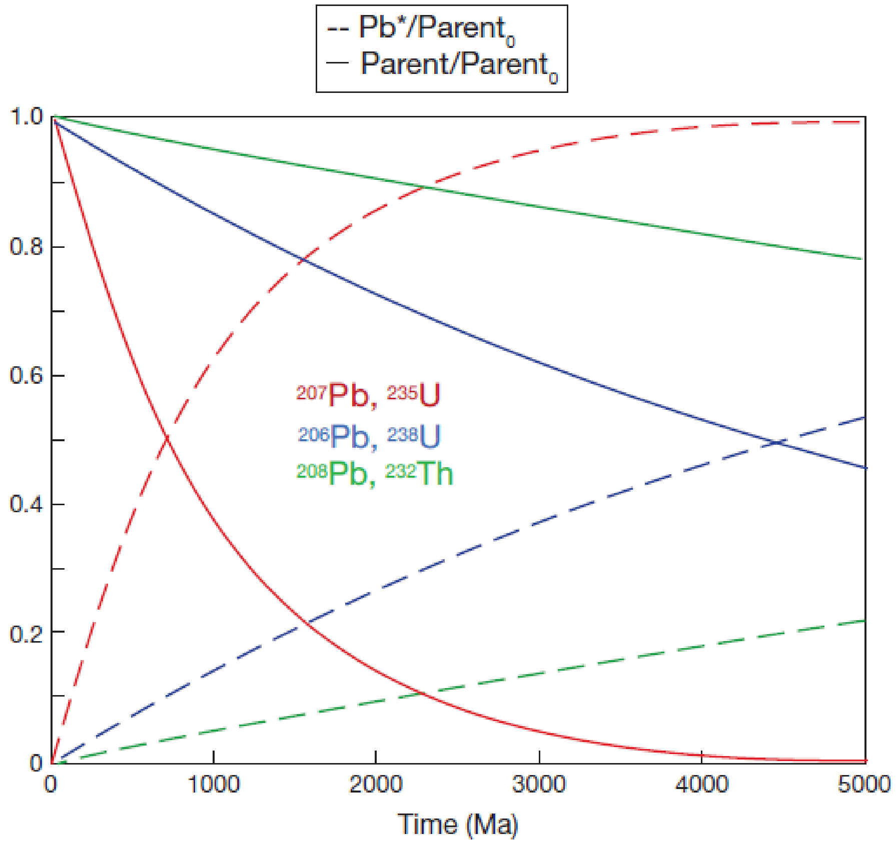


Image 2. 12 - Illustration of the different half-lives of ^{232}Th, ^{238}U, and ^{235}U through decay of the parent isotope and in growth of the daughter. Curves are color-coded by decay system. Image courtesy of Shoene (2013).

When it comes to using lead to pinpoint geochemical age, however, these techniques cannot confidently be used for anything except fresh crude oil samples. Several criteria must be fulfilled for successful analysis of geochemical age. One of those criteria is that the mineral must have remained closed to uranium, thorium and lead and all intermediate daughters throughout its history (Shoene, 2013). This not the case for the oil samples which have been drifting at sea for several years. Lead had become a very ubiquitous pollutant, most commonly spread by exhaust fumes from leaded gasoline, which is still sold in several countries. Thus lead can be used as an identifier only, not a measure of the age of the reservoir.

2.1.9.c Rare Earth Elements

The rare earth elements (REE's) commonly include the 15 lanthanide elements as seen in table 2.1.

Table 2.1 - Summary of the REE's and their atomic number.

Element	Abbreviation	Atomic number
Lanthanum	La	57
Cerium	Ce	58
Praseodymium	Pr	59
Neodymium	Nd	60
Promethium	Pm	61
Samarium	Sm	62
Europium	Eu	63
Gadolinium	Gd	64
Terbium	Tb	65
Dysprosium	Dy	66
Holmium	Ho	67
Erbium	Er	68
Thulium	Tm	69
Ytterbium	Yb	70
Lutetium	Lu	71
Yttrium	Y	39

Although initially difficult to isolate and study by 18th and 19th century scientists, REE's are gaining more and more widespread use today, especially in electronics and engineering. Despite their name, they are actually quite ubiquitous in the earth's crust, and are found in varying concentrations all over the world. Comparisons with chondritic (stony) meteorites, unaltered by activity on earth, provide valuable insight in relative enrichment or depletion of REE's in various materials (Castor and Hedrick, 2006).

As there are different chondritic meteorites, different measuring methods and different result within the chondritic meteorites, discussions persist about the best way to normalise anything against chondrites. The three different methods debated are averages, individual analyses, or grinding several chondrites into a standardised mixture, similar to any reference material. Although these are important discussions, it has been concluded that the within-chondrite variation is only relevant when comparing different chondrites. REE patterns in highly evolved materials would still show distinct differences (Evensen et al., 1978).

One of the first studies on REE's in crude oil was done by Li et al (1998). Recoveries in the study were found to be; 99.8 % - 107.7 %, with a relative standard deviation (RSD) of 4.36 % - 16.53 %. The method was successfully applied to various different Chinese crude oils.

Another novel study specifically on REE's in crude oils was posted as late as in 2007 (Akinlua et al., 2007). In this study of oils from the Niger Delta, light REE's (lanthanum through europium) were found in all samples, but heavy REE's (gadolinium through lutetium plus yttrium, due to chemical and physical similarities) were not found in offshore samples. Through chondrite normalisation (Castor and Hedrick, 2006), they were able to classify crude oils based on REE's.

Another recent study from Zhang et al. (2009) found that medium REE's (MREE's, neodymium through holmium) with an even number of f-electrons and HREE's were enhanced in some areas of the Dongying depression in eastern China. This was attributed to mantle derived fluids and possibly also due to how MREE's and HREE's show stronger affinity to organic matter than LREE's do.

REE's are also used as an additive and a catalyst during the oil refinery process. Thus is might be interesting to investigate levels of various REE's in weathered oils. Large spikes compared to chondrite might indicate that the oil has been through a refinery (Castor and Hedrick, 2006), while small fluctuations might provide a potential as an identifying factor (Akinlua et al., 2007).

2.1.9.d Other metals

Other metals or interest are expected to be found in much smaller concentrations compared to nickel and vanadium. Two of the main metal contaminations in crude oil is silicon and aluminium which originate from suspended clay particles (Zhang et al., 2009).Trace metal analysis in oil is gaining popularity, and several studies and different methods have been published on the subject (Duyck et al., 2002; Mónaco et al., 2002; Gondal et al., 2006; Aucélio et al., 2007; Duyck et al., 2007; Pereira et al., 2010, Mello et al., 2012, among others).

An overview of the most common metals in oils and their origin can be found in table 2.2, adapted from Sánchez et al (2013) and references therein. Other elements of interest could be any “binary” element which might provide information, simply by being present or not.

Table 2.2 -Summary of the origin of the presence of metals and metalloids in petroleum products and derivates. Table adapted from Sánchez et al. (2013) and references therein.

Origin	Element
Added as additive or catalyst	Al, As, B, Ba, Ca, Co, Cr, Mg, Mn, Mo, Ni, P, Sn, Si, V, Zn
Contamination by contact with drilling mud or seawater during extraction process	Ca, K, Mg, Na
Contamination during refining process	Al, As, Ba, Cr, Cu, Fe, Mn, Ni, Pb, Se, Zn
Natural	As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Si, Sn, Sr, V, Zn

2.2 CHARACTERISTICS AND WEATHERING OF SEABORNE OIL SPILLS

There are several effects taking place when an oil spill occurs at sea, commonly known as weathering. The main factors influencing the behaviour and weathering of the oil is chemical composition, weather (temperature, wind, waves, sunlight) and water properties (bacteria, temperature, salinity, oxygen, density, currents, nutrients, particles). The main effects to take place directly after an oil spill are evaporation of light components, drift due to currents, formation of the oil slick and mechanical mixing into the water column by wave action, dissolving the water soluble particles (Brandvik and Daling, 2012b).

Prolonged weathering has been shown to affect certain biomarkers, such as phenanthrenes, after more than 2-3 months weathering (Brakstad and Grahl-Nielsen, 1988), and should be taken into consideration. A study by Dutta and Harayama (2000) found that crude oil can be expected to degrade in the following order: N-alkane > naphthalenes > branched alkanes > fluorenes > phenanthrenes > dibenzothiophenes, which invites caution in the handling of highly weathered material.

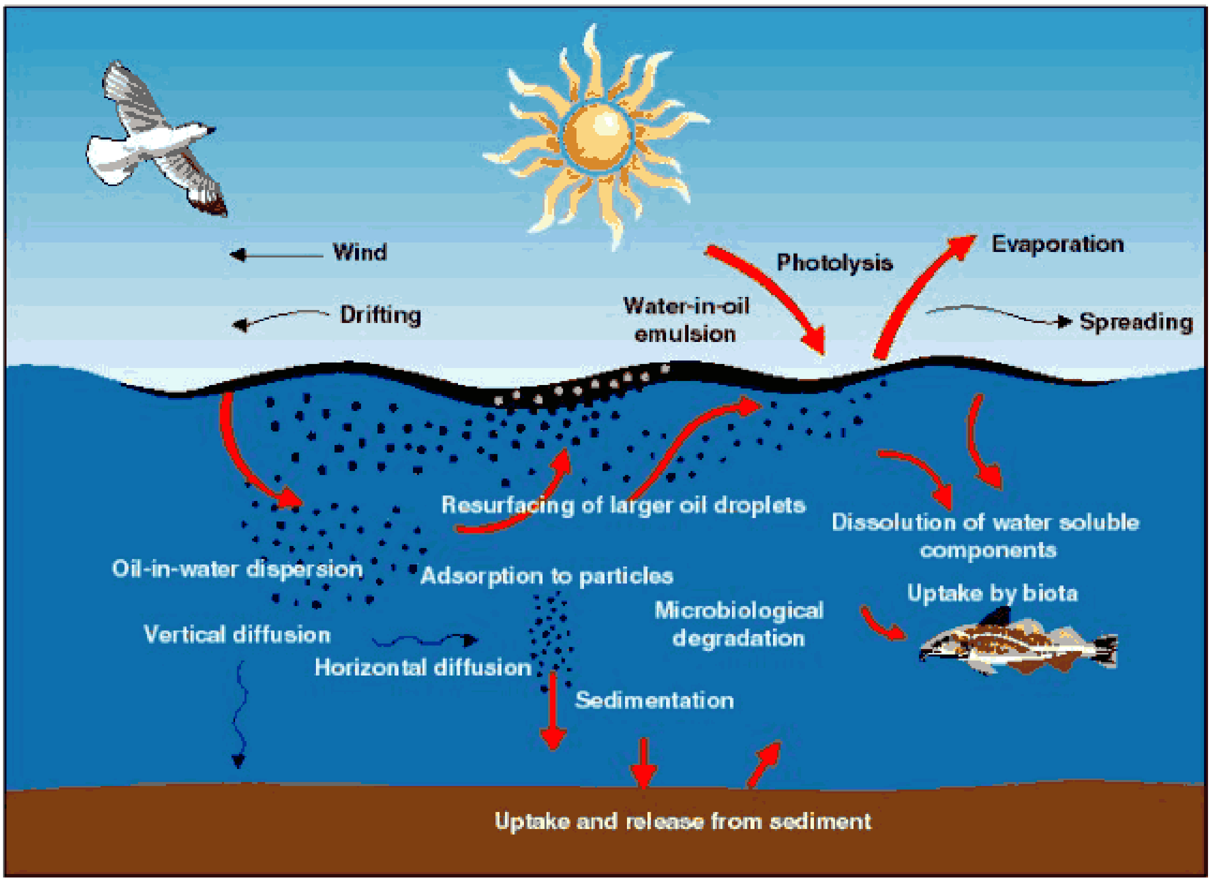


Image 2. 13 - Weathering processes taking place in a marine oil spill, image courtesy of SINTEF Marine Environmental Chemistry.

2.2.1 EVAPORATION

One of the first and most influential events to occur after or during and oil spill, is evaporation. Within less than a week most components with a boiling point below 270 ˚C will have evaporated (Brandvik and Daling, 2012b). Wind aids evaporation by removing gas and vapour, driving the equilibrium towards more evaporation.

Unless an oil spill is completely removed by evaporation after a couple of days, its properties can be greatly altered. Density has been seen to rise by 10 %, the flash point by 400 %, and the viscosity by as much as a thousand fold after only about 40 % of an oil has evaporated (Fingas, 2013).

If the weather is particularly still or the oil has been deposited onto rocks or the shore, evaporation can be greatly inhibited by formation of crust or "skin". This occurs when the lighter components on the surface of the oil evaporates, leaving the heavier components to cluster together. Such grouping of heavy components on the surface of the oil will act as a lid to retain lighter components inside the oil, potentially forming highly stable tar balls (Fingas, 2013).

2.2.1.a Density

The density of an oil affects how it is distributed as an oil slick, how it dissolves into the water column and is taken up by, or affecting, biota. For a few, specific, kinds of oil, enough evaporation of light components can push the density past that of seawater, brackish or freshwater, causing the oil to sink (sedimentation).

Sedimentation may cause adverse effects when the oil cover up the sea-bottom, interact with biota and vegetation and is very difficult to detect or clean up (Morales-Castelles et al., 2006). However, as long as the oil is only sedimented in small quantities, a large study has shown their toxicity is rapidly lost through weathering (Page et al., 2002). Sedimentation may also occur along shallow shorelines as a result of the oil taking up, or adhering to, sediment particles, pulling it down. Once on the bottom, the oil may be covered by another layer of sediment which stalls weathering.

2.2.1.b Flash point

The flash point of oil is a measure of the danger to the workers around an oil spill. It is a conservative laboratory feature, but still useful. It is a measure of when the oil has evaporated enough volatile components to explode by a spark. In the lab this is done in a sealed chamber or "bomb". Luckily, the volatile components are often carried away and diluted rapidly in real scenarios with low temperatures and a reasonable breeze present. Still, this is important to keep in mind, and for oils with a flash point below 60oC, specific vessels are required for storage. The flash point of oil will increase with evaporation (Brandvik and Daling, 2012b).

2.2.1.c Viscosity

Viscosity has been defined as a liquid's "resistance to flow". This is most commonly measured in the unit centipoise (cP). Thick, syrupy solutions like honey or mayonnaise have high viscosity, while thin, free-flowing liquids like water have low viscosity. The viscosity of oil will increase as the light components evaporate, or the oil takes up water (Fingas, 2013).

2.2.1.d Pour point

Pour point is related to, but different from, viscosity. It is chiefly affected by the wax content of the oil, as wax precipitation is largely responsible for deciding the pour point of oil. In practice, the oil is heated up to 50oC and then left to slowly cool down, which causes wax crystals to precipitate. For every 3 ˚C an attempt is made to "pour" the oil by tilting the container. Once the oil will no longer flow from this outside intervention, the pour point has been reached. As waxes are heavy, and do not suffer notably from evaporation, their concentration will increase as lighter components evaporate, leading to a higher pour point over time (Brandvik and Daling, 2012b).

2.2.2 EMULSIONS

Definition of emulsion from the Merriam Webster Dictionary:

> *A system (as fat in milk) consisting of a liquid dispersed with or without an emulsifier in an immiscible liquid usually in droplets of larger than colloidal size.*

An emulsion can be stable or unstable. For an emulsion to be stable, the dispersed droplets have to be small enough such that the surface tension from the surrounding, immiscible liquid has greater impact than gravity or buoyancy. Stable water-in-oil (w/o) emulsions are often referred to as "mousse", can easily double or triple the volume of spilled oil, even after evaporation, and display different characteristics from the original spilled oil. Unstable emulsions are more often referred to as water uptake. The major properties of oil which affects emulsification is viscosity and surface active components in the oil.

After evaporation, formation of emulsions is the second, large process to affect an oil after it has been spilled at sea, and it has a great impact on the properties of the oil (Nordvik, 1995). Notably the viscosity increases a great deal. Free flowing oil can turn solid upon emulsification. Solid emulsions are harder to evaporate, do not succumb rapidly to biodegradation, and cannot be removed by in-situ burning. They can remain stable for years at a time, and are harder to clean up (Fingas, 2013). Disposal is also a problem, as a mousse cannot readily be utilised by a refinery because of the high water content. High temperatures can break emulsions, but demand huge amounts of energy. Another option is to add chemicals to the oil which breaks up the emulsion and reduces the water content (Bridié et al., 1980).

Oil in Water (o/w) emulsions also exists, but because the volume of water is enormous compared to the volume of oil, this is more often known as dispersion.

2.2.3 DISSOLUTION

In general, small and/or polar molecules are the most prone to dissolution, such as small aromatics (benzene, toluene). However, evaporation is usually 10-100 times faster than dissolution which leads dissolution to only play a minor role in the removal of oil from the water surface. A more dispersed oil will demonstrate a higher rate of dissolution (Brandvik and Daling, 2012).

2.2.4 DISPERSION

Dispersion is the act of breaking an oil slick into smaller droplets. This is most commonly caused by wave action, but artificial addition of chemicals known as "surfactants" can also aid in this process. Dispersion is generally desired in cases where the volume of water is much, much larger than the volume of oil, like with an open sea spill. If the wave action is energetic enough and the oil is of the right type, it might eventually be broken into droplets so small that they will be pushed further down by the waves, long before they resurface, efficiently removing the oil from the surface. This will lead to less damage to shorelines, sea birds or otters on the surface of the sea, but might cause harm to fish eggs and reproduction if the water is too shallow (Fingas, 2013).

These smaller droplets lead to a greatly enlarged sum surface area of the oil, which in turn make them a lot more available to bacteria for biodegradation. Natural dispersion is generally more efficient for lighter oil types.

2.2.5 PHOTOLYSIS

Photolysis or photooxidation is caused by sunlight working on the surface of the oil. All components, but especially aromatics, are prone to oxidation by this method. The oxidised molecules often display different surface characteristics, stabilising water in oil emulsions and prolong the lifetime of an oil slick on the surface. Over time, the oxidised molecules can react with each other, creating heavy resins and asphaltenes. Long term weathering at sea can cause the formation of tar-balls; small, hard lumps with relatively high concentrations of resins and asphaltenes on the surface. When tar-balls have been formed, they have proven very resilient to most any types of further weathering. Some oils are more susceptible to photolysis than others, although it is not fully understood. It is not a major contributor to the net fate or behaviour of an oil spill (Fingas, 2013).

Under Arctic conditions though, things might be a little different. A study done by Sydnes et al. (1985), found that evaporation was only the major means of removal from October to February, the darkest months of the year. The rest of the year was dominated by oxidation from the sun and increased dissolution to the water column with increased toxicity to marine life. Photolysis might play a bigger role regarding the toxicity of oil spills than is yet fully understood.

2.2.6 BIODEGRADATION

Oil, as with most constituents in nature, can be utilised as an energy source and broken down (biodegraded) by various bacteria, fungi or yeast, given enough time. When exposed to an oil spill, microorganisms which are already present bloom in response to the sudden influx of fuel. With the addition of nutrients like nitrogen, phosphorous and potassium, these microorganisms have proven efficient in cleaning up oil spills, especially in hard to reach and sensitive areas (Nikopolou and Kalogerakis, 2008; Atlas and Hazen, 2011).

All components in oil, except asphaltenes, can be broken down by different by specified microorganisms. Straight-chained hydrocarbons are the easiest to break down and this process is usually faster in warmer weather, although there are bacteria which work better at low temperatures. For the aromatic group, small, water soluble molecules are usually broken down before the larger, lipid soluble molecules (Bastow et al., 1999).

Biodegradation takes place in the interface between oil and the environment (e.g. sea water), which is why dispersants may aid in the biodegradation of oil by drastically increasing the available surface area. Degraded products are usually oxidized, which may lead to further degradation, dissolution, accumulation in the remaining oil or higher toxicity compared to the parent compound (Fingas, 2013).

Biodegradation is not a fast pathway for the removal of oil after an oil spill. It demands significant amount of oxygen, nitrogen and phosphorous. As phosphorous reserves are diminishing (Cordell et al., 2009, among others), oil should first be cleaned up traditionally by skimmers and manual labour, before the remnants may be fertilized for faster degradation.

2.3 TWO RECENT OIL SPILLS IN NORWEGIAN WATERS

Prior to this study, the confounding effects weathering would have on the metal ratios in oil had not, to the author's knowledge, been investigated. For this reason, it was necessary to include some samples which had sustained some weathering, but where the source was known. The cases chosen were two incidents from within Norwegian shorelines; the cargo ship MS Server, and cargo carrier MV Full City, presented briefly in this chapter.

2.3.1 MS SERVER

Friday 12th of January 2007, the Cypriot cargo ship MS "Server" ran aground close to Fedje in Hordaland, Norway at 18.30, local time. The ship had 585 cubic tons of heavy oil and 72 tons of diesel when it grounded. The weather was rough, with a stiff wind from southwest (15-16 m/s) and waves as tall as seven meters (Melbye et al., 2008). After rescuing the crew, the ship broke in half where the largest oil tank was located, spilling its content into the surrounding sea. This tank contained about 290 cubic tons heavy oil. As this was heavy fuel oil, dispersion and dissolution did not occur to any major degree and long areas of coastline were oiled overnight.

In response to the accident, SINTEF performed a data simulation of the most likely way the oil might spread, taking into account the weather forecasts, ocean currents, oil type and other relevant factors. This can be seen in image 2.14.

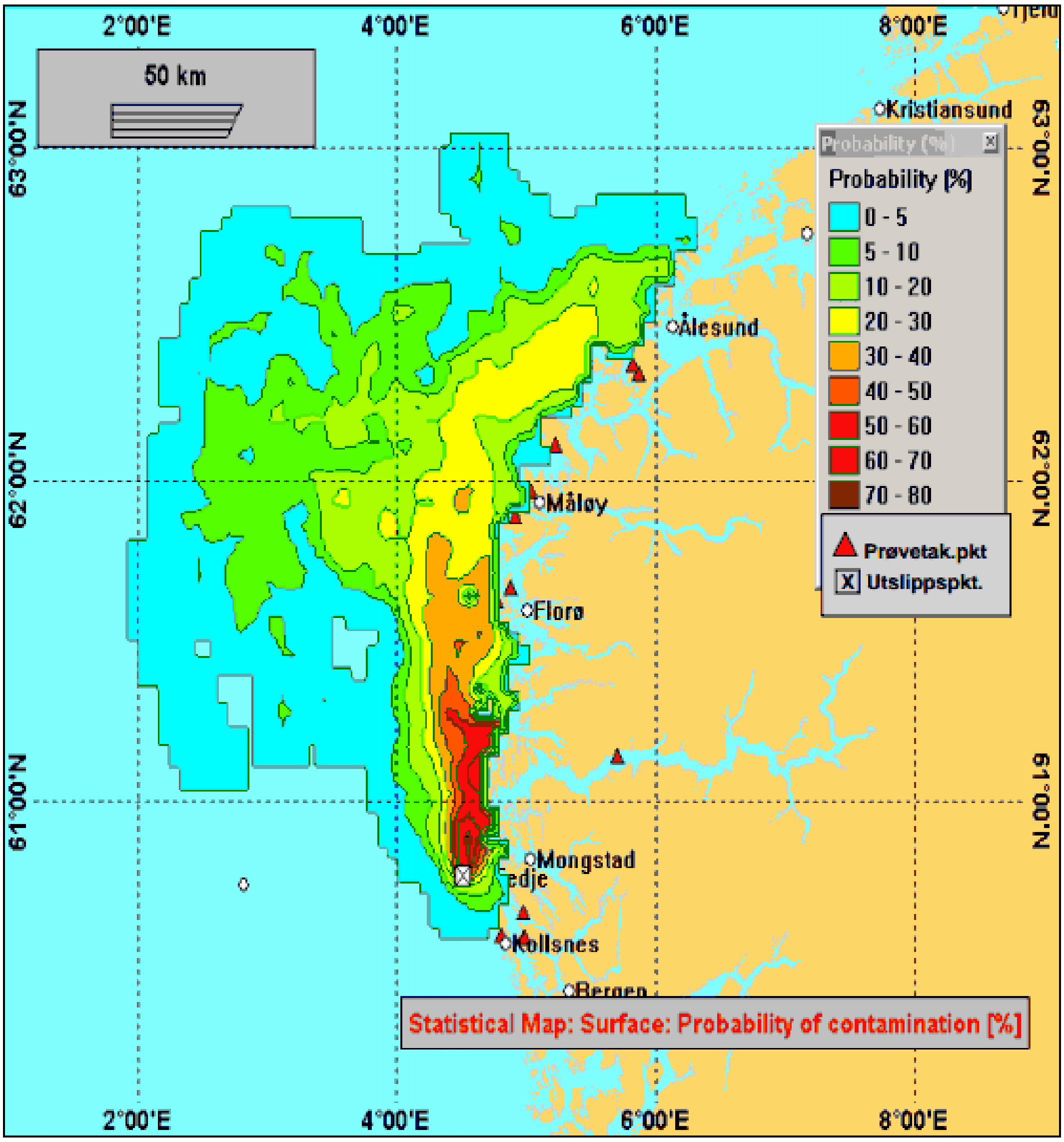


Image 2. 14 - 25 day model for probable contamination after the Server-accident using meteorological data. X marks the wreckage and triangles mark sampling spots for the SINTEF report (Almås et al., 2007).

After the spill, SINTEF received 45 different samples from and around the wreckage. Oil spill fingerprinting was performed on a selected number of these samples according to the CEN standard: Oil Spill Identification (CEN, 2012) to assess and confirm the extent of the spill.

2.3.2 MV FULL CITY

Friday 31st of July at 00.23, local time, Panama flagged bulk cargo carrier, MV Full City grounded close to the town of Langesund in Telemark. The ship was carrying 1000 cubic meters heavy oil (type IFO 180) and 120 tons light oil at the time of the accident (Kystverket, 2011).

Image 2. 15 - The oil carrier, MV Full City. Image courtesy of Kystverket.

SINTEF received 58 samples from The Norwegian Coastal Administration and another 67 samples from Bamble police station. This accident in particular is very relevant for multivariate statistical tools, as no single reference sample from the different tanks could be used. Oil spill identification analysis (CEN, 2012), showed that all oil outside the ship were mixtures of different oil sources. Furthermore, the concentration of the various sources differed between sampling points, making Full City a complex spill analytically. Instead of using references from the ship tanks, it was decided to use nearby sampling points which were so close that a match was undisputable (Faksness, 2009).

2.4 WITHERED SAMPLES

Included in this study are a substantial number of heavily withered samples. These samples have been deposited onto rocky shores during high seas. They have become, or are close to, tar-balls and can melt onto the rock on a sunny day where they might stay indefinitely. Any volatile content has long since evaporated from the surface and any water soluble fraction long since dissolved. They are expected to contain mainly asphaltenes and resins, little or no straight hydrocarbons, and most of the lighter biomarkers will be gone or be unreliable.

As these samples are not collected in relation to any known oil spill nearby, it is reasonable to assume that they are either a; very old (10-50+ years), or b; have spent a significant amount of time on sea before reaching this destination. Previous studies (Henriksen, 2012; Ďuricová, 2012, among others) have found any and all sorts of heavy oil spattered onto the shoreline. Samples are commonly divided into North-Sea crudes, non-North Sea crudes and bunker/other. Such studies underline the global responsibility of pollution. Just like air pollution and radioactive fallout, it will not stay where the accident took place, but spread across the world with wind and ocean currents.

2.5 REFERENCE OILS

Several reference oils have been included in this study. Although there are excellent libraries containing chromatographic GC-MS-SIM information about most crude oils and many other types of oils already at SINTEF, no such thing exists for ICP-MS analysis so far, to the author’s knowledge, and some investigation was required.

2.6 INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

As one of the last analytical instruments to be in commercial use today, ICP-MS is one where the results and maintenance are still heavily reliant on the skill and experience of the operator. For many, this means that the bar for purchasing such an instrument is significantly higher compared to other instruments. That being said, it is a valuable and powerful technique and one of the most sensitive on the market with detection limits down in the sub-ppt range (Thomas, 2004).

Successful applications can be found in diverse fields such as environmental and life sciences, food industry, chemistry, semiconductors, forensic science, archaeology and geochemistry. Especially the study of proteins is experiencing increased interest for the instrument, as an estimated 25 % of proteins contain some sort of metal (Becker et al., 2005; Ammann, 2007). It has also been used successfully to identify inorganic impurities in drugs and pharmaceuticals (Rao and Talluri, 2007) and ICP-MS analysis of various petroleum oils and crude oils have been employed with good results (Al-Swaidan, 1996; Duyuck et al., 2007; Akinlua et al., 2008; Pereira et al., 2010; Sánchez et al., 2013, among others).

2.6.1 THE INSTRUMENT

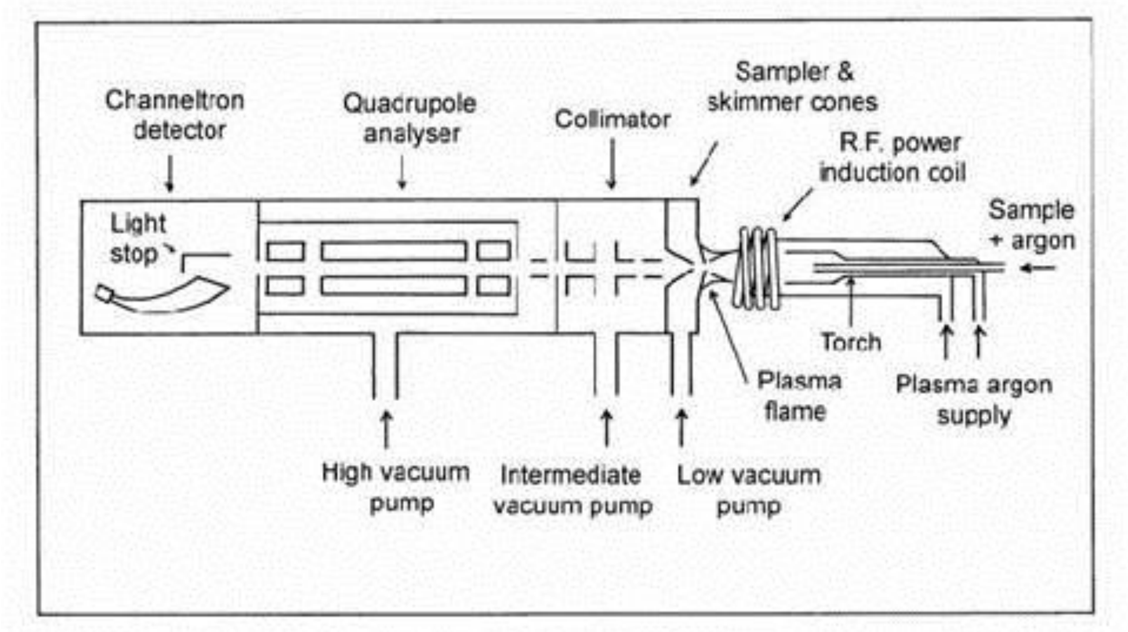


Image 2. 16 - The essential parts of an ICP-MS. Image courtesy of Alan P. Dickin (2005).

A sample, usually liquid, is first introduced into a nebulizer. There are several different nebulizer models available, but they all serve the same basic principle: To disperse the sample into fine aerosol mist. Typically only 1-2 % of the sample is used while the larger droplets are discarded. The aerosol is carried by a stream of argon into the plasma torch.

In the plasma torch, copper coils, radiofrequency (RF) and a power supply serves to ionize a different source of argon gas. When this gas is seeded with electrons from a high-energy spark, it ignites and creates an extremely hot, self-sustaining plasma discharge at about 10 000 K (Thomas, 2004), although the working area of the flame is "only" around 5800 K (Ammann, 2007).

When the finely dispersed aerosol droplets (< 10 µm diameter) are introduced into this flame, it is subsequently dried, vaporized, atomized and finally ionized. The majority atoms are ionized singularly (M^+). Negative ions such as halogens (X^-) are also formed, but an ICP-MS is optimized for positive ions, so most instruments cannot measure these. Because the plasma exerts such a high energy upon the sample, the information available will be elemental composition only. The element speciation information is lost in the process (Thomas, 2004).

The next, essential, part of the ICP-MS are the sampler and skimmer cones. They are, in essence, plates (usually nickel, but can also be other metals like platinum) with a tiny orifice (0.6-1.2 mm) in the middle and water-cooled to withstand the heat from the plasma torch. Behind the each cone is a vacuum pump, pulling a small amount of sample through. The pump is strong enough to maintain the vacuum which is lost by the system. The natural drawback with orifices of this size is its sensitivity towards salt and salt formation. It can tolerate salt concentrations up to 100 mmol/L salt. The addition of acid helps this disadvantage by rendering the salts volatile (Ammann, 2007).

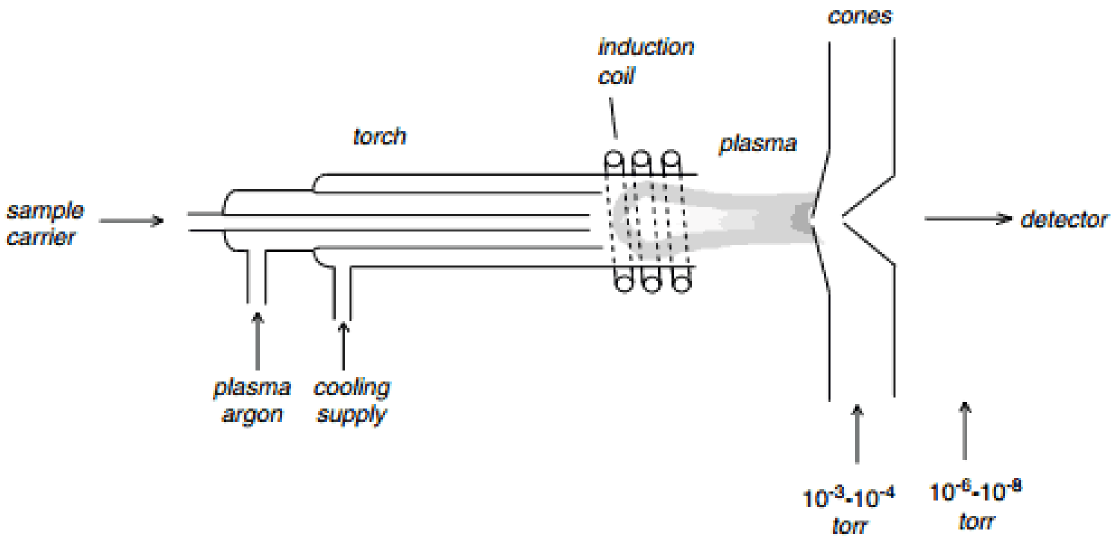


Image 2. 17 - A close-up of the plasma torch and sampler and skimmer cones, illustrating the reduction in pressure. Image courtesy of Adrian A. Ammann (2007).

As the ions exit the sample and skimmer cones, they enter into the Ion Focussing System, also known as Ion Optics. Several different designs are in manufacture, but their main task is to separate the desired analytes (M^+ ions) from the interfering matrix.

It is made up of metal plates, barrels or cylinders with a positive voltage. The Focussing System may, for instance, work at an angle, such that the ion beam must follow the curvature of the Focussing System in order to reach the mass analyser. In this way, undesired species such as non-ionic particulates, photons, neutral species or negative species are ejected from the ion stream and do not interfere with the mass analyser (Thomas, 2004).

2.6.2 THE QUADRUPOLE MASS ANALYSER

The quadrupole, in essence, consist of 4 parallel metal rods (typically about 1 cm diameter and 15-20 cm length), usually stainless steel or molybdenum, often with a ceramic coating to resist corrosion. Two of the rods have a positive direct current (DC), while the rods opposite have a negative DC. On top of that DC is an alternative current (AC). The currents can all be adjusted, meaning that these rods can be selective for high or low m/z. When all four rods work on the ion beam, it can choose a specific m/z to send into the detector. As the electrical currents can be remote controlled and programmed, the entire range of 1-300 atomic mass units (amu) can be selected and gone through in a manner of seconds (Thomas, 2004).

With the skimmer cones and mass analyser, it becomes obvious why the vacuum is needed. Too much interference from gravity would pull at the ion stream and ruin it, not because of the changed angle, but because heavier objects would be more attracted, and the beam would get pulled out of shape based on the weight of the atoms.

2.6.3 DRAWBACKS AND INTERFERENCES

Issues pertaining to ICP-MS analysis are generally related to ion-specificity or plasma generation. Argon species of sodium (ArNa m/z 63) interfere with copper, chlorine (ArCl m/z 75) with asbestos, calcium (ArCa m/z 78 and 82) with selenium and carbon species (C2 m/z 24 and ArC m/z 52) with magnesium and chromium, respectively. Oils high in sulphur might also suffer additional interference from different sulphur-species, for instance $^{32}S^{32}S$ (m/z 64) and $^{34}S^{32}S$ (m/z 66) which coincides with zinc. This can be avoided by using other minor isotopes of the affected elements, which in turn requires instruments with higher sensitivity (Duyuck et al., 2007). These and other matrix effects might be enhanced by organic solvents (Liu and Beauchemin, 2006), reduce ionisation energy in the plasma torch (Caumette et al., 2009).

Another serious instrument concern with ICP-MS is always the small size of the sampler and skimmer cones. High concentrations of organic solvents and salts might deposit on to the cones and eventually lead to clogging which might in extreme cases blow out the plasma (Dreyfus et al., 2005). Improvements on these issues have been suggested by several authors, usually addressing the nebulizer technology (Kahen et al., 2003; Giusti et al., 2006; Caumette et al., 2009).

Although clogging, matrix effects, ionization energy and nebulizing issues are of concern with all ICP-MS analyses, they are especially prominent with direct injection of whole oil. Wet-digestion of the oil in acid prior to sample introduction reduces the risk of serious implications with the instrument, but increases the limit of detection. Other issues can generally be mediated by correct use of quality reference material and several blanks throughout the analysis (Ammann, 2007).

2.7 GAS CHROMATOGRAPHY

Chromatography is an old technique which, in essence, revolves around separating a mixture of chemicals by letting a mobile phase work on a solid phase. One of the simplest, yet most illustrative, examples is to stain a thin layer chromatography (TLC) plate (silica on aluminium) with black ink and then submerging it into a mixture of ethanol and water. As seen in image 2.18 below, the dye of the ink travels up by capillary forces, and by inspecting the result it becomes evident that there is no one chemical making up the colour black, but several compounds together. All chromatographic techniques build upon this basic principle; separation and analysis.

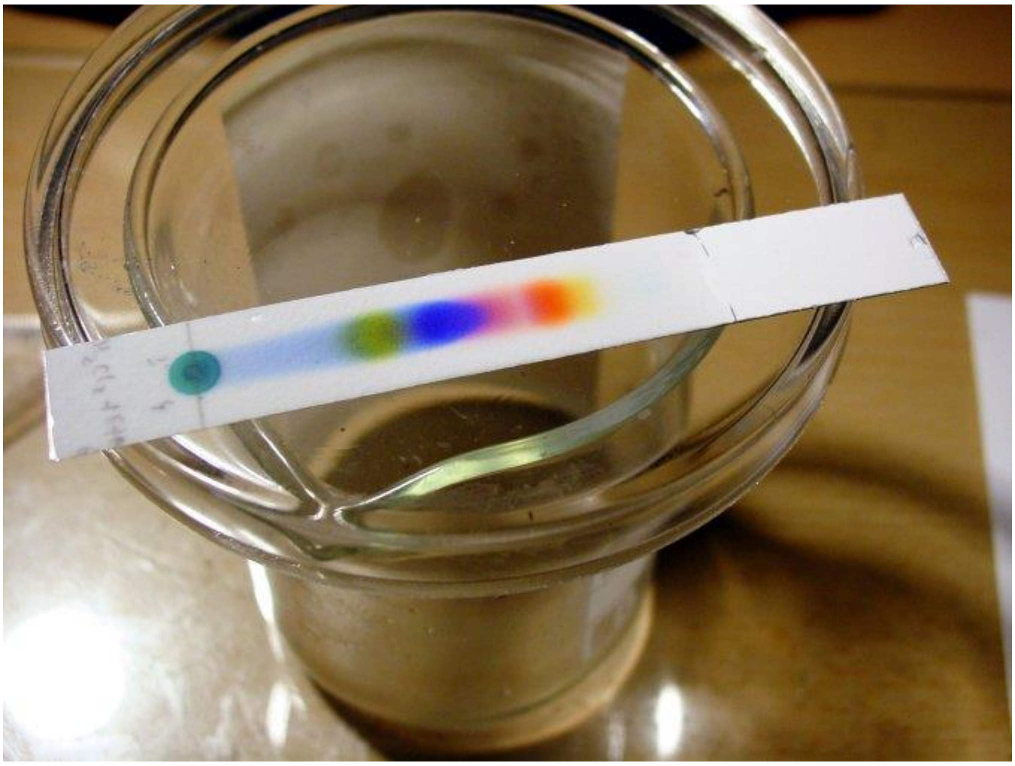


Image 2. 18 - Separation of black ink on TLC plate. The photo was taken after experimenting with black ink from a permanent marker (Stabilo OHPen universal) and ethanol + water mixture as solvent. Image courtesy of the webpage Wikipedia (wikipedia.com).

In more recent years, chromatography has become a lot more sophisticated. In theory, a stationary phase could be as long as the scientist desires, although increase in analyse time would have to be expected, which allows for analysis of increasingly complex mixtures (Christensen et al., 2005a). Dependant on the analyser at the other end of the GC-column, almost anything could be analysed. Applications range from analysis of specific phytohormones in plants (Müller et al., 2002), detection of herbicides (Djozan and Ebrahimi, 2008), or even the use of hair to investigate drug related sexual assault where the drug has already been removed by the body (Pascal et al., 2003).

In this study, GC-FID/MS-SIM has been used to investigate organic petroleum samples of various compositions. The method has previously been applied successfully to investigate both degree of weathering an oil has suffered (Hughes and Holba, 1988, Malmquist et al., 2007) and classification of similar/dissimilar oils (Abu-Elgheit et al., 1998; El-Gayar et al., 2002; Faksness et al., 2002; Nielsen et al., 2012).

2.7.1 THE INSTRUMENT

In theory, any kind of substance can be analysed by a gas chromatograph, provided it has a vapour pressure of approximately 0.1 Torr at the working temperature of the instrument and interacts with the column material. The carrier gas must also be capable of carrying the substance through the column, without altering it significantly. As different components interact with the column material, equilibrium constants will cause some to adsorb slightly to the column material, while others prefer the gas phase. This will lead to staggering or retention of certain components, while other pass through more or less unhindered. Because these columns are very long and very thin (0.250 mm diam. 15m long, with a film thickness of 0.25µm in this study, but 60m columns are not unusual) the constituents of the sample order themselves after retention time. If the conditions are just right, components pass into the detector at the end one after the other and can be successfully analysed (Grob and Barry, 2004).

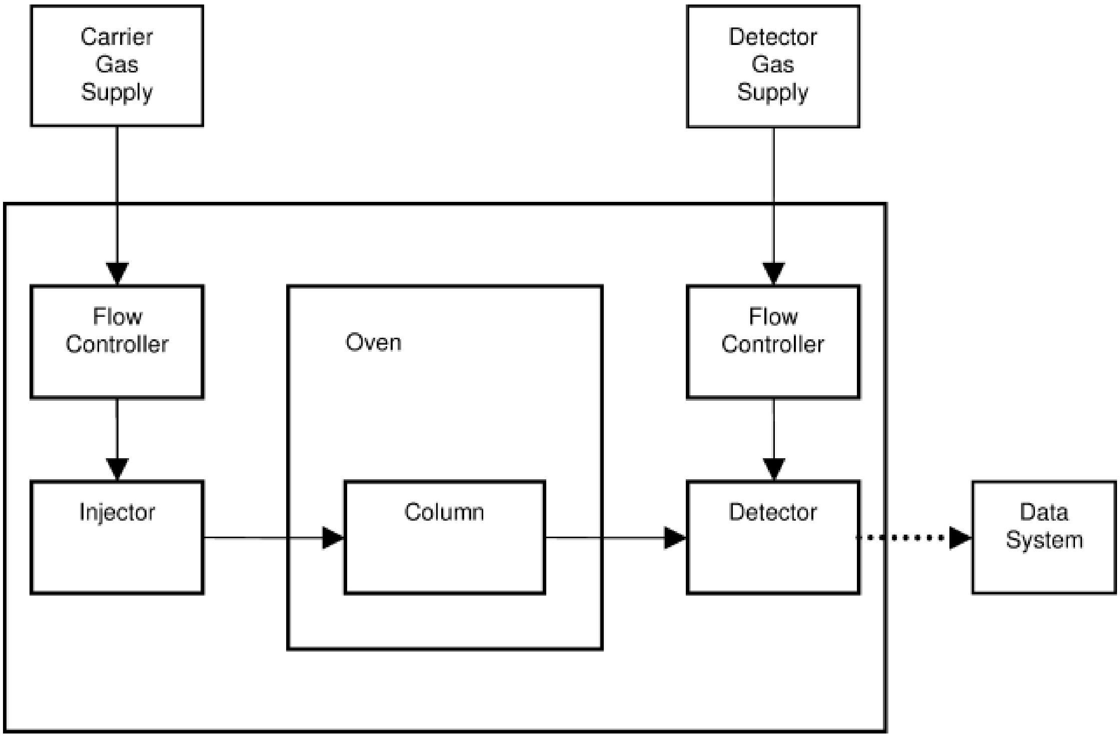


Image 2. 19 - A schematic representation of the main parts in a GC. Image courtesy of the University of Tromsø.

A carrier gas, usually an inert gas such as Argon, Helium, Hydrogen, Nitrogen or air, is introduced into the system through a flow controller, making sure the gas is introduced at constant speed and pressure.

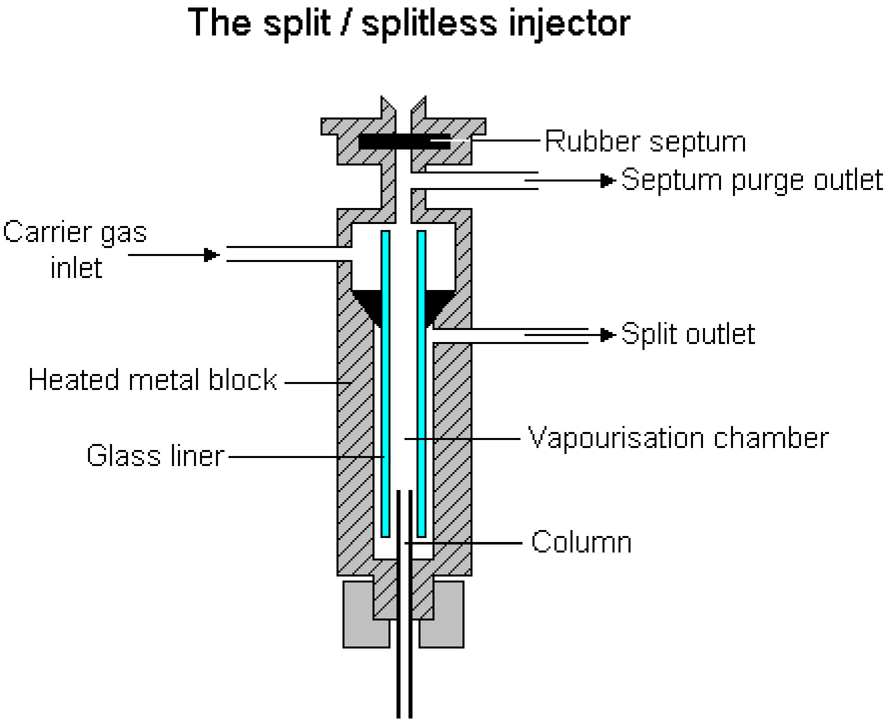


Image 2. 20 - Basic parts of an injector in a GC instrument. Image courtesy of Sheffield Hallam University.

The injector is an important part of the GC. The sample is introduced with a syringe through the rubber septum and into the heated chamber. The sample vaporizes near instantly and is carried into the column by the carrier gas. In a split injector, only a fraction of the sample is introduced into the column while the rest goes into a separate outlet and into a waste container.

Once the sample is inside the column, the rest is done by the carrier gas and the oven. A temperature program is set from cold to hot which ensures separation of the interesting components, while keeping runtime down as much as possible. At the end it is common to “burn out” any remaining sample matrix on the column by heating the oven above program parameters for a set amount of time.

Once the sample matrix has travelled through the column, it is introduced to the detector. Several different detectors exist, one of the simplest being the Flame Ionization Detector (FID). The data is then translated into a readable format through a data system.

2.7.2 GAS CHROMATOGRAPHY-FLAME IONIZATION DETECTOR

The Flame Ionization detector is the most common detector in commercial use today. It is destructive and very specific in that only combustible elements can be detected, which makes it ideal for organic analysis.

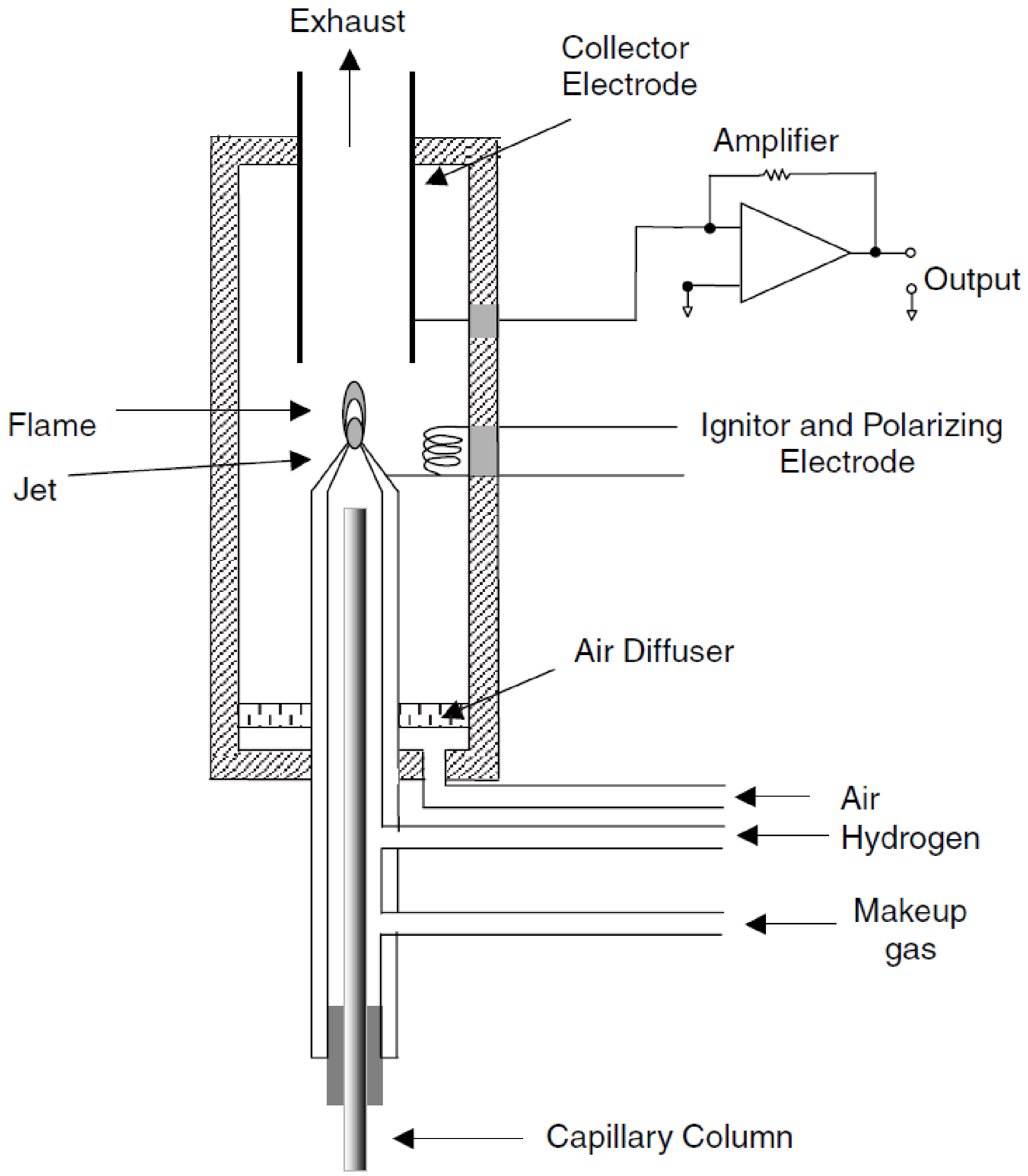


Image 2. 21- Schematic illustration of a FID. Image courtesy of Grob and Barry (2004).

The flame has its own supply of hydrogen which keeps it burning regardless of what comes out of the capillary column. When the sample matrix reaches the flame and is consumed, the flame creates ionization energy which can be detected. The flame can only combust a certain amount of matter per second, or there will be formation of soot which discriminates the results. The FID response is proportional to the number of carbon atoms, rather than the compound weight or moles (Grob and Barry, 2004).

It is worth mentioning that the FID system only generates a signal based on the intensity of the ionization. For any comparable information, it is dependent on pure samples of specific analytes and calibration curves.

2.7.3 GAS CHROMATOGRAPHY-MASS SPECTROMETRY-SELECTIVE ION MONITORING

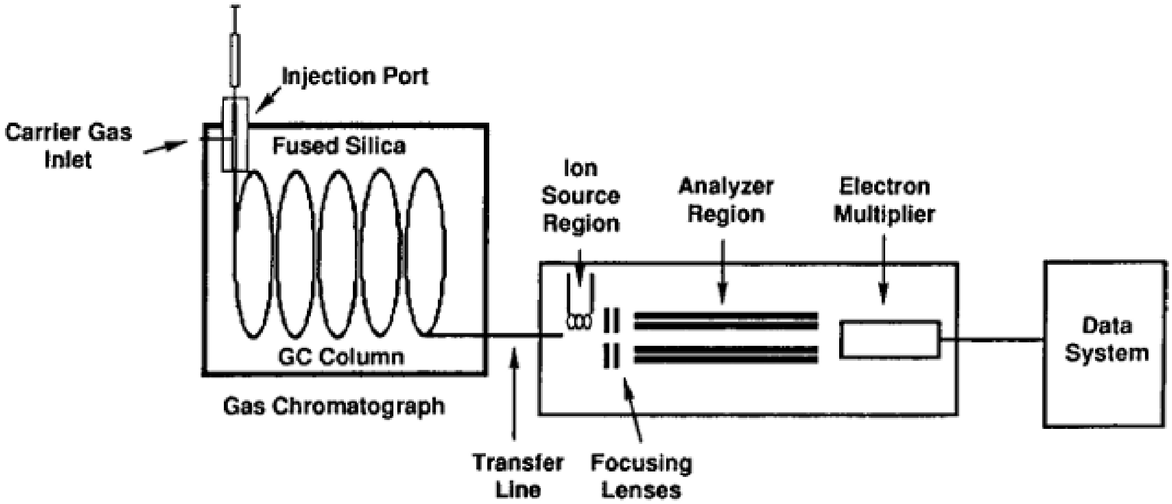


Image 2. 22 - Schematic illustration of a GC-MS system.

As discussed in chapter 2.6, MS needs vacuum conditions to function properly. This is in contrast to a GC, which requires carrier gas and pressure to push a sample through the system. For standard instruments, this means a GC-MS setup can tolerate no more than 1 mL/min from the GC and into the MS vacuum system (Grob and Barry, 2004).

In the ion source, rather than the destructive FID or high energy plasma torch, analytes are ionized either by chemical ionization (CI) or electrical ionization (EI). This ionization is “softer” compared to an ICP-MS and rather than M+ fragments, what reaches the detector after going through the mass analyser are molecular fragments such as CH_3^+. After ionization, they are sped up by focusing lenses and into the analyser region (typically a quadrupole). The temperature has to remain high enough to avoid condensation of the analytes (Grob and Barry, 2004).

2.7.4 SELECTIVE ION MONITORING

By the nature of an MS-system, the GC-MS can also be set up to scan for specific m/z ratios rather than all masses in range, known as Selective Ion Monitoring, or SIM. This can increase the sensitivity by up to three orders of magnitude. SIM is incredibly useful for quantification of analytes and routine analyses. A drawback of SIM is that you are only looking for what you expect to see, and thus might miss new and potentially important factors (Sauer and Boehm, 1991).

2.7.5 DRAWBACKS AND INTERFERENCE

Recurring issues encountered in GC analyses mainly focus around co-eluting compounds and signal to noise ratios. If co-eluting is not discovered or dealt with, results may be overrepresented and wrong. This was the case with gammacerane during the first round robin test done during the revision of the Nordtest method (Faksness et al., 2002), where several labs mislabelled a co-eluting peak as gammacerane in samples where no gammacerane was present. The issue was remedied by inspecting a different m/z chromatogram where the co-eluting peak showed no signal.

The traditional way to deal with co-elution is to change the different oven settings or replacing the chromatography column for one with a different solid phase. This is often time consuming and leads to longer run-time. Methods are being proposed where the use of multivariate statistics might help resolve co-eluting peaks, while still keeping runtime low or even drastically reducing it (Statheropoulos et al., 1998).

Other issues which usually surface over time with several runs are baseline drifts, non-Gaussian (normal) peaks and changing elution time. Consistent use of good internal standards is a traditional way to deal with these problems, although multivariate modelling methods are emerging to help as well (Amigo et al., 2008).

When it comes to signal/noise ratios, unless there is something wrong with the sensitivity of the instrument, you would often have to go beyond the instrument to remedy the issue. Extraction, purification and concentration of the sample are all methods which could be tested prior to the analysis, although just concentrating the sample might concentrate the noise/interference as well. It is generally accepted in all analysis that you can’t get excellent results from poor samples, but there are methods being developed to reduce signal/noise issues. A paper written by Statheropoulos et al. (1999), presents a PCA model which extrapolates data to reduce noise levels.

2.8 DATA ANALYSIS

Some 30 years ago, the field of chemometrics and multivariate data analysis was really starting to come into its own. Principal component analysis PCA and PLS-R are among the techniques which were developed to cope with rapidly growing size of available data. Now, over 30 years later, the data sets created are even larger, generally increasing in size more than tenfold each decade and making comprehensive multivariate data analysis more relevant than ever (Kettaneh et al., 2003).

2.8.1 CEN-METHODOLOGY

The CEN-methodology is based on the Revised Nordtest (Faksness, 2002) report. The most recent guideline is CEN (2012). The main reason for the guideline is to provide a simple, unified method which demands little specialised equipment and provides enough information to help analysts and laboratories that are new to oil spill analysis make a sound and court defensible conclusion.

Encouraging different countries to agree on one method is also beneficial in regards to comparisons, sharing of knowledge, international accidents and large, collective databases. Included in the methodology are annual round-robin tests where laboratories from all over the world participate.

Most alternatives to the CEN-method include MVA methods (Nielsen et al., 2012) based on similar or different biomarkers from GC-MS analyses. A potential method which is still being investigated is the use of Electrospray Ionization-Mass Spectrometry (ESI-MS). Rostad (2006) found promising results during a study focusing on light petroleum fuels, and adaptation to higher weight, weathered oils might be interesting. Elemental analysis using ICP-MS (Akinlua et al., 2007), Atomic Adsorption Spectrometry (AAS, Akinlua and Torto, 2006) and neutron activation analysis (Duewer et al., 1975) have also been investigated, although increased classification might be acquired by combining the methods.

2.8.1.a The method

The CEN-methodology was developed primarily as an analytical method. It values efficacy and lab resources, both time and money. The goal is to label all samples into four different categories: Match, probable match, non-match and inconclusive. As soon as a sample is labelled non-match, it is removed from subsequent analyses, as illustrated by the step-by-step flowchart presented in image 2.23.

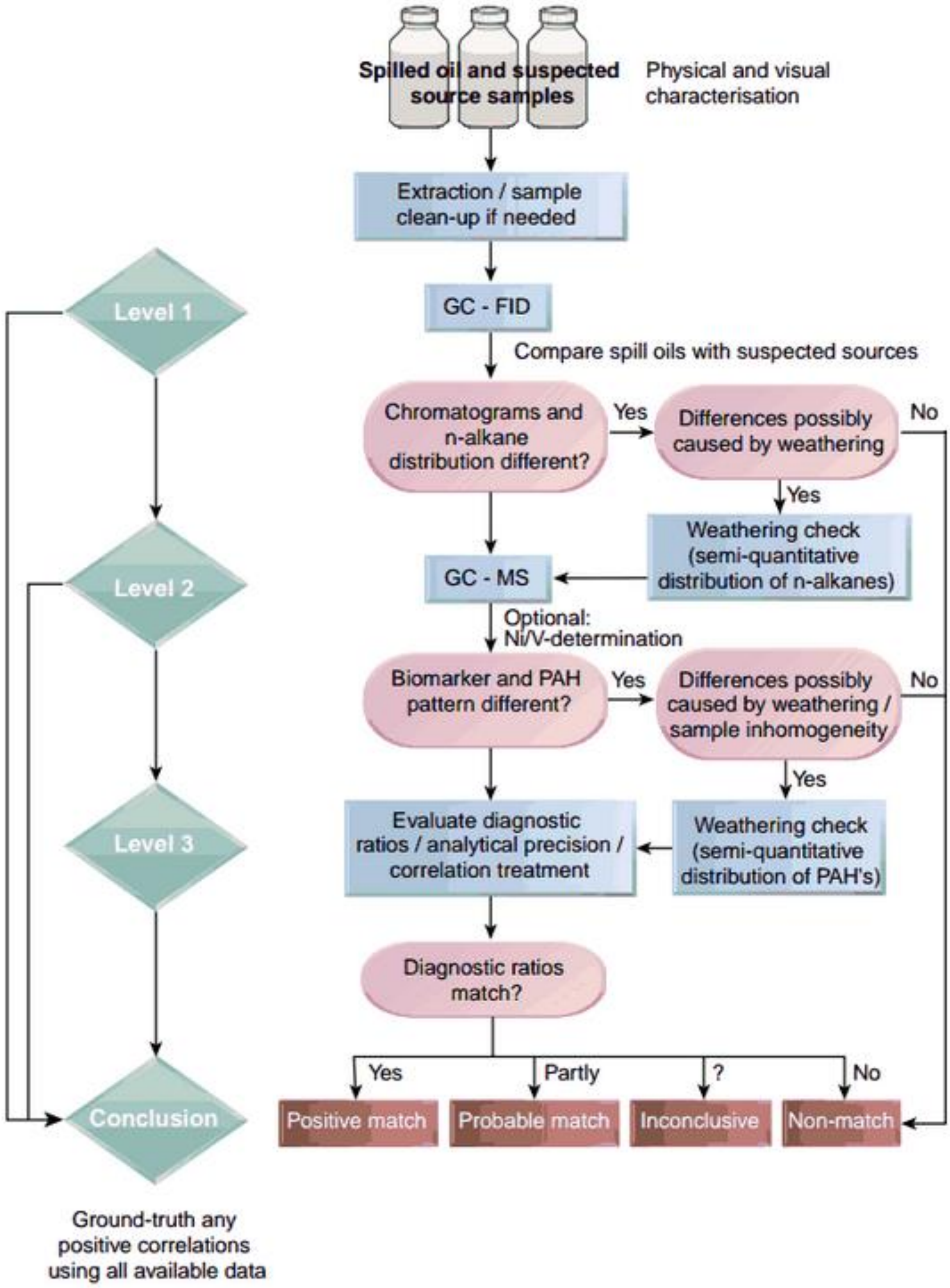


Image 2. 23 - Steps in the CEN-methodology. Image courtesy of Wang and Stout (2007).

The way this categorization is done is first to inspect all the GC-FID chromatograms for similarities. A skilled analyst can here rule out samples based on the overall distribution of hydrocarbons, as well as keep those samples which are different, but differences are caused by weathering.

The next step is then to send all remaining samples to further GC-MS-SIM analysis. Traditionally, the analyst would here inspect all relevant mass spectra, chose suitable biomarkers from a suite of commonly used ones, and then integrate all samples by hand before plotting into a spreadsheet and calculating critical differences between samples. Although critical difference can be computed individually, depending on instrument, noise and other specific factors, CEN has put a cut-off at 14 % for all labs. Relative difference (RD) between two samples can be calculated thus:

$$RD = \frac{|y_r - x_r|}{\mu} * 100 \tag{2.9}$$

Where y_r and x_r are the ratios of x and y respectively (in percent), µ is the mean between the two percentages and RD is relative difference. If RD exceeds 14 %, the two samples are significantly different (CEN, 2012).

The general rule is, for the 29 most common biomarkers, only 2 can be above critical difference if the sample is to defensibly be concluded as a positive match (CEN, 2012). Researchers are continually looking for robust statistical methods which can aid in the classification of samples, thus reducing the impact of analyst experience and rendering the method more objective.

Although the comparison of ratios is established and acknowledged, it does have certain limitations. If there is more than one different source of oil contamination, for instance as with MV Full City, there could be the issue with mixing, which would force the conservative demands of the CEN-method to render most samples “non-match” to individual sources. This issue was addressed specifically in the Full City case by Faksness et al. (2009), where PCA was successfully used to deal with the mixing issue.

Other oil identification methods have focused more specifically on MVA, PCA and pattern recognition (Duewer et al., 1975; Brakstad and Grahl-Nielsen, 1988; Nielsen et al., 2012) and this might present a natural evolution of the CEN-methodology. Another intriguing possibility might be to look into 2D GCxGC or even GCxGC-MS runs for even more extensive separation of possible markers of interest (Medeiros and Simoneit, 2007).

2.8.2 COSIWEB

COSIWeb (COSIWeb, 2014) is a large oil spill database which belongs to the German Bundesamt für Seeschifffahrt und Hydrographie (BSH). It was quite recently hosted on a server and published online where it is quickly growing. The brilliance of the system lies in how the user can export and upload a chromatogram directly, only providing a few key retention times. The algorithm then integrates the remaining components based on the key information, but allows the user to make changes based on personal experience and knowledge about the data.

After a chromatogram has been visually inspected and accepted by the user, the 29 basic CEN DR are displayed. As the oil is uploaded into the rest of the database, users can search for matches by comparison with all other chromatograms in the database, critical differences included and clearly displayed. Simultaneously, the chromatogram which was just uploaded also becomes available to other users. Once up and running, the database is a self-sustaining system which will only get better as it grows. All DR's presented in this study was obtained by this software. COSIWeb measures all ratios in peak height.

A possible limitation of the database is that it calculates only the 29 most used DR's. It does not give the user control to investigate other, possibly interesting biomarkers present in the oil, for instance if an oil was depleted of certain biomarkers.

2.9 MULTIVARIATE STATISTICAL METHODS

MVA is a relatively young, but rapidly expanding field. Its power lies in finding latent or underlying information in huge data sets often consisting of several hundred samples and variables. With such vast amounts of information, it quickly becomes clear that plotting one sample or variable against another at a time, as with traditional statistics, quickly becomes both time consuming and near impossible.

In general, multivariate analysis methods are highly graphical in nature, and have the power to explain with an image what might otherwise demand several pages in text or tables. It can quickly identify units which correlate or co-vary, although it does not say anything about why, which is why background knowledge, or domain knowledge, is essential (Swarbrick, 2012).

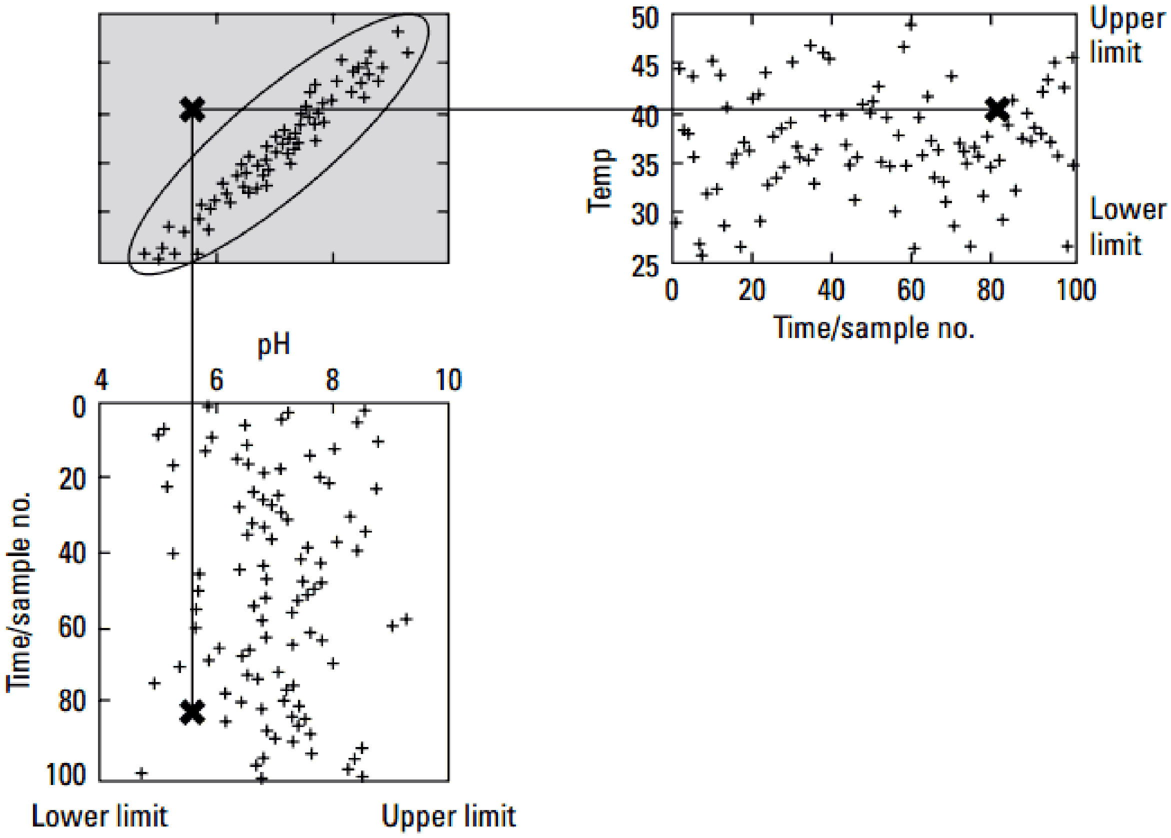


Image 2. 24 - A simple example, illustrating how temperature and pH depend on each other, successfully identifying an outlier which was not detectable in either plot by themselves. Image courtesy of Brad Swarbrick (2012).

With sensor technology and computer power rapidly increasing, the challenge today is often not to acquire data, but rather to analyse and understand it. Sampling a chemical process more than once per minute is not uncommon today, compared to one an hour or fewer 30 years ago. This creates huge datasets which cannot be interpreted by traditional, univariate methods (Kettaneh et al., 2005).

2.9.1 PRE-PROCESSING

As with any research, steps should be taken to ensure, as much as possible, continuity in the analysis. To work-up and analyse the samples over a short time span, by the same analyst and with the same laboratory facility and chemicals. Similarly, for the data analysis, it is important that all samples be given the same treatment to ensure the samples are as similar as possible, such that any variation with reasonable safety can be said to come from the samples themselves, and not their pre-treatment. This detail is worth pointing out, as low reproducibility in data is often the most recurring impediment with oil analysis (Christensen and Tomasi, 2007).

Inspection and pre-treatment of raw data is an important step to get a defensible result with multivariate analysis. Several methods, such as PCA and PLS, presented later in this chapter, rely on their data to be approximately normally distributed. If this is not the case, results can be unreliable or even directly faulty (Ebenesen et al., 2001).

One particularly interesting statistical feature is the relative standard deviation (RSD), which is a measure of the variance in a data set, given in percent (equation 2.10).

$$RSD = \frac{SD}{Avg} * 100 \qquad (2.10)$$

Where RSD is relative standard deviation, SD is standard deviation, and Avg is the average of the data set. Standard deviation is calculated by equation 2.11.

$$SD = \sigma = \sqrt{\frac{\sum_{i=1}^{n} x_i - \mu}{n-1}} \qquad (2.11)$$

Where SD is the standard deviation, n is the number of samples, x_i is each of the samples in the data set and µ is the average.

2.9.1.a Scaling

There are countless different ways to scale data sets for analysis. There is no clear-cut method which will work for everything, and a suite of suggestions are often tested before arriving at something which works for that, specific data set. The purpose of scaling is to emphasize the important variation, while trying to keep noise at a minimum. Some methods are listed below.

2.9.1.b The log-normal distribution

Although mathematically more complex, life- and nature-science data and economics often fall into log-normal distribution rather than the normal distribution. This sort of skewed distribution is often seen in cases where values cannot be negative, the mean values are low and the variance is large (Limpert et al., 2001). Any log-normal distribution can be transformed into a normal distribution by either taking the log x of all the samples, or plotting the samples on a logarithmic scale, as seen below.

$$X_{log} = log(x) \tag{2.12}$$

Where x is the sample which is to be log-transformed and X_{log} is the log-transformed sample.

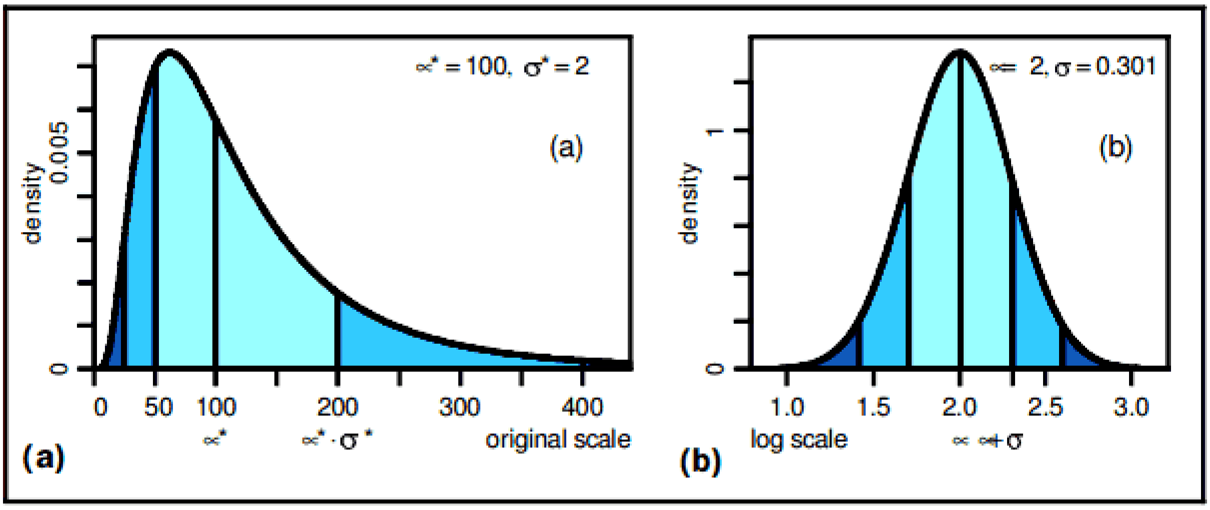


Image 2. 25 - The same log-normal distributed data set, but plotted on (a) the original scale and b) a log scale. Image courtesy of Eckhard Limpert et al. (2001).

2.9.1.c Kolmogorov-Smirnov test of normality

In essence, the Kolmogorov-Smirnov test of normality is a comparison tool. It takes one theoretical distribution, for instance the normal distribution, and compares it to a dataset to see if there is significant difference between the two. The difference between the two is calculated, and a threshold or significance level in % determined whether the difference is significant.

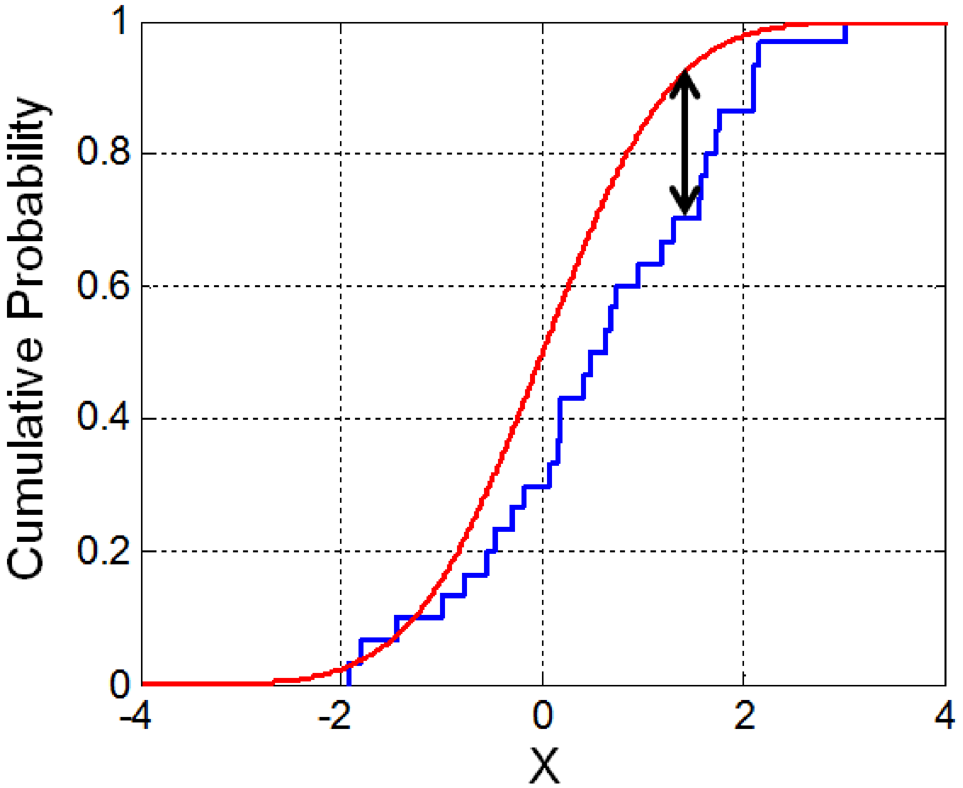


Image 2. 26 - An illustration of the Kolmogorov-Smirnov test of normality. A theoretical distribution is compared to a dataset.

In practice, this is done by the following formula (equation 2.13):

$$T = \sup_x |F^*(x) - F_n(x)| \tag{2.13}$$

Where “sup_x” stands for supremum or “greatest” of the set of distances, F* (x) is the a sample in the theoretical distribution and F_n (x) is the empirical distribution function of the corresponding sample in the dataset (Razali and Wah, 2011).

2.9.1.d Standardisation

Standardisation is another, common transformation where each variable has their variance set to 1. It is a useful transformation which allows each variable in the data set to influence the model equally, no matter if they are measured in mg or kg. It does, however, assume the data follows a Gaussian fit, and is sensitive to noise and risks giving too much emphasis on outliers (Ebenesen et al., 2001).

$$x_{new} = \frac{x-\mu}{\sigma} \tag{2.14}$$

Where X_{new} is the new, standardised value, x is the old value, μ is the average and σ is the standard deviation for each variable.

Standardisation was preferred over normalisation, as normalisation is sensitive to extreme outliers which might very well be present in the data. The drawback of standardisation is that it assumes a normal Gaussian distribution of variables. This assumption is already implicit in dealing with PCA and PLS-R, which means little additional uncertainty, is added by performing this transformation.

2.9.1.e The Pearson correlation coefficient

In this study, the Pearson correlation coefficient is calculated automatically using COSIWeb, but it is still useful to have some insight into how this is done. A Pearson correlation coefficient is a single number representing the covariance of two samples and all their variables, or in other words, indicating how similar they are. Two perfectly co-varied samples would have a Pearson correlation of +1 (positive correlation) or -1 (negative correlation). The formula for this can be seen in equation 2.15 below.

$$r = \frac{n(\Sigma xy)-(\Sigma x)(\Sigma y)}{\sqrt{[n\Sigma x^2-(\Sigma x)^2][n\Sigma y^2-(\Sigma y)^2]}} \tag{2.15}$$

Where r is the Pearson correlation coefficient, x is the first sample to be compared, y is the second sample to be compared, and n is the number of variables (Walpole et al., 2007).

2.9.2 PRINCIPAL COMPONENT ANALYSIS

PCA is one of the main workhorses in multivariate analysis. It is often one of the first things done to the data after some pre-treatment has been done. It can also be used to get an impression about how well a certain transformation has worked and can be used as basis for several more advanced methods. PCA is gaining credence as a forensic tool in oil spill investigation and assessment of weathering through an increasing number of cases (Christensen et al., 2005b; Malmquist et al., 2007; Faksness et al., 2009).

At its core, PCA is a matrix decomposition, as illustrated by equation (2.16) below.

$$x = TP^{T} + E \tag{2.16}$$

Where X is the original matrix, T is the scores matrix, P^T is the transposed loadings matrix and E is the residual error matrix which should contain mostly noise.

PCA seeks to explain the variance in the data as efficiently as possible. It does this by projecting the original data onto a new coordinate system based on explained variance. In this coordinate system, the first axis, known as principal component 1 (PC1) unfolds along the plane which explains the most of the variation in the data. The second PC (PC2) is orthogonal to the first, and explains the second most variation in the data. One may extract as many PC's as there are variables in the data set, but if that is necessary, PCA has provided no simplification to the data (CAMO, 2006).

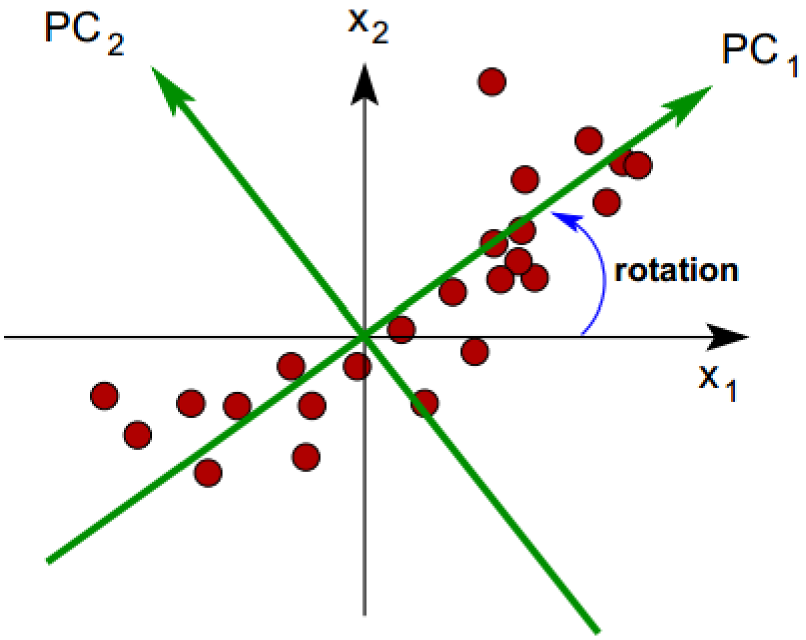


Image 2. 27 - A simple 2D example illustrating the difference between traditional coordinates and principal components. Image courtesy of Bjørn Kåre Alsberg.

In addition to rearranging the samples in what is known as a scores plot, PCA also explains which variables are responsible for the variation in the complementary loadings plot. Here, all variables are plotted in a similar graph in the ranges -1 to +1. The two plots can then be superimposed on top of each other, and it is possible to identify which variables are important for the separation of specific samples or groups of samples. Variables in the same area are positively correlated, while variables 180˚ away (relative to the origin) are negatively correlated. Variables around 90˚ have no correlation to each other and variables close to the origin have little or no influence over the model (CAMO, 2006).

In addition to the regular rotation where PC1 explains the most variance, PC2 the second most and so on, there are also a number of possible rotations available. One of these rotations is called the Varimax rotation. This rotation does not necessarily explain the most variance first, but looks for a solution which explains the most total variance. In table 2.3 below, an example illustrating the differences between the two methods is illustrated. Varimax can illuminate features which might get “dwarfed” or hidden by a very dominating PC1 in a regular PCA plot.

Table 2.3 – Example illustrating the difference in explained variance between Varimax rotation and regular PCA rotation.

%	Normal PCA	Varimax PCA
PC1	45	32
PC2	15	25
PC4	6	17
Total %	66	74

2.9.3 PARTIAL LEAST SQUARES REGRESSION AND DISCRIMINANT ANALYSIS

PLS-R is a method which takes two matrices and looks for correlation between the two. One matrix (Y) is fixed, while the model attempts to find the pattern which linearly correlates the other matrix (X) to Y as well as possible. Y being fixed is why this is a partial regression method. The robustness of the method means X and Y can be different types of data with different scales (Geladi and Kowalski, 1986). The two matrices can be represented thus:

$$X = TP^T + E \tag{2.17}$$

$$Y = UQ^T + F^* \tag{2.18}$$

Where X and Y are the respective matrices, T and U are decomposed scores matrices, P^T and Q^T are transposed loadings matrices, and E and F* are residual error matrices.

The mixed relation between these two matrices can be seen in equation (2.19):

$$Y = TBQ^T + F \tag{2.19}$$

Where B is estimated through $\hat{u}_h = b_h t_h$, and F is to be minimised.

A better relation can be achieved by an iterative algorithm, giving the blocks each other's scores. X scores are not always orthogonal in the result though, which is addressed by weighting the variables until a best fit can be found (Geladi and Kowalski).

The model needs both a calibration dataset to make the model and a validation data set to test the accuracy of the calibrated model. For small to medium sized data sets, it is common to use cross validation, where part of the data set is taken out and used as a validation set for one iteration, before it is re-inserted into the calibration data set and a new part is taken out to be the validation data set. This is repeated until all parts of the data set has been taken out and re-inserted. The smallest number of samples you can take out at a time is 1, which is also known as "leave one out" (Wold et al., 2001a).

An important point in PLS-R is that it is only accurate within the defined model. It cannot safely predict anything outside the parameters whence it was made. This means the calibration samples have to be representative, and preferably a little outside, expected values for future samples. Issues with PLS-R naturally emerge if the relationship between X and Y is not linear, but maybe exponential. As with anything, a model can never be better than the data used to create it (Wold et al., 2001b).

Because PLS-R deals with linear relationships, it does not handle clusters well. If there are clear clusters in the data, it is often advised to split the samples, modelling each cluster by themselves (Kettaneh et al., 2005).

Another alternative is to run PLS-DA. The PLS-DA model uses the exact same algorithm as the PLS-R model, but rather than using two data matrices X and Y, PLS-DA takes one data matrix X and one classification matrix Y. In this classification matrix, samples are given an ID based on knowledge about the samples, for instance labelling crude oils -1 while bunker oils are +1.

2.9.4 DATA EVALUATION

When data sets have been scaled and modelled, they have to be evaluated. For PCA, this is often done by visually inspecting the scores and loadings (Christensen and Tomasi, 2007). Are the samples clearly distinguishable into groups? Are the loadings dominated by overly influential variables/noise? What are the different PC's explaining? Does the classification make sense? Are there clusters of positive and/or negative correlation? Of course, classification might not always be clear cut. Fuzzy groups might mix with each other, groups might have different shapes, and samples where it is not clear if they are true outliers or very important samples often give further difficulties with interpretation.

For PLS-R, in addition to the visual inspection described above, there is the added information of R^2. As with traditional statistics, an R^2 close to ± 1 indicates a reliable model of good fit, while anything closer to 0 indicates a model with bad predictability. An approximately linear relationship between X and Y both from the calibration dataset and the validation dataset indicates a good model (Wold et al., 2001a).

With a lot of multivariate analysis work, the model building and data evaluation is often a circular process, repeating itself several times until an acceptable model with good quality has been achieved within the provided timespan. In addition to the multivariate evaluation, it is always a good idea to return to the original data set at this point to inspect interferences such as noise, standard deviations and reliability of the data.

3. MATERIALS AND METHODS

3.1 FIELDWORK

The fieldwork in which this author assisted was performed late September in 2012 in the Froan nature reserve as a student of the annual Organic Marine Environmental chemistry course at NTNU (course code KJ3050). Earlier fieldwork from 2011 had been performed by a previous class of students whose samples had been stored at 4 ˚C. This study would not have been possible without the help and hard work of students from both classes. Image 3.1 illustrates the combined sampling points of the two field trips which were used in this study.

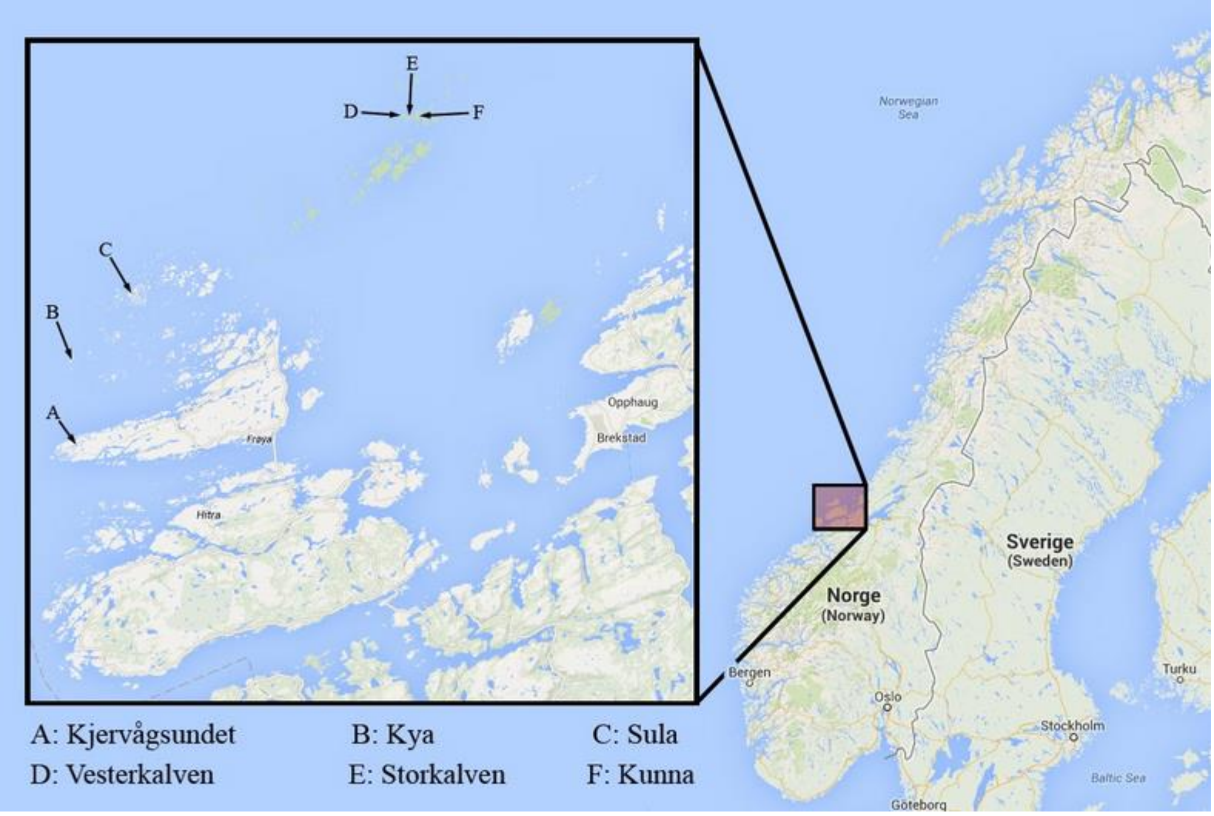


Image 3. 1 - Map showing the six islands withered samples were taken from, all are far at sea and exposed to the forces of nature. Location A, Kjervågsundet, is a specific location on the larger island, Frøya, all other sampling points are island names.

The withered samples used in this study were collected off rocky shorelines along the Trøndelag coast. Their age and source are not known. The Froan nature reserve has never suffered any known, severe oil spill. Meaning any oil found here must have travelled quite a distance. The samples were collected in containers optimised for organic analysis; stainless steel spatulas and aluminium containers with paper lids. The origination of the various weathered samples can be seen in table 3.1.

Table 3.1 - The weathered samples in this study, sorted by island of origination.

Sula	Kunna	Storkalven	Kya	Kjervågsundet (Frøya)
01	07	12	28	38
02	08	13	29	39
03	09	14	30	40
04	10	15	31	44
05	11	16	32	45
06	17		33	46
	18	Vesterkalven	34	
	19	23	35	
	20	24	36	
	21	25	37	
	22	26	41	
			42	
			43	

Samples were typically small, black and melted onto the rock surface. Some were old enough to have grown white mould or moss. As seen in image 3.2, the oil sample is obviously highly weathered as it has formed a cracking pattern from prolonged weathering after rock deposition. In several samples, a protective “skin” had been created on the oil sample, leaving the oil still sticky underneath.

Image 3. 2 - An example of a large oil sample from the field work.

All samples were stored at 4 ˚C directly upon arriving at the lab. Details about all samples in this study can be found in Appendix A.

3.2 SAMPLE DISCRIMINATION

The samples in this study are made up from several individual studies/sample sets, all of which were too large to be included in full. For this reason, each sample set had to be condensed by removing several samples. The process and reasoning behind this for each sample set is explained in this chapter.

3.2.1 SELECTED SAMPLES FIELDWORK IN 2011 AND 2012

Samples were chosen from the large amount of total samples gathered, based on getting an even geographical spread throughout the sampling areas, but also based on a minimum required volume (0.5 g) to be able to do both GC-FID, GC-MS-SIM and ICP-MS analyses. The samples from 2011 and some samples from 2012 had been analysed once already (Henriksen, 2012; Ďuricová et al., 2012), which could be used to choose samples based on sample type and, to a certain degree, weathering ratio.

3.2.2 SELECTED SAMPLES FROM SERVER AND FULL CITY

For samples from the Server and Full City spill, having a real spill sample and a matching reference sample was crucial for any verification of the ICP-MS analyses. For this reason, samples were chosen based on the published reports (Almås et al., 2007; Faksness et al., 2009), in such a way that there was at least one or more reference samples with a corresponding spill sample classified as a “match” from both spills. For Full City, there was no single reference sample as the oils were a mixture of sources from different tanks. In this case, two reference samples and corresponding matching spill samples were chosen. Details can be found in Appendix A.

3.2.3 SELECTED SAMPLES FROM SINTEF CRUDE OIL STORAGE

For the reference oil samples, a more arduous method was used. All available fresh crude oils which had been already analysed at SINTEF and were classified as open to the public had their data entered into a multivariate table and then plotted into a dendrogram by senior scientist Trond Størseth at SINTEF. Any identifiers which might bias the selection were then removed, and a subset of oils which were as different from each other as possible were chosen. The original dendrogram and chosen (highlighted) samples can be seen in image 3.3 below:

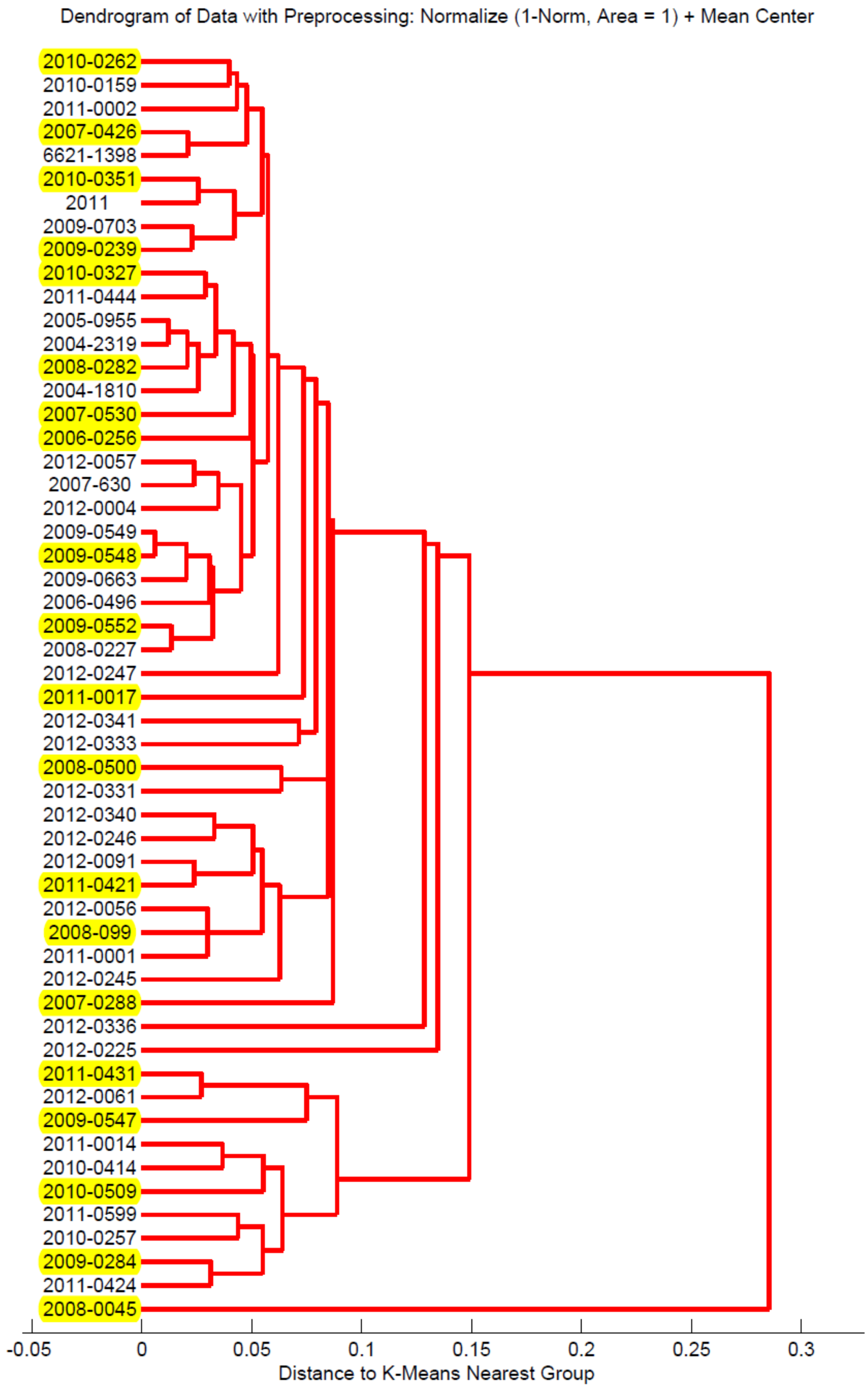


Image 3. 3 - Dendrogram of various fresh crude oils with their SINTEF-ID's. Samples used in this study are highlighted with details in Appendix A.

3.3 LAB WORK

All chemicals used were of analytical grade.
When the word “baked” is used, it is referring to heating up glassware and chemicals to 450 ˚C (increasing temperature by 250 ˚C/hour) and then keeping that temperature for 3 hours in a muffle furnace before allowing it to cool down again, removing any organic matter which might interfere with the results in the process.

3.3.1 GC-FID AND GC-MS PREPARATION

For the GC-samples, a small but homogenised sample of oil was taken, approx. 0.1 g. For spill samples, an effort was made to make sure this sample consisted of as much oil as possible, and preferably little or no matrix from other contaminants. To each sample was added approx. 10 mL dichloromethane (DCM) such that the concentration was approx. 10 mg oil/mL DCM. The bottle was capped, and the sample shaken vigorously. All samples were left at least overnight at room temperature to make sure as many compounds as possible were dissolved properly.

In a baked Pasteur pipette was first packed a small ball of baked Bilsom watt before 4-5 cm of baked, water free, sodium sulphate (Na_2SO_4) was added on top. Each sample was applied on top of such a filter with a baked Pasteur pipette and allowed to filter through into marked 2 mL vials. This served both as a means of removing water from the solution and a filter to exclude any large pieces of matrix from the sample.

The solvent was then exchanged from DCM to hexane by means of a nitrogen sample concentrator (Stuart block heater SBH130D/3 and Stuart sample concentrator SBHCONC/1). Samples were de-capped and put on a heating block (35 ˚C) over which a gentle stream of nitrogen (0.5 bar) was passed to speed up the evaporation. When approx. 0.5 mL was left in the bottle, hexane was added, the bottle capped and shaken, before it was put back in the heating block and evaporated to 0.5 mL again to remove the remaining DCM. The samples were then ready to be applied to the pre-packed silica columns.

3.3.1.a Bond Elut

The vacuum manifold was washed with DCM between each sample. Pre-packed silica columns (Bond Elut, 3 mL columns, 500 mg. silica) were marked and put on top of the manifold with negative pressure through water suction. 3 mL hexane was applied and flushed through to condition the columns. Between 2-3 mm hexane was left above the silica of each column, and they were never allowed to run dry as this ruins the column once it has been conditioned.

The washing tubes were then exchanged for marked and baked sample tubes and each sample was applied to their own silica column with a baked Pasteur pipette. The glasses were washed 2-3 times with small amounts of hexane and this too was transferred to the columns until the total applied volume was close to 3 mL. The sample was then passed through the column, and when only 2-3 mm sample remained on top an additional 2 mL hexane was added to wash the column. Additional hexane was added a total of 2 mL x 3 times.

Each tube was then evaporated down on the nitrogen sample concentrator and transferred with a baked Pasteur pipette into clean, marked GC-vials. Each tube was washed 2-3 times with small amounts of hexane which was then transferred to the GC-vial until the GC-vial was full. Each vial was then capped and turned upside down a few times for homogenisation. The samples were stored dark and cool (4 ˚C) awaiting further analyses.

3.3.1.b GC-FID analyses

The column chosen for the GC-FID analyses was a 0.250 mm diameter, 15 m long Narrowbore column with a film thickness of 0.25 µm. The gas (Helium, grade 4.6) was adjusted in such a way that the flow through the column was held constant at 2 ml/min and the temperature rose by 15 ˚C/min from 40 ˚C to 250 ˚C where it was held for 10 minutes to burn out remaining residue. In addition, for every 20th sample, a standard “SINTEF mix” of various oils was run (3 replicates) to ensure stable data quality, followed by a wash run with DCM and then an n-alkane standard for reproducibility.

3.3.1.c GC-MS analyses

Before GC-MS analyses, all chromatograms from the GC-FID were inspected. If response on the GC-FID exceeded 200 pA, the sample was classified as too concentrated, and appropriately diluted with hexane. The procedure for GC-FID/GC-MS follows the specifications given in the technical report CEN/TR 15522-2:2012, Oil spill identification for Waterborne Petroleum and Petroleum Products (CEN, 2012).

3.3.2 ICP-MS PREPARATION

For preparing the samples for ICP-MS analyses, 20 mL quartz (SiO_2), glass tubes had been stood overnight in a 50 % HNO_3 solution. These glasses were then rinsed twice in ultrapure milli-Q (Millipore corporation) water and violently shaken “dry”. Between 50 and 200 mg of sample was introduced and weighed into each glass depending on the sample size and 6 mL 50 % HNO3 was added. The samples were then capped with glass lids which allowed the escape of gases and placed in an Ultraclave.

The Ultraclave was sealed tightly, pushed up to a pressure of 50 bar (Nitrogen grade 2.6) and slowly heated up to 225 ˚C over the course of 1 hour and 20 minutes in order to digest all organic matter. The same amount of time was then needed afterwards in order for the Ultraclave to cool down and release the pressure in a controlled fashion. Details of the program can be found in Appendix B. Although element concentrations in the reference oils were expected to be low, increasing the sample size beyond suggested values was not advised, as the build-up of gases and pressure during Ultraclave procedure might have posed a safety risk.

Image 3. 4 - A set of digested samples emerging from the Ultraclave.

After digestion, the samples emerged in various degrees of light yellow solutions as seen in image 3.4. No solution showed any remaining fragments of undigested oil.

The samples were diluted to 60 mL in a small Teflon bottle which had been stood with milli-Q water and approx. 4 mL HNO_3 overnight to remove any residues. The same bottle was rinsed twice in milli-Q water and shaken dry between each sample. Dilution was done by taring the weight with the bottle on, adding the sample, rinsing the sample glass twice with milli-Q water, adding this rinsing water to the same bottle and then filling it up until 61 ± 0.3 g. was reached and the bottle was capped and lightly shaken. The quartz sample glasses were then filled with milli-Q water and 1 mL HNO_3 and stood overnight awaiting the next round of samples.

15 mL, marked PP-vials were then rinsed twice with the diluted solution before they were filled up with the last 15 mL, capped and stored for ICP-MS analysis. Blanks were included to calculate a baseline and ensure instrument stability.

3.3.2.a Reference material

The following reference material for the ICP-MS was used:
Conostan oil analysis standard, a paraffin oil spiked with 22 different metals;
Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V and Zn.

Ekofisk crude oil Alpha, a real but thoroughly homogenized crude oil suitable for metal analyses.

Three blanks were run each day (a total of six blanks), to ensure data quality, and investigating and correcting for baseline shifts.

3.4 DATA TREATMENT

After analysing all samples according to the description above, the results had to be modified and interpreted. This is briefly explained in the following subchapter.

3.4.1 COSIWEB

All chromatograms were visually inspected for trends and anomalies before anything else was conducted. Some information about degree of weathering can be inferred from the distribution or lack of hydrocarbons in the GC-FID chromatogram. Weathered oil will typically contain no significant amount of hydrocarbons below C15 (CEN, 2012). Another interesting feature is the unresolved complex mixture (UCM), where several humps might indicate a mixture of oils, typically bunker oils. This has, however, been seen in crude oils as well, after wax precipitation (Wang and Stout, 2007). Large UCM humps are often indicative of a large degree of biodegradation and photooxidation of the sample (Dutta and Harayama, 2000).

The retention time of pristane and phytane for all GC-FID chromatograms were noted before the files from both GC-FID and GC-MS-SIM were converted to .AIA files, renamed according to COSIWeb protocol, and uploaded into the COSIWeb database. The reference oils and spill oil samples were inspected first, and an average retention time for the various biomarkers used by the database could be identified and labelled. This was then used as a guideline to label the more difficult cases with some of the heavily weathered oils, and was possible because all the samples were analysed under the same conditions over a short period of time.

Patience and accuracy during identification was important as all the data and ratios used later stem from this peak identification and adjustment. For cases of doubt, the original GC-MS-SIM files were inspected, and the average m/z for the peak in question identified. COSIWeb then integrated the marked peaks, calculated all the 29 most common diagnostic ratios and was able to compute a correlation matrix to the other oils in the database using the Pearson correlation coefficient (Faksness et al., 2002; CEN, 2012, COSIWeb, 2014). This could be used to compare different oils to each other. The SINTEF-mix and n-alkane standard oils were used to calculate a signal/noise ratio, which could be used to estimate certain peaks as below the detection limit.

Certain ratios were not always present in all the oil samples in the study, but not to such a large degree that they should be excluded from the study based on statistical precautions (Reimann and Filzmoser, 1999).

3.4.2 CEN-METHODOLOGY

Despite limited experience with the method, a visual inspection of the chromatograms along with the diagnostic ratios was attempted in order to identify the weathered oils. Unknown oil samples from the field work were classified as "non-NS crude", "crude", "bunker" and "unknown" to the best of the author's ability and by using the correlation comparisons provided by COSIWeb. Some samples were also labelled as "not oil", because they didn't show the typical n-alkane pattern common to hydrocarbons, or significant levels of biomarkers. Examples of the typical n-alkane pattern can be seen in image 3.5 and 3.6 below.

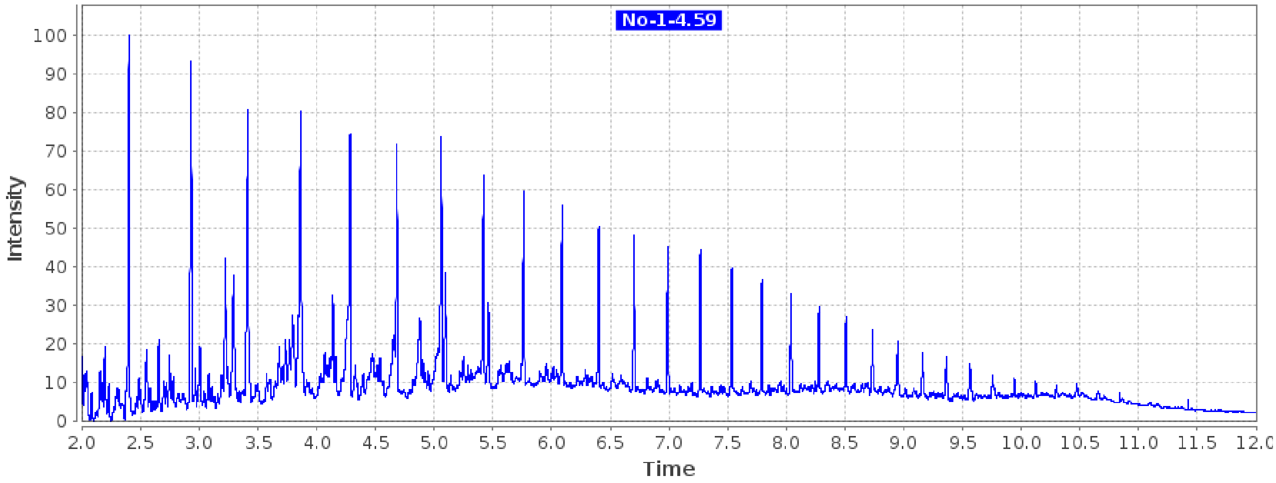


Image 3. 5 - A GC-FID chromatogram of the fresh crude oil Luno, showing the n-alkane pattern.

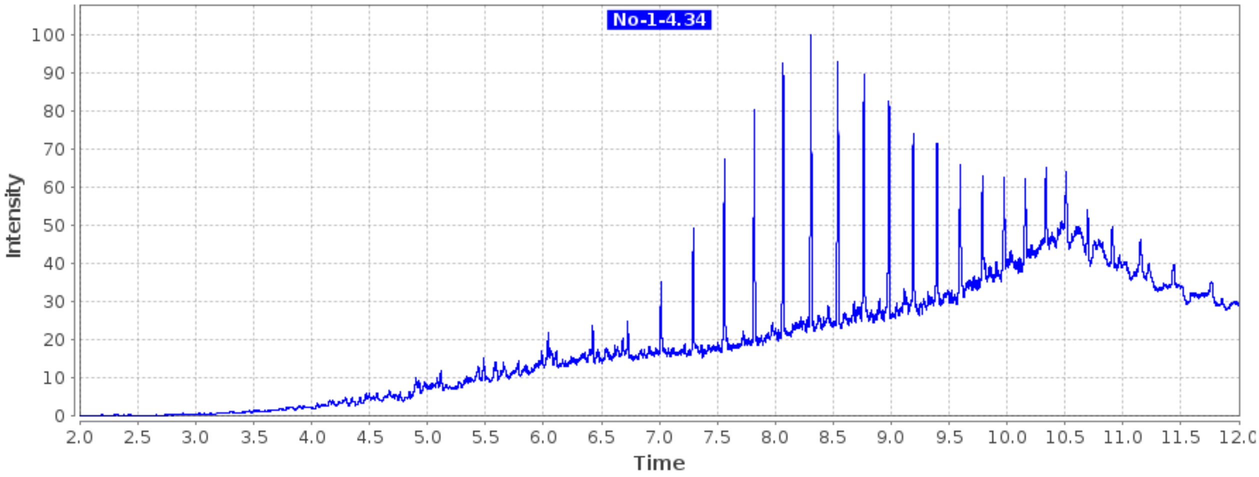


Image 3. 6 - A GC-FIC chromatogram of unknown sample 37 from the field work.

Despite being heavily weathered, the n-alkane pattern in image 3.6 is still obvious. Image 3.6 also displays a much more distinct UCM hump compared to image 3.5, which is typical when comparing fresh crude to weathered oil. Some key factors for determining class can be found in table 3.2. All biomarker abbreviations used in this study are explained in Appendix C. An example of “not oil” can be seen in image 3.7. The lack of n-alkane pattern and unconnected peaks along with lack of response in the GC-MS ion-specific chromatograms classifies this as a “not oil” sample. The oscillating peaks seen past 9 minutes are mainly column bleed and noise from the instrument.

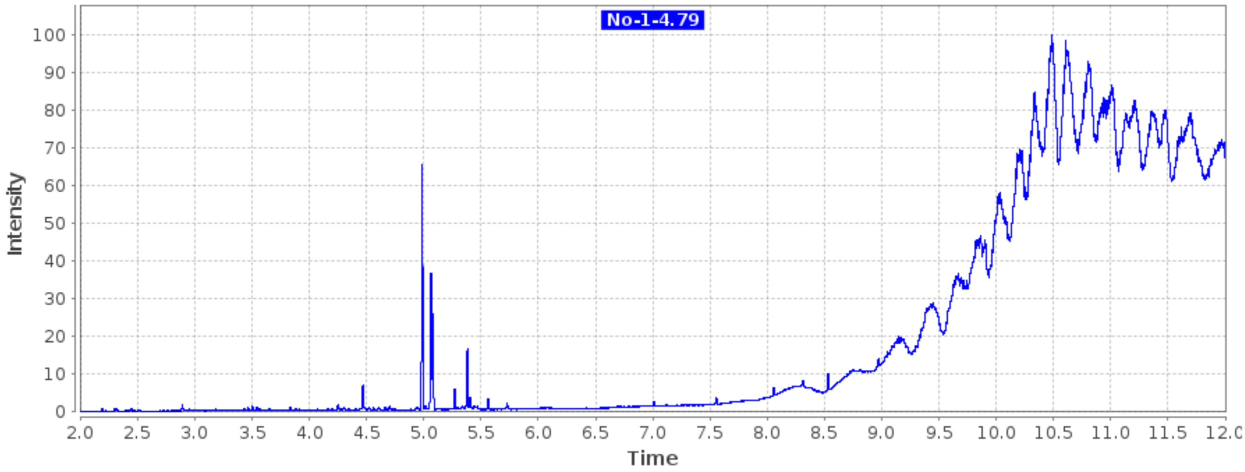


Image 3. 7 - A chromatogram of unknown sample 43 classified as “not oil”.

Table 3.2 - Particularly identifying biomarkers with regards to classification.

Biomarker	M/z	Explanation
Oleanane (30O)	191	Rarely found in NS oil and considered a marker for “non-NS” (Faksness et al., 2002).
Gammacerane (30G)	191	Indicates stratification of the water column and most commonly found in oils from the Middle East (Sinninghe-Damasté et al., 1995).
Retene	234	Broken down during oil refining, only found in crude oils, but is not present in all crude oils (Peters et al., 2005).
MetylPhenanthrenes (MP’s)	192	If 3MP and 2MP are taller than 9/4MP and 1MP it is generally considered a bunker oil and vice versa (Faksness et al., 2002).
MetylAntracene (MA)	192	Formed during refinery processes, high levels indicate bunker fuels (Faksness et al., 2002).

Once each unknown oil had been assigned to a class (“non NS crude”, “Crude”, “Bunker” and “unknown”), this information could be imported into a spreadsheet for further work in the multivariate analysis statistical tool, The Unscrambler X 10.3.

Throughout the identification, comparison to samples previously identified by experienced scientists was indispensable. Several examples can be found in CEN (2012) and Wang and Stout (2007).

3.4.3 METALS

All results from the ICP-MS instrument were corrected for their corresponding blanks and converted from µg/L to µg/g by senior engineer Syverin Lierhagen at NTNU. Mr. Lierhagen also calculated lead isotope ratios and the Pearson correlation between each measured element.

Subsequently, the LOD was calculated for each metal. This was either the Practical-LOD (P-LOD, 3 * standard deviation for the blanks) or Instrument-LOD (I-LOD, determined by the make and brand of the instrument), whichever is greater. All LOD's can be found in Appendix D. Measurements below the LOD were removed from the sample set. After inspecting the distribution of samples, all sample concentrations were log-transformed as per equation (2.12).

The metals were then inspected, first by descriptive statistics and histogram to get a feel for the data, and later by the Kolmogorov-Smirnov test of normality (equation 2.13). Variables were not carried through to PCA or PLS-R analysis, unless they were normally distributed within a 5 % significance level. Samples exceeding this level were either subject to more pre-processing, or eventually excluded from the analysis. Samples carried through for more analyses were standardised per equation (2.14).

3.5 ANALYSIS OF MULTIVARIATE DATA

MVA was done with the program The Unscrambler X, which is a user friendly program developed by CAMO Software AS. MVA was performed on all samples in this study and is an important tool to support the inherently more subjective classification by the CEN-methodology. Work on implementing MVA on DR's has previously been initiated by Kamalia (2011). After building a model, MVA could also be used to suggest another classification for the samples labelled "unknown" or help defend or change the classifications made by the analyst.

3.5.1 PRE-PROCESSING OF DATA

Pre-processing of data was primarily done in excel. All data was inspected visually and through descriptive statistics, which contains parameters like average, median, SD, RSD and skewness, to look for outliers or extreme RSD values, indicating unreliable data.

Samples below LOD (ICP-MS) or biomarkers having a response no more than 3 times the signal to noise ratio (GC-MS) were removed, and any variable where more than 25 % of samples were missing were removed from subsequent analysis, and the remaining samples below the LOD were given values at 50 % of the LOD in question (Reimann and Filzmoser, 1999).

Normal distribution was investigated by histogram plots and Kolmogorov-Smirnov tests for the different variables. Non-normal variables were not carried through to PCA and PLS-R analyses, because both these techniques assume normally distributed data, and might return a faulty result if that is not the case. For ICP-MS, all data was log-transformed to approach normality. To allow each variable to contribute equally to the model, data was typically standardised after an initial inspection of the data.

3.5.2 PRINCIPAL COMPONENT ANALYSIS

PCA was done early with all data sets to get an initial impression of the data after descriptive statistics. If large skewness or obvious outliers were observed, the data either needed more pre-processing, or the outliers were removed in an attempt to look for trends underneath the outlier. Typically seven PC's were considered more than enough to cover the most interesting trends. The scores plot distribute the samples according to their variance, while the loadings plot distribute variables in a similar fashion; similar samples cluster together, while different samples keep a distance.

Various rotations of the PCA plots were attempted to look for hidden structures in the plots, as well as the most common form of rotation, Varimax rotation, which rotates the PCA in such a way that the total sum of variation in the scores and loadings are maximised, as opposed to normal PCA, which seeks to explain the most variation in a subsequent fashion.

3.5.3 PARTIAL LEAST SQUARES

After finding an agreeable PCA model for the biomarker analysis, the metal ratios were used as the fixed response matrix Y, while the DR PC's were plotted against as the predictor matrix X using the "leave one out" method. This is the PLS-R method, and can be used to investigate if variation found in X can explain variation found in Y.

To investigate whether clusters observed in PCA are really different, PLS-DA can be used. It uses the exact same algorithm as the PLS-R model, but rather than using PC's for DR's to investigate the information found in the metal ratios, the PLS-DA takes a classification matrix in the response matrix Y. This classification matrix could for instance be -1 for crude oils and +1 for bunker oils, but the numbers don't really matter, as long as they are different.

The data set was also split into smaller parts in order to simplify and investigate particular trends.

3.5.4 RARE EARTH ELEMENTS

Another promising classification method included using REE's. To account for variation and concentration increase caused by extensive weathering, the REE samples were normalised against the average chondritic meteorite samples analysed by Evensen et al (1978). To approach normality, the data was log transformed and inspected for normality by Kolmogorov-Smirnov tests of normality. The data could then be plotted, manipulated and explored. After the assessment of normality, the data was plotted by PCA and inspected.

4. RESULTS

In the chapter, an attempt to present the most essential results of the data treatment and multivariate analysis is made. Data is typically presented in plots with a short description illuminating the key features in the data.

The method chosen for this study was sadly not optimal for the metal analysis of the fresh crude oils, which contain concentrations significantly smaller compared to their weathered counterparts. With an average of 67 % of the measurements of the fresh crude oils below the LOD, which accounted for more than 86 % of the samples below LOD in the total sample set, the fresh crude oils had to be excluded from the study. Since metal analysis was the key focus in this study, they have also been excluded from biomarker analysis as such data on fresh crude oils is presented extensively elsewhere.

4.1 CEN-METHODOLOGY

The 46 unknown oils in this study were identified according to CEN guidelines with the author's limited experience in table 4.1 as follows. All GC-FID chromatograms can be found in Appendix E. The group "Crude" has previously been coined as "NS crude" by Henriksen (2012) and Ďuricová et al. (2012), but the author feels more comfortable just calling them (possible NS) crude oils, while oils with 30G and 30O peaks are coined non-NS crude oils.

Table 4.1 - The 46 unknown oil samples and their classification. NS = North Sea.

Classification	Sample
Non-NS crude	01, 05, 07, 11, 12, 16, 17, 19, 22, 26, 29, 39, 44, 45
Crude	03, 09, 18, 21, 23, 30, 32, 35, 38
Bunker	02, 04, 06, 20, 25, 28, 31, 34, 36, 37, 42
Unknown	08, 13, 15, 33, 40, 41, 46
Not oil	10, 14, 24, 27, 43

For the Full City and Server samples, the previous work done by Almås et al. (2007), Faksness et al. (2009) and Kamalia (2011) was used, a summary can be seen in table 4.2 and 4.3.

Table 4.2 - The chosen spill samples in this study from Full City. N/A indicates no information was available.

Sample	Information	Distance from wreck (Kamalia, 2011)	Description taken from Faksness et al (2009).
47	Reference 1	3.3 km	Krogshavn. “20L smooth emulsion pumped up from the sea in Krogshavn.”
48	Reference 2	N/A	Såstein. “Oil from within havarist”
49	Match to ref. 2	9.8 km	“1-15 mm thick, taken in Steinvik in Ødegårdsfjord, Nevlunghavn.”
50	Match to ref. 1	3.7 km	Langesund. “Langesund bad, 1 mm. Krogshavn.”
51	Match to ref. 2	190 km	“Oil with traces of free water.”
52	Partial match to ref. 2	115 km	N/A

Table 4.3 - The chosen spill samples in this study from Server. N/A indicates no information was available.

Sample	Information	Distance from wreck (Kamalia, 2011)	Description taken from Almås et al (2007).
53	Reference	N/A	“Sample taken from tank 3.”
54	Reference	N/A	“Emulsion taken from skimmer head on board KV Eigun.”
55	Match	N/A	“Emulsion taken from the sea by KV Ålesund.”
56	Match	180 km	“Oil sample, Kvamsøy, Sande county.”
57	Non-match by CEN, match by MVA	165 km	“Oil sample from sandy shore, Selje county.”
58	Match	N/A	“Emulsion from crack in the rocks. Only patch wise oil in the area around the crack.”
59	Match	N/A (far, far off)	“Oil sample, Stongholmviksjø, Bømle county.”
60	Match	125 km	“Oil sample from Vetvika, Bremanger county, Nordfjord.”

In the table 4.4, all ratios used by COSIWeb are explained. Explanations for all abbreviation used can be found in Appendix C.

Table 4.4 – Explanation of the 29 DR's used by COSIWeb, all abbreviations are explained in Appendix C.

DR	Ratio	DR	Ratio
C17/Pr*	C17/Pr (GC-FID)	TARC28	TARC28/TARC26+TASC27
C18/Ph*	C18/Ph (GC-FID)	C17/Pr	C17/Pr (GC-MS-SIM)
Pr/Ph*	Pr/Ph (GC-FID)	C18/Ph	C18/Ph (GC-MS-SIM)
Ts	Ts/Hop	Pr/Ph	Pr/Ph (GC-MS-SIM)
Tm	Tm/Hop	2MP	2MP/1MP
28ab	28ab/Hop	MA	MA/1MP
29ab	29ab/Hop	4MD	4MD/1MD
30O	30O/Hop	2MF	2MF/4MPy
31abS	31abS/Hop	B(a)F	B(a)F/4MPy
30G	30G/Hop	B(b+c)F	B(b+c)F/4MPy
27dbR	27dbR/27dbS	2MPy	2MPy/4MPy
27bb	27bb/29bb	1MPy	1MPy/4MPy
TASC26	TASC26/TARC26+TASC27	Retene	Retene/Tm-Phe
TASC28	TASC28/TARC26+TASC27	BNT	BNT/Tm-Phe
TARC27	TARC27/TARC26+TASC27		

After importing the DR's from COSIWeb and separating the samples into the classes in tables 4.1-4.3, RSD was calculated and presented in table 4.5. Several trends can be observed in this table, such that the RSD for Full City and Server are generally much lower, showing a stronger trend, compared to the average.

This is expected from samples with a common source. The group non-NS crude oils display larger variation compared to the other weathered samples, indicating a large within-sample variation and probably a lot of noise and very different samples. If these samples have travelled by currents as opposed to being released by ships, they would have had to travel quite the distance, and this result would not be surprising. Variables with a low RSD for one group compared to the total are expected to play a role in the differentiation of that specific group in the later MVA.

Table 4.5 - RSD of DR’s of the samples classified in tables 4.1-4.3. Abbreviations are explained in Appendix C.

RSD %	Total n=54	non-NS n=14	Crude n=9	Bunker n=11	Unknown n=7	Full City n=6	Server n=7
C17/Pr*	63.1	47.5	40.3	36.8	45.0	30.6	11.7
C18/Ph*	78.0	127.2	51.9	65.8	41.2	31.2	12.9
Pr/Ph*	112.7	173.7	30.2	48.1	48.8	16.4	7.2
Ts	31.4	27.4	26.0	31.2	42.4	11.1	4.5
Tm	29.6	24.3	41.3	28.7	35.2	8.5	4.7
28ab	94.8	129.2	36.6	46.1	76.3	6.4	7.2
29ab	14.2	22.7	37.6	16.6	19.8	4.5	4.3
30O	72.4	92.7	282.8	54.7	140.7	48.6	9.3
31abS	13.9	16.4	14.7	21.2	16.0	5.2	5.2
30G	35.7	38.3	40.7	28.6	54.4	4.4	5.2
27dbR	4.2	20.2	14.6	33.3	26.7	5.7	4.8
27bb	13.6	19.1	25.8	18.7	30.4	6.4	5.7
TASC26	46.1	41.0	53.5	20.3	66.1	11.9	4.4
TASC28	18.6	19.6	20.7	23.1	20.8	5.5	1.4
TARC27	11.7	14.7	5.4	8.8	27.2	4.8	3.1
TARC28	13.9	19.2	18.9	23.6	12.3	7.2	3.4
C17/Pr	145.0	92.4	145.9	98.8	74.7	38.1	14.2
C18/Ph	143.3	113.3	148.5	114.2	150.2	36.2	13.3
Pr/Ph	64.5	45.7	30.9	40.5	55.7	14.3	3.6
2MP	45.3	72.5	58.2	41.7	88.5	13.2	12.4
MA	177.3	132.0	204.3	71.1	158.1	43.2	20.0
4MD	37.2	46.6	40.7	48.0	37.4	11.3	8.1
2MF	46.6	97.7	52.3	53.5	127.0	5.8	0.0
B(a)F	60.7	81.1	61.7	63.8	140.6	13.1	10.1
B(b+c)F	91.7	100.8	126.7	83.2	186.0	10.8	16.6
2MPy	41.1	48.7	26.6	34.7	58.0	3.4	3.8
1MPy	21.5	45.9	38.3	24.2	53.9	3.8	3.9
Retene	193.1	266.3	72.3	N/A	N/A	N/A	N/A
BNT	56.1	69.0	62.1	44.8	48.9	9.5	10.7

4.1.1 COSIWEB

One of the many interesting things about using a database such as COSIWeb, are the many possibilities it offers beyond the original dataset. For instance, when comparing any sample, COSIWeb will calculate and return the Pearson correlation for 50 of the most similar oil samples in the entire database. This is very useful when working with a spill or doing Round Robin tests, but could also show underlying trends of oil spill migration, and help identify unknown “mystery” spills.

In this chapter, the spills Full City and Server are first presented with their COSIWeb correlations to give an impression about what a normal range for similar samples might be expected to be, before some of the most interesting correlations for the weathered samples are presented. The correlation values are calculated by COSIWeb based on RD between the DR's of two samples.

4.1.1.a Full City

In the table below (table 4.6), the two reference samples 47 and 48 are presented with their corresponding "best match" correlation values.

Table 4.6 – Reference sample 47 and 48 from Full City with the ten most similar matches according to Pearson correlations in COSIWeb. FC = Full City, S = Server.

Sample	Best match	Correlation	Sample	Best match	Correlation
47	48 (FC)	0.9974	48	47 (FC)	0.9974
	50 (FC)	0.9952		50 (FC)	0.9962
	Lv-1-101.7	0.9943		51 (FC)	0.9950
	49 (FC)	0.9934		49 (FC)	0.9950
	Lv-1-101.3	0.9929		59 (S)	0.9928
	51 (FC)	0.9918		Uk-1-332.2	0.9923
	Fi-1-3.7	0.9910		De-1-985.6	0.9914
	De-1-1117.6	0.9907		De-1-184.1	0.9913
	De-1-184.1	0.9904		De-1-178.1	0.9906
	De-1-178.1	0.9901		Fi-1-3.7	0.9906

These samples are not all from the same oil but it is interesting to look at the similarities.

Addressing sample 47 first, the samples Lv-1-101.7, Lv-1-101.3 and Fi-1-1117.6 are all from the same Round Robin test (RR 2013, source 3), and the results indicate that this sample was indeed from Full City. The samples 48, 49, 50 and 51 are scoring high, as one would expect from samples of similar origin. Inspection of the DR's and m/z chromatograms of De-1-1117.6, De-1-184.1 and De-1-178.1 reveal that De-1-1117.6 might very well be from Full City as well, while De-1-184.1 and De-1-178.1 are displaying some important differences, such as different 30O ratios. Even so, the last two are very similar to sample 47 in several other aspects.

Sample 48, on the other hand, is matching up with samples 47, 49, 50 and 51 from Full City before anything else. Next on the list at 0.9928 is sample 59 from Server. Inspection of the m/z chromatograms indicate that they are quite similar, with only differences in 30O and 30G pulling them apart. This does not have to mean that anything beneath sample 59 in correlation is not Full City. On the contrary, sample Fi-1-3.7, which was identified as a Round Robin sample probably from Full City, can be seen at the bottom of the table.

Between sample 59 and Fi-1-3.7 are some interesting samples. First off, Uk-1-332.2 is a sample which was taken off Fulmar Feathers in Eshaness on the Shetland Isles. In this sample, most biomarkers are similar (within the 14 % RD defined by CEN), with some differences including MA, 30O and 28ab. Both the Shetland Isles and the West coast of Norway are close to each other, and lie along the North-Atlantic current, making it quite likely that samples could migrate to and from these two sampling spots.

It is interesting and invites caution to see that samples De-1-184.1and De-1-178.1shares the majority of DR's with Full City (21 out of 29 have less than 14 % RD), but are bunker fuels from a different ship.

As interesting as similar samples are, it might be just as interesting to investigate the sample which is missing. Sample 52 is also a sample from the Full City accident, but neither of the reference samples lists this sample among the 50 samples COSIWeb presents correlation data on. Sample 52 was identified as partial match by the report made by Faksness et al. (2009). Even so, not even one of the other Full City samples show up among the 50 best correlations presented by COSIWeb. The five best for sample 52 are presented below in table 4.7.

Table 4.7 - Sample 52 from Full City with the five most similar matches according to Pearson correlations in COSIWeb.

Sample	Best match	Correlation
52	37	0.9594
	Nl-1-3307.5	0.9571
	Uk-1-332.5	0.9526
	De-1-155.43	0.9399
	De-1-1015.2	0.9391

One of the first things to notice here is how none of these correlations come even close to the correlations for sample 47 and 48, where the 10 best correlations were all above 0.99. The first sample on the list, sample 37, does actually show some striking resemblance to sample 52. The general pattern of biomarkers and GC-FID are all quite similar, although small variances due to weathering cannot conclude these as more than "partial match".

Sample 52 was sampled far from the original spill (115 km), 19 days later (Appendix A). Sample 51 was sampled further from the spill (190 km), indicating that other factors such as contamination or mixing might play a role as well. The little information which could be gathered about the other samples indicates that Nl-1-3307.5, De-1-155.43 and De-1-1015.2 are all heavy fuel oils (HFO's) from different spills or ships.

The Uk-1-332.5 sample is from a Gannet feather off Burravoe in Shetland and displays several similar characteristics. Even with heavy weathering, the two are considered "partial match".

4.1.1.b Server

For Server, there was only one reference sample, sample 53, which can be seen in table 4.8 below.

Table 4.8 – Reference sample 53 from Server with the ten most similar matches according to Pearson correlations in COSIWeb. S = Server.

Sample	Best match	Correlation
53	56 (S)	0.9987
	60 (S)	0.9984
	55 (S)	0.9980
	58 (S)	0.9968
	54 (S)	0.9958
	De-1-981.9	0.9953
	Ee-1-6.6	0.9948
	De-1-1012.4	0.9946
	Ee-1-6.1	0.9934
	Ee-1-6.8	0.9932

The first five correlations are other Server samples and strong matches. For the remaining samples, it is interesting to see that all samples from Estonia (Ee) are from the same project and are categorised as HFO's. The Estonian samples do, however, all have 30O DR's well over twice that of sample 53, indicating that the samples are not from the same source. The two German samples (De) do not show any 30O peak, which makes them a non-match as well, along with other differences in the chromatograms.

Similar to the Full City samples, the samples which are not present might be just as informative as those that are present. Sample 57 shows up in the correlation list all the way down at number 46 with a correlation of 0.9842, while sample 59 does not show up at all. The five most correlating samples for sample 57 and 59 can be seen in table 4.9 below.

Table 4.9 – Server samples 57 and 5 with their five most similar matches according to Pearson correlations in COSIWeb. FC = Full City and S = Server.

Sample	Best match	Correlation	Sample	Best match	Correlation
57	54 (S)	0.9911	59	48 (FC)	0.9928
	55 (S)	0.9897		De-1-155.55	0.9924
	58 (S)	0.9897		De-1-155.44	0.9905
	60 (S)	0.9895		50 (FC)	0.9900
	56 (S)	0.9889		Uk-1-332.2	0.9899

It seems that even though the reference sample 53 did not match well with sample 57, sample 57 is correlating well with the other samples. This could be due to sample 57 being sampled from a sandy shoreline after travelling 165 km. The reference sample might have been too different, making it easier to correlate with the other spill samples which had suffered some weathering.

Sample 59, on the other hand, was found so far from the accident, that they stopped counting km. The sample was concluded a match to the other Server samples by Almås et al. (2007), but looking at the chromatograms and DR's from sample 48 (Full City), they are overall similar, with only 2 samples above the 14 % cut-off, which is below the "positive match" threshold.

The German samples do not share these similarities, and although the chromatograms share similarities, the DR's clearly indicate non-match. Similar to sample 48, sample 50 shares several chromatographic features with sample 59, but here the subtle differences possibly caused by weathering means a positive match cannot be concluded. Lastly, the Fulmar feather sample from Eshaness, Shetland is too weathered or diluted to conclude anything from the chromatograms.

4.1.1.c Weathered samples

When looking at the correlation data and chromatograms for the weathered samples, there are a lot fewer relevant matches. After looking at the correlation data and chromatograms for the Full City and Server samples, a cut-off at 0.95 was decided when deciding which correlations to inspect further. With this cut-off level, 13 out of the 46 weathered samples returned correlation values above the cut-off. These are presented in table 4.10 along with their CEN-classification.

Table 4.10 – Weathered samples with correlation above 0.95 and their corresponding matches. C = crude, N = non-NS crude, B = bunker, U = unknown and FC = Full City.

Sample	Best Match	Correlation	Sample	Best Match	Correlation
04B	06B	0.9824	34B	De-1-178.23	0.9817
05N	04B	0.9565		De-1-178.25	0.9787
06B	04B	0.9824	36B	46U	0.9565
08U	De-1-199.1	0.9792	37B	Uk-1-332.5	0.9737
09C	Uk-1-231.4	0.9923		52FC	0.9594
	23C	0.9899	38C	De-1-56.16	0.9515
21C	De-1-1042.1	0.9726	40U	De-1-200.1	0.9620
23C	09C	0.9899	46U	36B	0.9565
	Uk-1-231.4	0.9844			

The first sample pair, 04 and 06, displays some overall similarities, but also too many differences for them all to be caused by weathering. The same can be said about the next pair, 05 and 04, which are quite different. All three samples were found on the same island, and mixing between them might account for some of the similarities.

For sample pair 08 and De-1-199.1, nothing conclusive can be said. De-1-199.1 is a crude oil, and lacks all hopanes and most of the other biomarkers. Sample 08 is too weathered and no conclusion can be reached either way.

The sample set 09, 23 and Uk-1-231.4 is the most highly correlated group among the weathered samples. They all share hopanes below the 14 % cut-off and the main differences are with the C17/Pr, C18Ph and Pr/Ph ratios, which are all gone in the weathered samples. The British (Uk) sample is another sample found on Fulmar feathers on the Shetland Isles. Weathering has altered some ratios too much to conclude a positive match, but they can all be concluded “probably match” to each other.

In sample pair 21 and De-1-1042.1, the majority (20 out of 29) of the biomarkers exceed the 14 % cut-off difference and it is a non-match. Comparing this result to the others in table 4.10, it does give the indication that perhaps correlation should be at least 0.98 for similar samples, but as seen by sample 52, weathering and contamination will have a detrimental effect on this number.

For sample 34, neither of the correlating samples (De-1-178.23 and De-1-178.25) can be concluded as matches because of weathering and low response of certain biomarkers. But both De-1-178.23 and De-1-178.25 are HFO’s, strengthening the CEN classification of sample 34 as bunker oil.

Sample pair 36 and 46 share several features, the first being heavy biodegradation and photooxidation leading to strong depletion of hydrocarbons and large UCM humps. 12 out of 29 biomarkers are slightly above the 14 % cut-off, and the samples are a classified as probable match, even though their correlation is only 0.9565.

With sample 37 and Uk-1-332.5, several features are similar. Sample Uk-1-332.5 has already been mentioned in the investigation of Full City sample 52, which is the other match of sample 37 and has already been presented. As probable matches, both sample 37 and Uk-1-332.5 might be remnants from the Full City spill.

Sample 38 does not match De-1-56.16 upon visual inspection of the chromatograms and no conclusion could be reached for sample 40 and De-1-200.1, because De-1-200.1 lacked the majority of the biomarkers.

In summary, out of the 12 weathered biomarkers which displayed Pearson correlation in COSIWeb above 0.95, 5 samples were probable matches, of which there were two pairs (09 to 23 and 36 to 46).

4.2 PRE-PROCESSING ICP-MS DATA

A fair amount of information can often be inferred by an attentive inspection of the raw data and descriptive statistics. In the first run, samples 10, 14, 24, 27 and 43 were excluded from the analysis based on GC-FID and GC-MS chromatograms because they contained little or no detectable traces of oil. Although small oil concentrations can be successfully used in biomarker studies, it is not desirable for metal studies, because it indicates that the sample contains something other than oil which might influence the results.

Another sample which was removed in preliminary analyses was the sample 58. This sample was too small to be properly analysed by ICP-MS, and data could not be acquired.

4.2.1 ON LIMITS OF DETECTION

For ICP-MS, two LOD’s are generally used; the I-LOD which is determined by the make and brand of the instrument and cannot be changed, and the P-LOD, which is found by taking the standard deviation of the blanks multiplied by 3. Neither of these is more or less wrong compared to each other; whichever number is the largest for the sample in question is the relevant LOD. All LOD’s in this study can be found in Appendix D.

After applying the LOD to all ICP-MS samples, variables with more than 25 % of the values below LOD were excluded from the sample set, as they were incapable of a normal distribution. Remaining samples which fell beneath the LOD were set to 50% of the LOD. That way they could still be included for the statistical treatment (Reimann and Filzmoser, 1999).

4.2.2 DESCRIPTIVE STATISTICS

Because biomarkers are well known descriptors of oil while metals are not, descriptive statistics were measured on the ICP-MS dataset after removing the aforementioned samples. A large difference was observed between average and median in all variables, in 33 out of 55 variables the median was less than half of the average, and in none of the variables was the median larger than the average, indicating a large skewness in the dataset and a non-normal distribution. This was confirmed by plotting histogram plots of all the variables and inspecting them visually. The concentrations of metals did not follow a normal distribution, and could not be used in their raw state to perform PCA or PLS-R.

To remedy this, a log-transformation, was performed on the raw data. This returned an average difference of 0.61 between median and average, or 10.9 % of the STD. In contrast to the raw data, which had an average difference between median and average of 75.5, or 29.3 % of the STD. The majority of the medians were still below the average values, indicating some skewness in the data still, but greatly reduced.

4.2.3 ASSESSING NORMALITY

After the log-transformation, the variables were inspected through simple histogram plots to gain a first impression. When this returned plots similar to bell curves, the more rigorous Kolmogorov-Smirnov test of normality was performed. With a significance level of 5 %, most variables were scored “Assumption of normality cannot be rejected” by the Unscrambler X.

13 variables were scored “Assumption of normality not supported” (Cd114, Ho165, Er166, Tm169, Yb172, Lu175, Au197, Mg24, V51, Ni60, Ag109, Sb121 and Ba137). Out of these, only magnesium and barium showed a “non-normal” trend among the majority of the samples, while the rest suffered from outliers. Sample 16 alone caused vanadium, nickel and antimony to fall outside the significance level due to extremely low concentrations, while sample 18 was responsible for holmium, erbium, thulium, ytterbium and lutetium. Both samples were removed as outliers and new Kolmogorov-Smirnov tests now scored cadmium, vanadium and nickel as “assumption of normality cannot be rejected”, the rest were still outside the threshold. Magnesium, barium and antimony were removed after these tests.

Although the HREE’s holmium, erbium, thulium, ytterbium and lutetium are showing signs of a non-normal distribution, it is interesting to note that it is the three Server samples 53, 54 and 55 which cause the most skewness in the lower end of the scale. It is also interesting that it is only the HREE’s which fall outside the threshold, although all the REE’s show the same trend. The REE’s are of special interest, and were not removed, but this does indicate something about the reliability of the data.

4.2.4 A SPECIAL COMMENT ABOUT THE BIOMARKER DATA

Because the biomarker data is already neatly presented in well-documented ratios, not much pre-processing is required apart from standardising the data to allow each variable to influence the model. Investigating the data through histograms and the Kolmogorov-Smirnov test did reveal that most of the data is not normally distributed. Only a handful (31abS, 30G, TASC26, TASC28, TARC28 and 4MD) were classified as “assumption of normality cannot be rejected”, within the 5 % significance level. None of the biomarkers were removed from the data set because of this, but it is worth mentioning.

This leaves a sample set of n = 52 for further analysis. This is on the borderline for defensible statistical analyses, but is assumed to be appropriate for providing assumptions and indications about trace metals in oil.

4.3 PRINCIPAL COMPONENT ANALYSIS

After inspecting the data and making sure it is of a reasonable quality, the MVA analyses can be conducted. The two are often not strictly performed one after the other, as a preliminary PCA model can often highlight issues, outliers or inconsistencies in the data. Testing different scaling and pre-processing methods such as normalisation, autoscaling, quantile normalisation, as well as different rotation modes in the PCA are all part of trying to piece together a coherent analysis. Here, some of the most essential results are presented.

4.3.1 DIAGNOSTIC RATIOS

To get a first impression of the data, it is common to plot the raw data before any scaling. This can help illustrate important elements in the dataset, although it would tend to dwarf potentially important variables. It could also help indicate whether or not the big variables are also important in classification. A PCA of the raw DR's, straight from COSIWeb, can be seen in image 4.1.

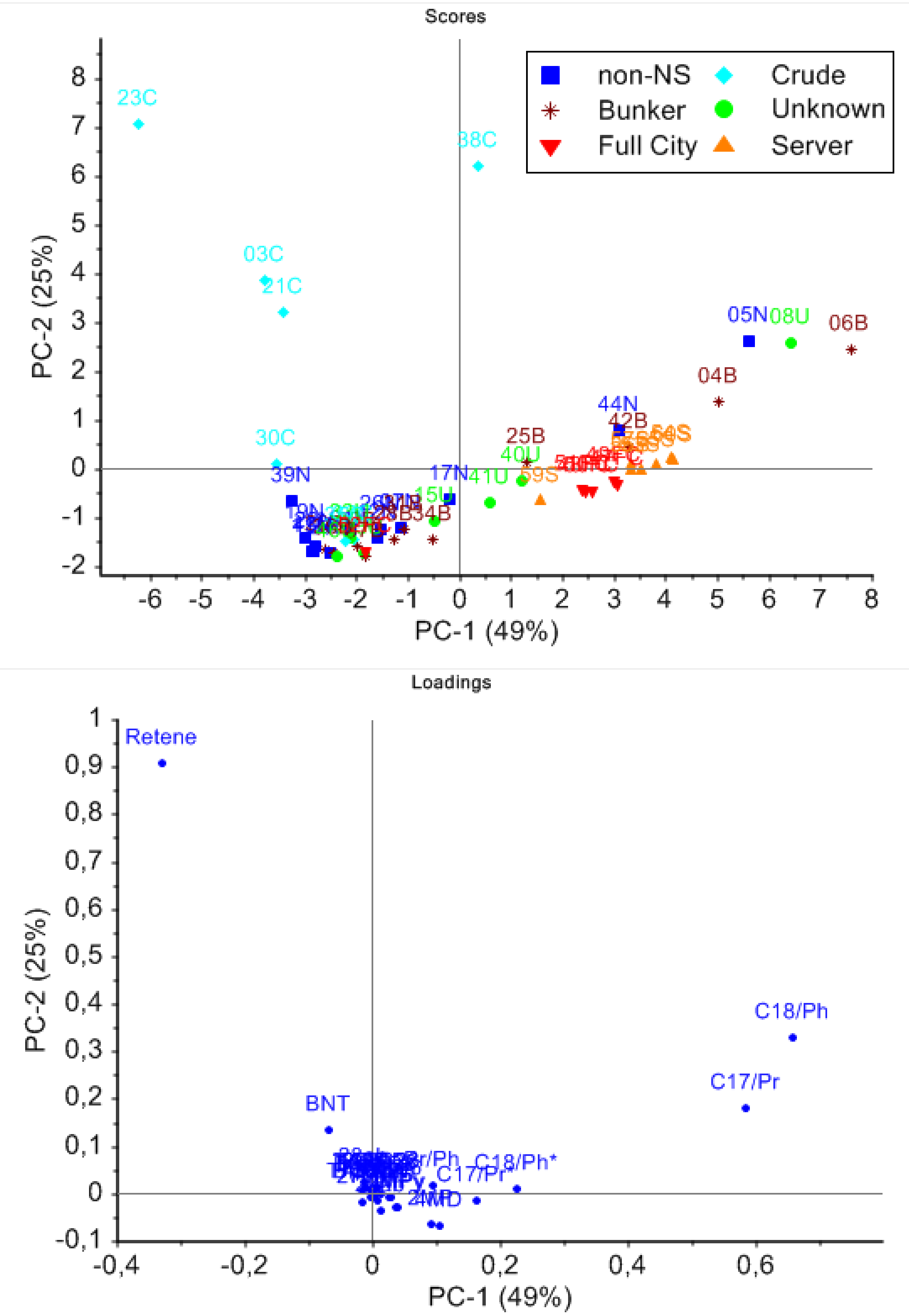


Image 4. 1 - PCA scores and loadings of DR's, PC1 and PC2. C = crudes, N = non-NS crudes, B = bunkers, U = unknown, FC = Full City and S = Server.

At least two things can be read from image 4.1. The first is that the plot is clearly dominated by 3 variables, retene, C17/Pr and C18/Ph. The other variables are largely bunched up around the origin, indicating that they have little influence over the model.

We know from inspecting the GC-FID and GC-MS m/z 85 that C17/Pr and C17/Ph are highly weathered in the weathered samples, and are not very reliable. Thus this model is far from ideal and using raw data is not feasible.

The second thing about the plot is that there appears to be a strong correlation in this dataset between the (possibly NS) crude oil group and retene. With a data set like this, it is not obvious if this could be a trend or an anomaly due to the small sample size.

After inspecting the plot for the raw DR's, the data was standardised to give each variable equal chance to influence the model. Pre-determined groups from the CEN-methodology, as well as the different spill samples can be seen in distinct clusters (image 4.2), with the exception of one Full City outlier and overlap between bunker oils and non-NS crudes. A much better classification can now be seen compared to image 4.1.

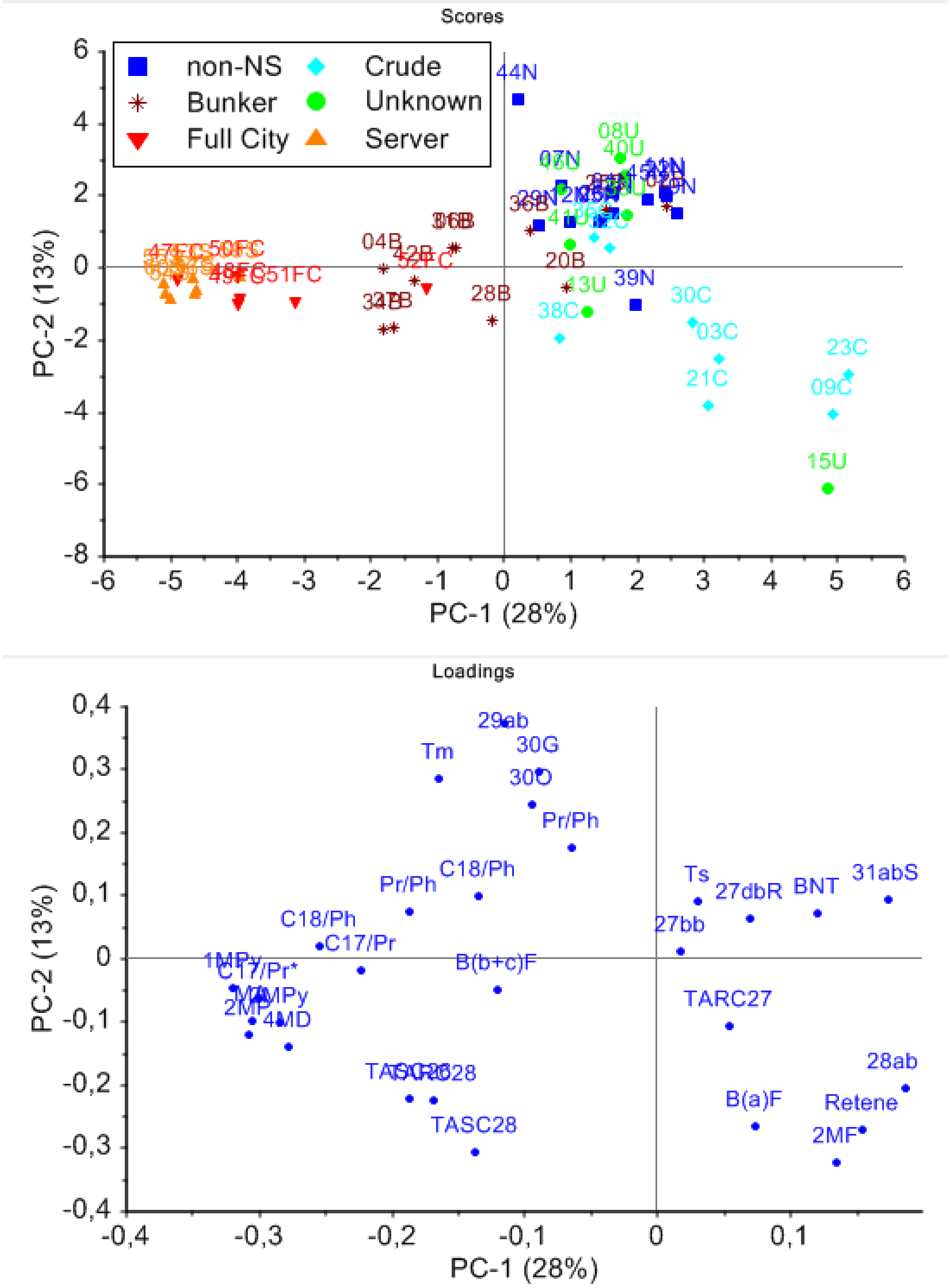


Image 4. 2 - PCA scores and loadings of standardised DR's, PC1 and PC2. C = crudes, N = non-NS crudes, B = bunkers, U = unknown, FC = Full City and S = Server.

As can be seen in image 4.2 above, PC1, which explains 28 % of the variance, appears to have something to do with weathering of the samples, while PC2, which explains 13 %, is separating the two classes of crude oils from each other. There are some variables close to the origin which are contributing little to the model (27bb, Ts, 27dbR), but most variables can be found some distance from the origin, indicating that they have an impact on the model.

Apart from sample 15, which seems to share several characteristics with the crude oil group, most of the unknown samples are found within the cluster of the non-NS crude oil group. The oils cannot be identified by this feature however, because there are also bunker oil samples and crude oil samples mixed in with the non-NS crude oil group. The spill oil samples from Server and Full City are both distinguishable and separated on the left, apart from sample 52, which has already been identified as significantly altered by COSIWeb.

The ability PC2 has to separate crude oils from non-NS crude oils can be seen even better when plotted against PC3, image 4.3. At 11 %, PC3 is still explaining a good deal of variation in the data.

In image 4.3, the non-NS crude oils are clustering along PC2, on the right. This is in contrast to the other crude oil group, which is a lot more separated. Important factors which were known previously are 30O, 30G and retene. Less known contributors are other factors along PC2, such as 28ab, 29ab and Tm.

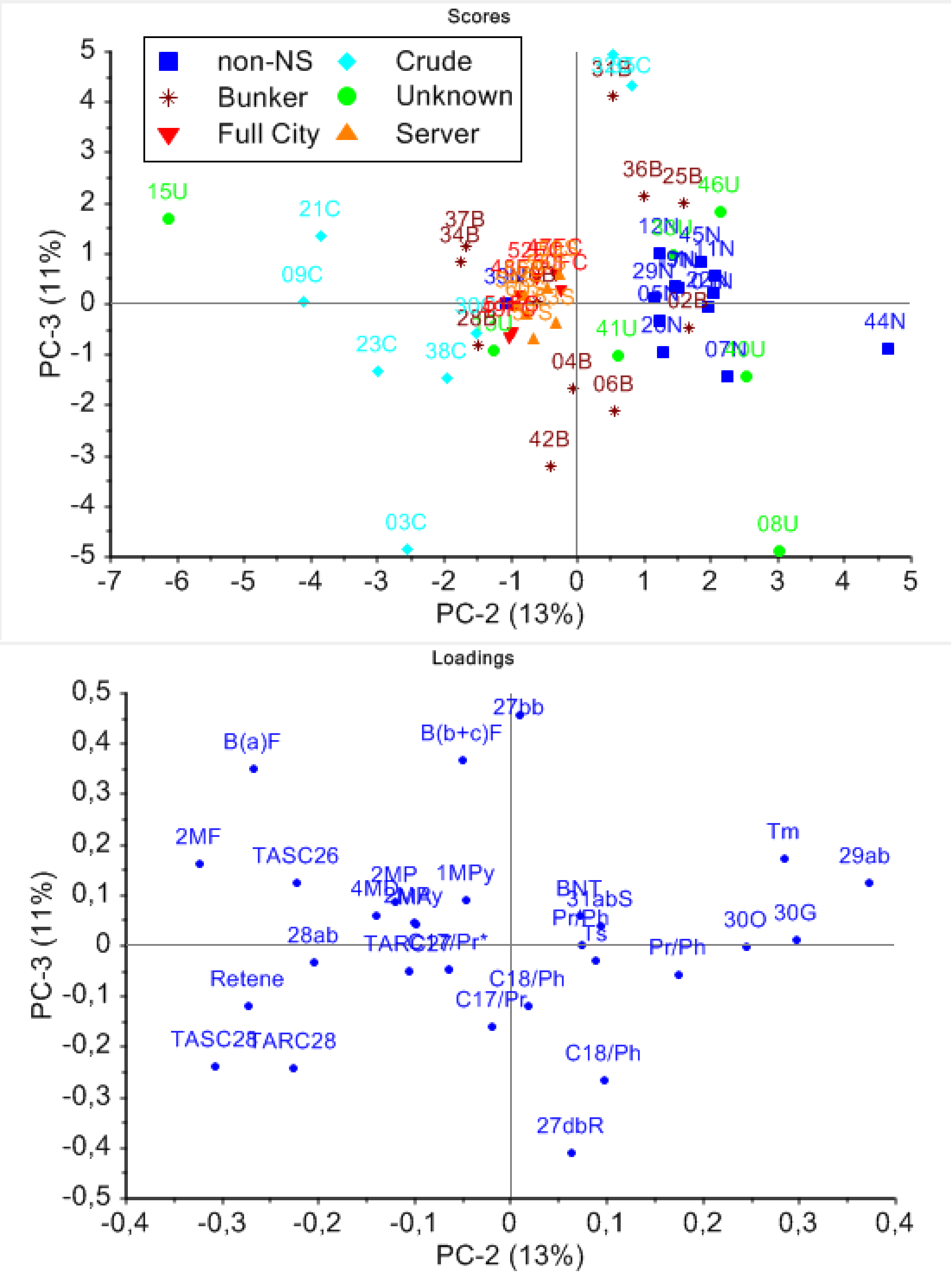


Image 4. 3 - PCA scores and loadings of standardised DR's, PC2 and PC3. C = crudes, N = non-NS crudes, B = bunkers, U = unknown, FC = Full City and S = Server.

In this plot of PC2 and PC3, all of the variables which identified the Server and Full City samples from the rest of the oils are gathered in the middle, contributing little to the plot. This strengthens the observation that PC1 is separating the different bunker oils, while PC2 is separating different crude oils. The two crudes on the top are samples 32 and 35, and are more influenced by PC3, perhaps indicating outliers, a different subgroup or just variation in the data.

4.3.2 RAW METALS

Before doing MVA on the metal data, it had to be inspected and pruned. Several metals could not be included, and the reasons are listed below.

The metals aluminium and silicon were removed due to contamination from sample containers and lab equipment. Magnesium, barium and antimony were removed because they lacked a normal distribution. Calcium, potassium and sodium were removed due to low reproducibility on the ICP-MS and their relative abundance in seawater. Wolfram, platinum, tantalum and iridium were removed because more than 25 % of the samples were below the LOD.

Of the samples left after the fresh crude oils had been excluded, only 3.7 % were below the LOD on average, which is well below the 25% required by Reimann and Filzmoser (1999) for defensible statistical analysis. The remaining samples below LOD were given values at 50% of the LOD.

In image 4.4 of log transformed metals, the classification is a lot more muddled compared to the DR analysis. This should be expected, as biomarker analysis has been optimised for their purpose, while these metals are simply being inspected for their potential use in the same field. With this in mind, it is encouraging to see that there appears to be a separation between the bunker oils in various shades of red and crude oils in shades of blue.

One thing to point out though, is that this data has not been standardised, and as such, presents only positive values. This is illustrated by the loadings plot in image 4.4, where there is no y-axis, because all variables are on the right side of the plot. This indicates that PC1 is mainly explaining the concentrations in the samples. Seeing how the Full City and Server samples are mainly plotting on the lower left, it seems as if both PC1 and PC2 are explaining some degree of weathering in the samples.

In literature, high metal content in oil is generally associated with a marine source input. If this is still reliable for heavily weathered oil samples, it might be an explanation for why the non-NS crude oil samples are divided in image 4.4, with one group (samples 11, 12, 17, 19 and 22) in the upper left, left of the crude oil samples, and the other group (samples 01, 05, 07, 26, 29, 39, 44 and 45) below the crude oil samples. It could also be indicative of weathering, as metal content would expect to increase with increasing weathering time.

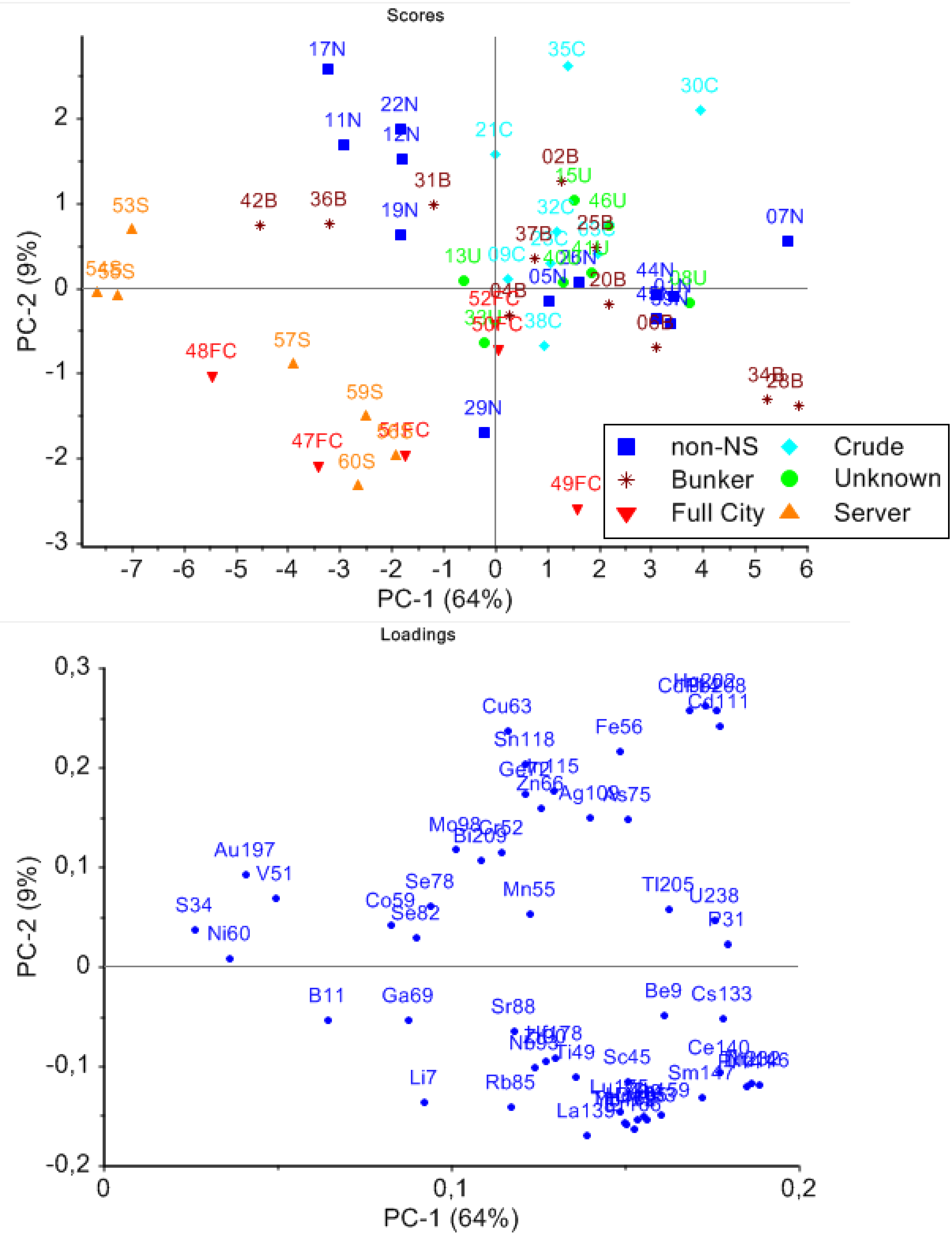


Image 4. 4 - PCA scores and loadings of log transformed metal concentrations, PC1 and PC2. C = crudes, N = non-NS crudes, B = bunkers, U = unknown, FC = Full City and S = Server.

Interestingly, PC2 and PC3 (image 4.5) appear to show some of the same ability to separate crude oils and non-NS crude oils seen by the DR's.

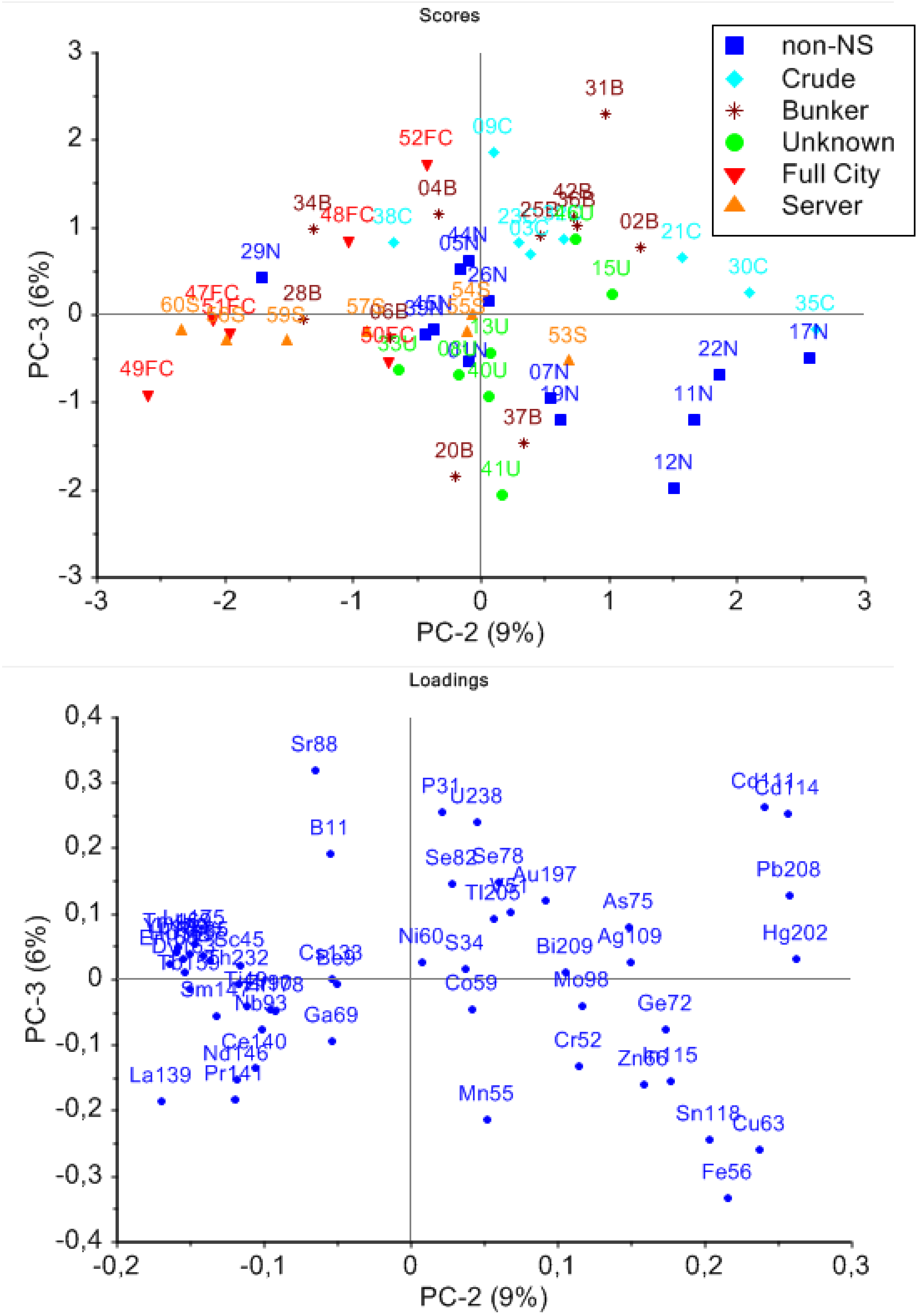


Image 4. 5 - PCA scores and loadings of log transformed metal concentrations, PC 2 and PC3. C = crudes, N = non-NS crudes, B = bunkers, U = unknown, FC = Full City and S = Server.

In image 4.5, a separation can be seen between the crude oils and the non-NS crude oils along the vertical axis of PC3. There appears to be a correlation between iron, copper and tin with several of the non-NS crude oils. These plots confirm that there is information in the metals as well.

A similar trend can be seen when standardising the metals (image 4.6). Concentration effects appear even more significant, while the metals vanadium, nickel, sulphur and gold separate slightly from the big bulk of metals on the right.

In PC2 and PC2 (image 4.7), the standardisation has caused some distinct changes. Here, PC3 appears to be able to separate Full City and Server samples on the left hand side, while nickel, vanadium, sulphur and selenium appear to correlate with some of the weathered bunker oils (samples 02, 04, 25, 31, 36 and 42). Several metals along the bottom right of the plot appear to correlate with several non-NS crudes (samples 01, 05, 07, 26, 29, 39, 44 and 45), while the crude oil samples show no distinct correlation.

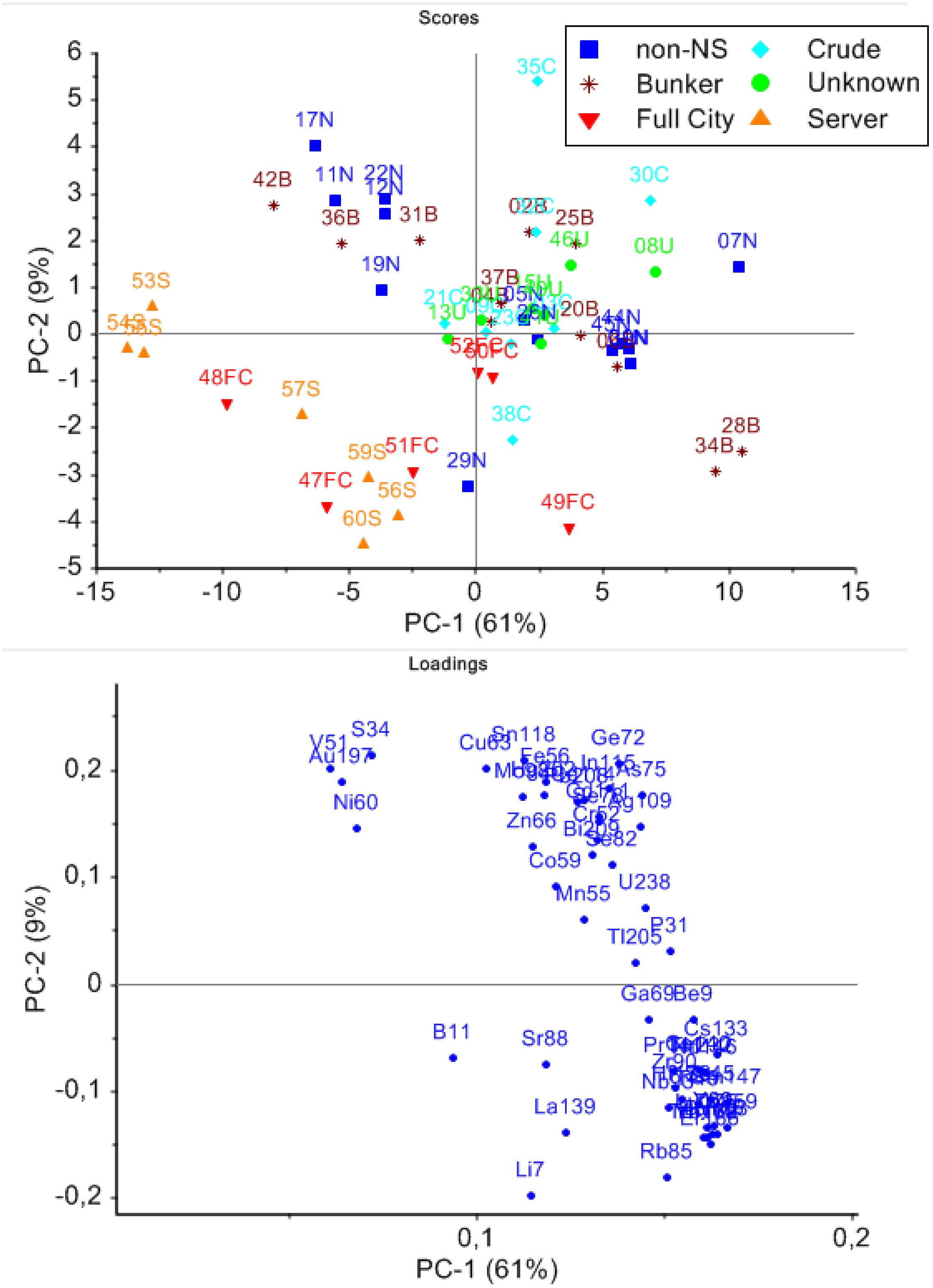


Image 4. 6 - PCA scores and loadings of standardised log transformed metal concentrations, PC 1 and 2. C = crudes, N = non-NS crudes, B = bunkers, U = unknown, FC = Full City and S = Server.

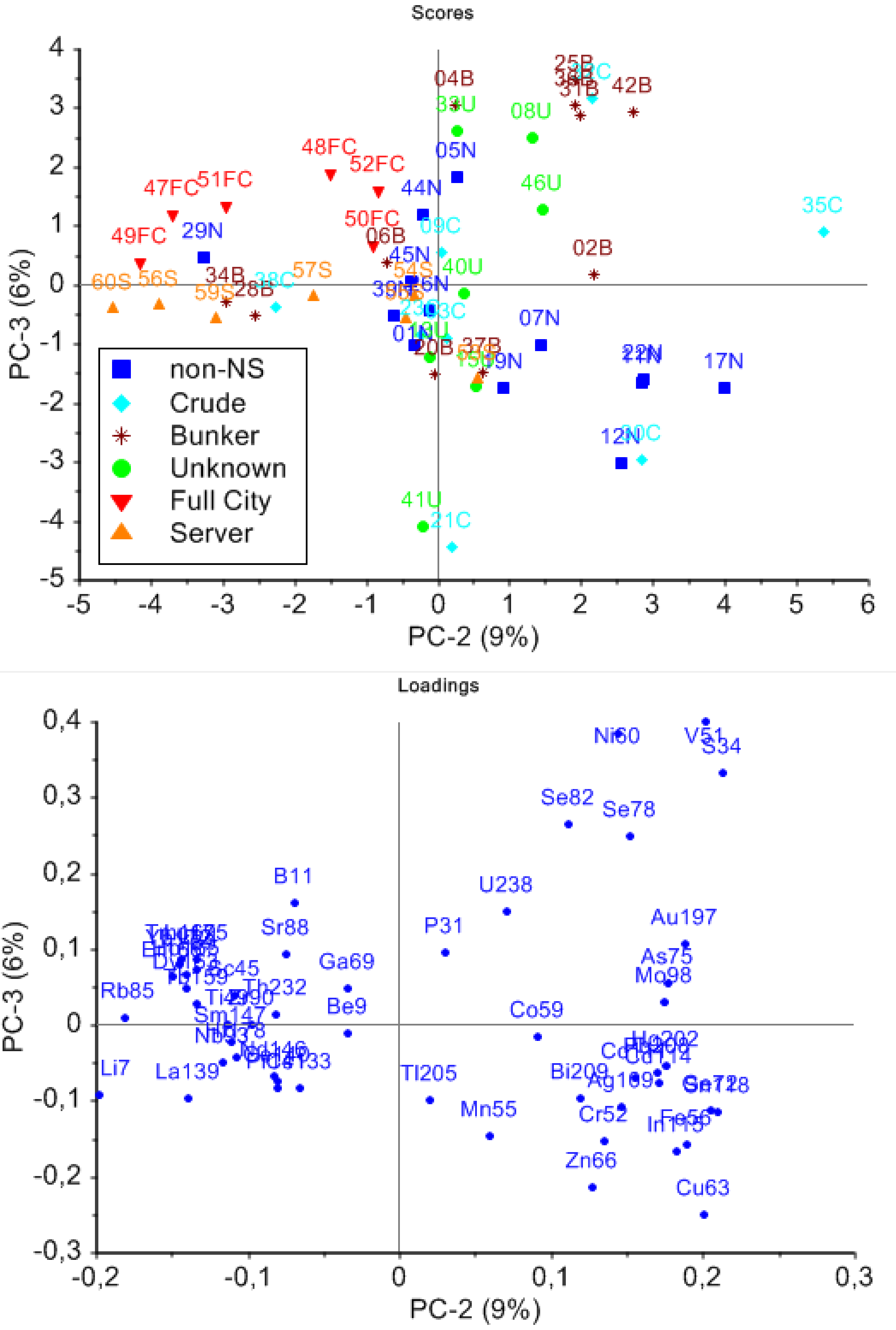


Image 4. 7 - PCA scores and loadings of standardised log transformed metal concentrations, PC 2 and 3. C = crudes, N = non-NS crudes, B = bunkers, U = unknown, FC = Full City and S = Server.

The trends seen in the metals are by far not as clear cut as seen in the DR PCA's and contains a lot of noise, but there is potential. In all plots, the REE's are clustering closely together and will be mentioned specifically in chapter 4.5.

4.3.3 METAL RATIOS AND LEAD ISOTOPES

For the ratios, choosing the most relevant ratios in a reasonable and timely fashion proved to be the most challenging. Where isotopes were available (lead, selenium and cadmium), these were preferred. From the literature, the most common elements to measure against (the denominator) in oil are sulphur, vanadium and to some degree nickel, because of their stability, relative abundance in oil and increasing concentration with increasing overall metal concentrations (Curiale, 1978; Frankenberger, 1994; Greibrokk et al., 1994, El-Gayar, 2003 among others).

Several well established ratios related to vanadium and nickel were considered especially important and given special attention. Attention was also given to copper and iron, where elevated concentrations might indicate time spent in pipelines (Dekkers and Daane, 1999). The REE's are treated separately. Lithium, beryllium and boron were excluded at this point due to the inherent uncertainty associated with measuring low mass elements. Also, because robustness is essential if one is to identify oil types with confidence, any variable with an average RSD (%) above 10 % were excluded (silver, germanium and gold). Some ratios found in the literature can be seen in table 4.11.

Table 4.11 - Suggested ratios from the literature for oil analysis with their respective source attached.

Ratio	Source
V/Ni, V/(Ni+V), Fe/V	Curiale, 1987, among others
Mn/Fe, Co/Ni, Co/Mn	Frankenberger, 1994
V/Cu, Ni/Cu, Ga/V, Co/V, Mn/V, Cu/V, Cu/Ni, Mo/(Mo+Cr)	Greibrokk et al., 1994
Ni/S, V/S	El-Gaydar, 2003 among others
U238/Pb206	Holmes, 1911

After some trial and error, the log transformed samples were organized into the following ratios, seen in table 4.12, where abbreviations used in the text are also explained. The UPb* ratio was calculated especially by senior engineer Syverin Lierhagen at NTNU, and separate concentrations of these isotopes are not available.

Table 4.12 – Explanation of metal ratio abbreviations used in images and the text.

Ratio	Abbreviation	Ratio	Abbreviation
U238/Pb206	UPb*	Ni/V	NiV*
Se78/Se82	Se*	Sc/(Sc+V)	Sc*
Cd111/Cd114	Cd*	Ti/(Ti+V)	Ti*
Mo/(Mo+Cr)	Mo*	Cr/(Cr+V)	Cr*
Zr/(Zr+V)	Zr*	Mn/(Mn+V)	Mn*
In/(In+V)	In*	Fe/(Fe+V)	Fe*
Sn/(Sn+V)	Sn*	Mn/Fe	MnFe*
Cs/(Cs+V)	Cs*	Co/(Co+V)	Co*
Hf/(Hf+V)	Hf*	Cu/(Cu+V)	Cu*
Hg/(Hg+V)	Hg*	Zn/(Zn+V)	Zn*
Pb208/(Pb208+V)	Pb*	Ga/(Ga+V)	Ga*
Bi/(Bi+V)	Bi*	Rb/(Rb+V)	Rb*
Th/(Th+V)	Th*	Sr/(Sr+V)	Sr*
P/(P+V)	PV*	As/(As+V)	As*
V/S	VS*	Nb/(Nb+V)	Nb*

Similar to the metal concentration PCA's, one of the first things to pop out in the standardised metal ratio plot (image 4.8) is the division between the different bunkers in shades of red, and the different crude oils, in shades of blue. The weathered bunker oils (stars) are making things a bit more confusing by mixing with the crude oils, indicating that the ratios might say something about degree of weathering as well.

In image 4.8, there appears to be a correlation between the MnFe* and UPb* ratios and the bunker fuels, possibly Mo* as well. On the other hand, a large amount of various ratios appear to correlate with crude oils. This could be due to the heavy legislation on desulphurisation and other removal of metals which is put on the oil refineries. The VS* ratio appears along the same axis as this cluster of metals, but on the opposite side of the loadings plot.

The reference samples for Full City (47 and 48) and Server (53) do not appear to correlate closely with their respective samples, indicating that larger sources of variation or noise is explained before more subtle factors such as this.

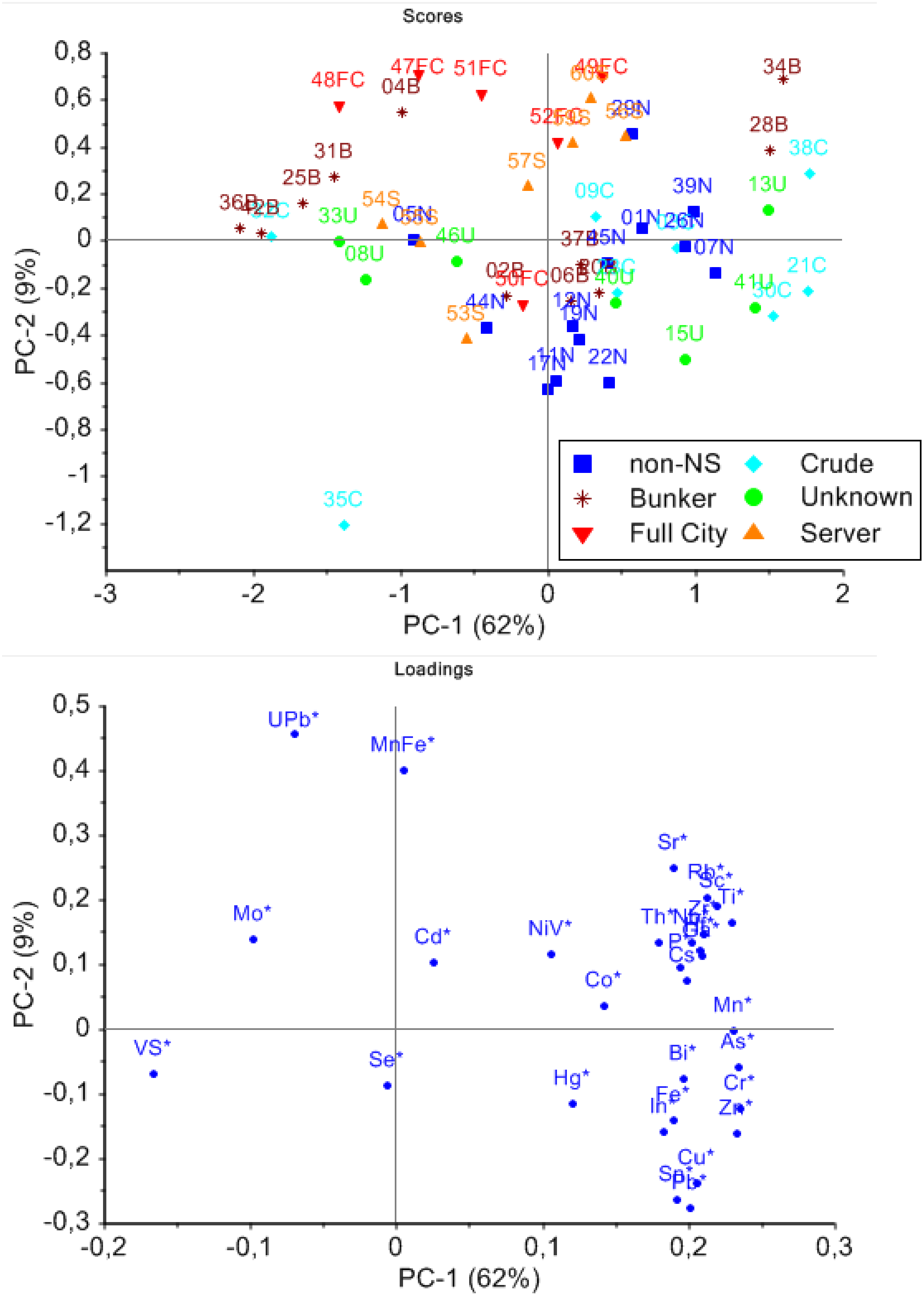


Image 4. 8 - PCA scores and loadings of standardised metal ratios, PC1 and PC2. Abbreviations explained in table 4.12. C = crudes, N = non-NS crudes, B = bunkers, U = unknown, FC = Full City and S = Server.

In PC2 and PC3 of the same plot (image 4.9) more separation between Full City and Server can be seen, compared to similar DR plots (image 4.3). It is not certain why sample 50 is and outlier, but reference samples 47 and 48 are correlating more strongly to the other Full City samples in this plot. Reference sample 53 is still not associating strongly with the other Server samples.

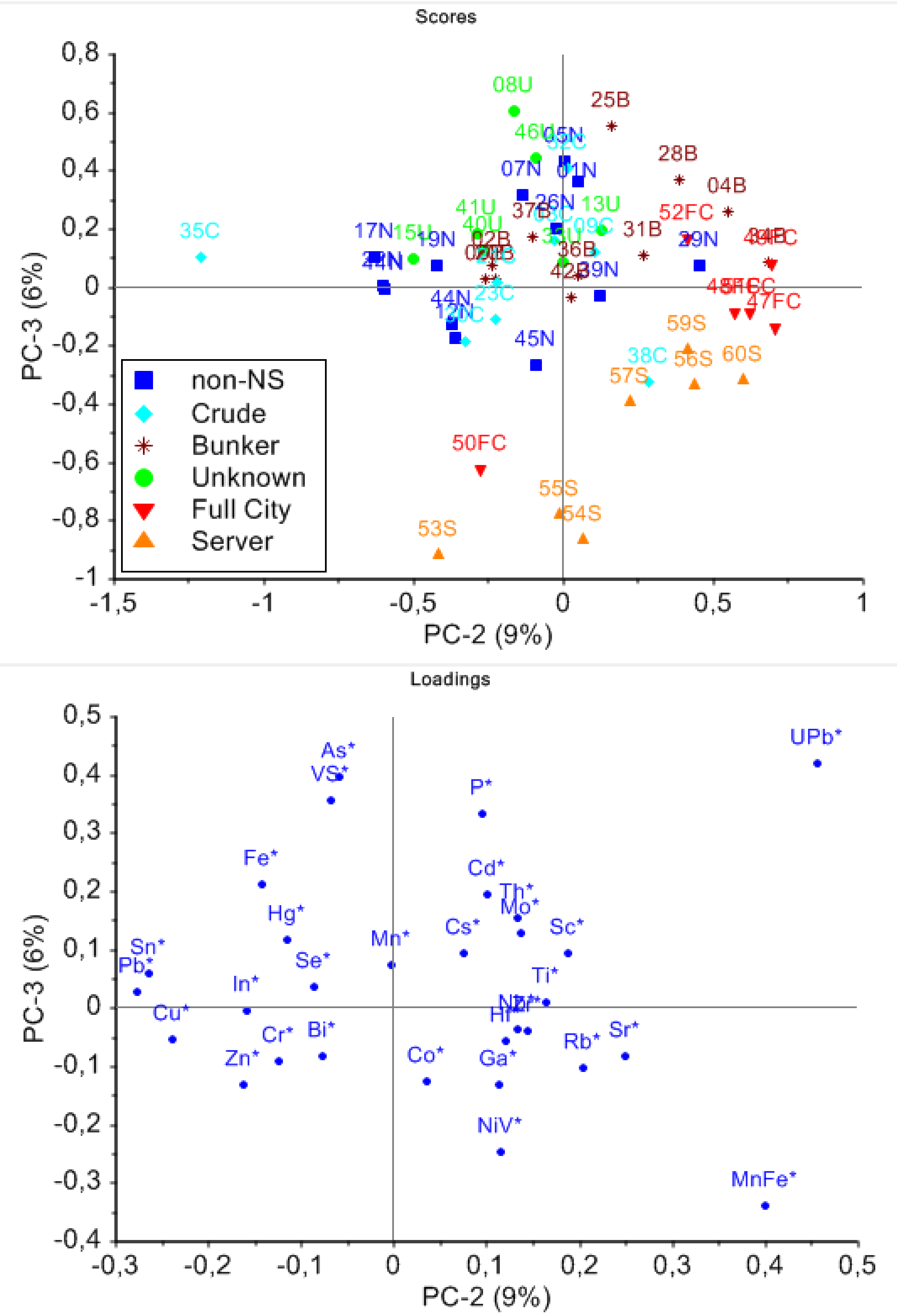


Image 4. 9 - PCA scores and loadings of standardised metal ratios, PC2 and PC3. Abbreviations explained in table 4.12. C = crudes, N = non-NS crudes, B = bunkers, U = unknown, FC = Full City and S = Server.

In an attempt to gain shed light over some potentially “hidden” data, a varimax rotation PCA was also performed (image 4.10).

In this plot, no new relations were discovered, except a reinforcement of the significance of MnFe* and separating bunker and crude oil samples. In the loadings plot, a cluster of Ga*, Nb*, Cs*, Rb*, Ti*, Sc*, Th*, Hf* and Zr* can be seen on the right hand side. This might have something to do with the crude oil samples in the same area.

On the lower right, a group of non-NS crude samples can be seen. Apart from sample 44 which is on the left, all the non-NS samples on the right hand side (01, 07, 26, 29, 39, 45) are the same samples pointed out in image 4.4 with respect to high and low metal concentrations in oil and a possible indicator for marine/terrestrial source input.

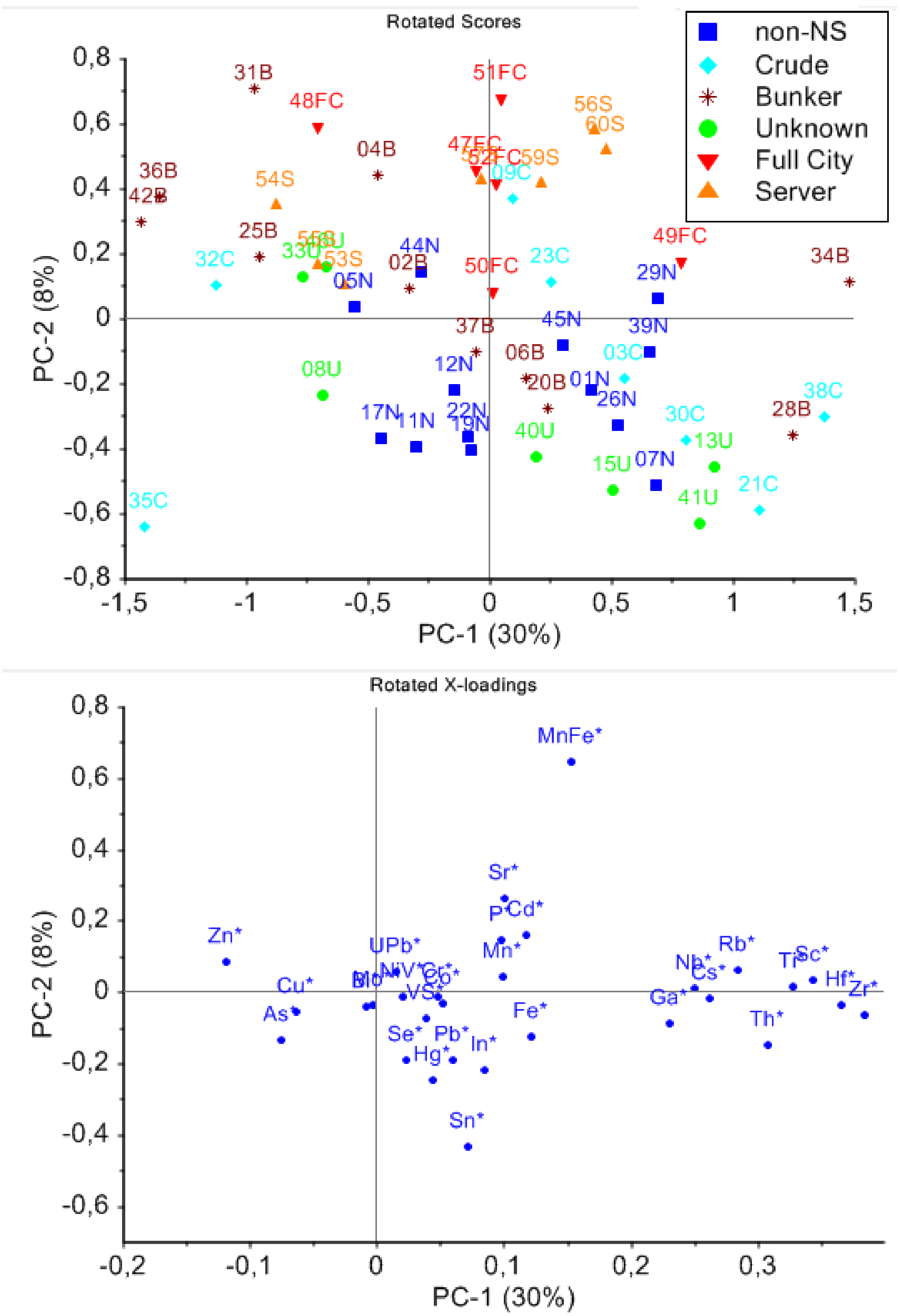


Image 4. 10 - Varimax PCA scores and loadings of standardised metal ratios, PC1 and PC2. Abbreviations explained in table 4.12. C = crudes, N = non-NS crudes, B = bunkers, U = unknown, FC = Full City and S = Server.

4.4 PARTIAL LEAST SQUARES

The PLS methods are powerful tools which can provide a lot of information. In this chapter, both PLS-R with metals and biomarkers are explored, as well as PLS-DA methods with only the metal ratios from table 4.12.

4.4.1 PARTIAL LEAST SQUARES REGRESSION

The PLS-R model was used as a continuation or second step after the PCA analyses to assess robustness and potential of the metal ratios.

For the model, the 30 metal ratios from table 4.12 were used as the response matrix Y, while the seven PC's from the DR PCA in image 4.2 were used as the predictor matrix X. In all cases, the validation method chosen was "leave one out", because there is big differences between the samples, and the sample set is small. The result can be seen in image 4.11.

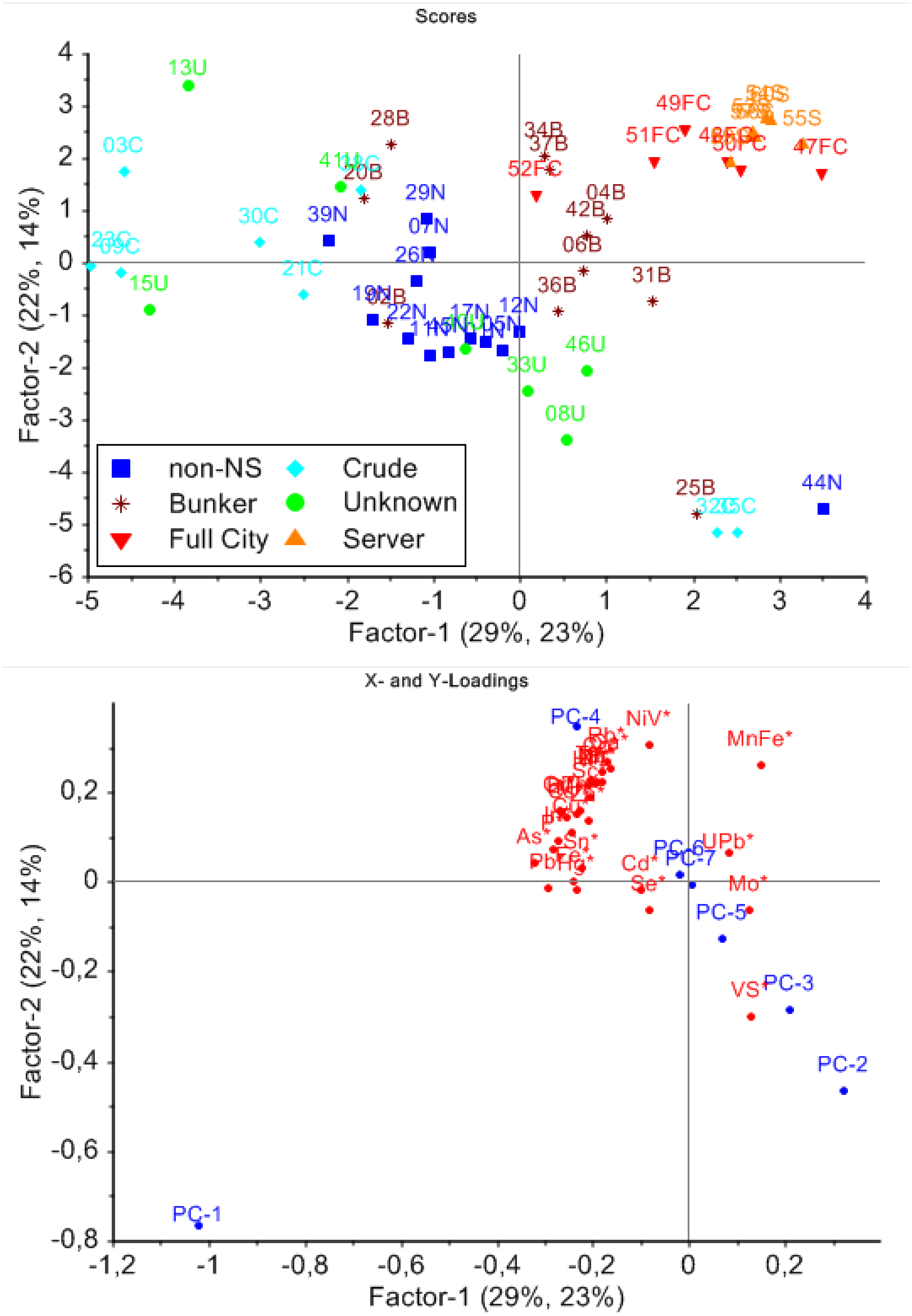


Image 4. 11 - PLS-R scores and loadings of metal ratios (Y matrix) and standardised DR PC's (X matrix), factor 1 and 2. Abbreviations are explained in table 4.12. C = crudes, N = non-NS crudes, B = bunkers, U = unknown, FC = Full City and S = Server.

In image 4.11, the same trends which were seen in the PCA plots are evident and PC1 is dominating the plot a fair bit.

Image 4.11 also displays less overlap between the weathered bunker fuels and the spill samples from Server and Full City, compared to previous plots. The ideal number of factors is two, according to the explained variance plot (image 4.12). Although PC1 is very influential on the model, there is also an influence gradient for the rest of the PC's as well, starting with PC1 and sequentially down to PC7, reflecting the % explanation of the model in each PC.

Crude oil samples 32 and 35 are separated from the rest of the crude oil group, similar to previous plots, while the other groups are displaying an interesting gradient starting in the top right with Server, through Full City, weathered bunker fuels, non-NS crude oils and ending with the scattered crude oils, the unknown samples being spread throughout the plot. This indicates that there is variation seen in the metal ratios which can be explained by the DR's.

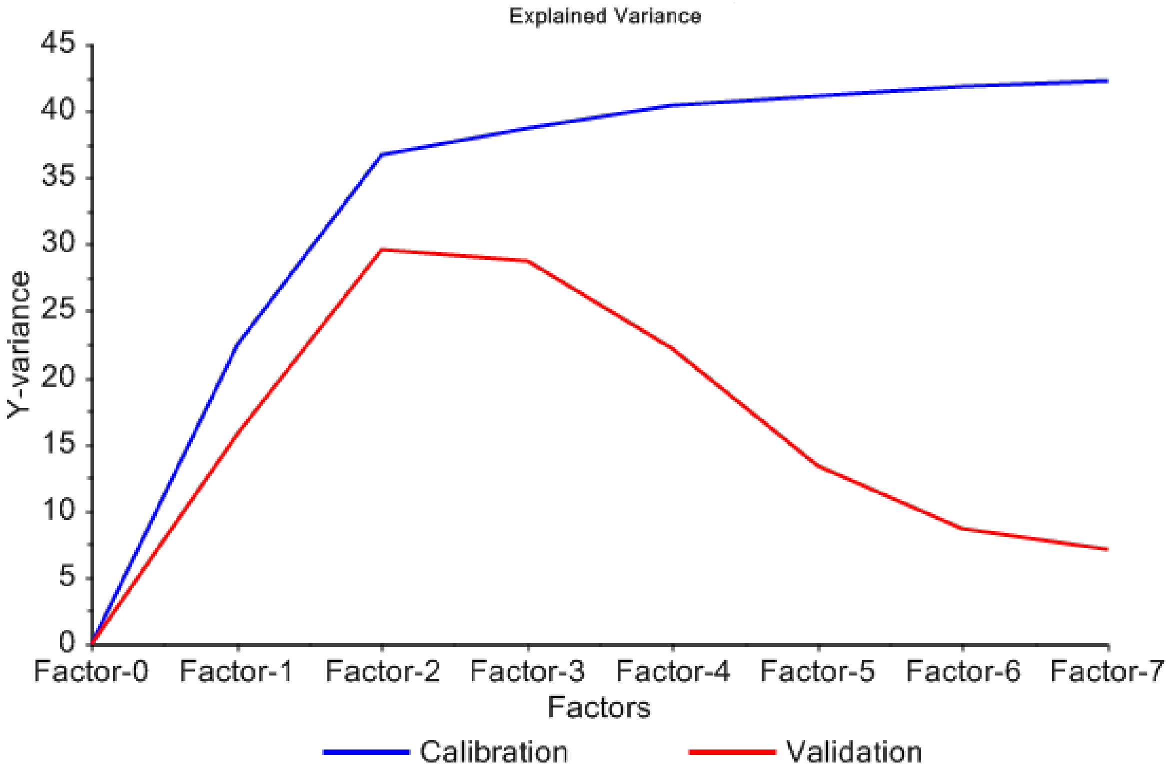


Image 4. 12 - Explained variance plot to the PLS-R model in image 4.13.

Using PC's as predictors rather than hard classification is expected to introduce an inherent "fuzziness" into the model which might account for some of the variation. Variation is also expected because there are several classes, and not a traditional single class, concentration gradient (such as a calibration curve) or yes/no classification. Similar to the PCA, the most variation can be found between the weathered samples, especially bunker oils from crudes.

A plot with standardised metal ratios was also attempted, but this performed less favourably compared to the model in image 4.11, using non-standardised metal ratios, and is not presented.

One set of samples which did not need the full PLS-R, was the Full City and Server samples. Inspection of the different "predicted vs reference" of a PLS-R analysis with metal ratios as the response (X) matrix and DR PC's as the predictor (Y) matrix, revealed that the NiV* ratio was the most important in separating the two groups of spill samples (image 4.13).

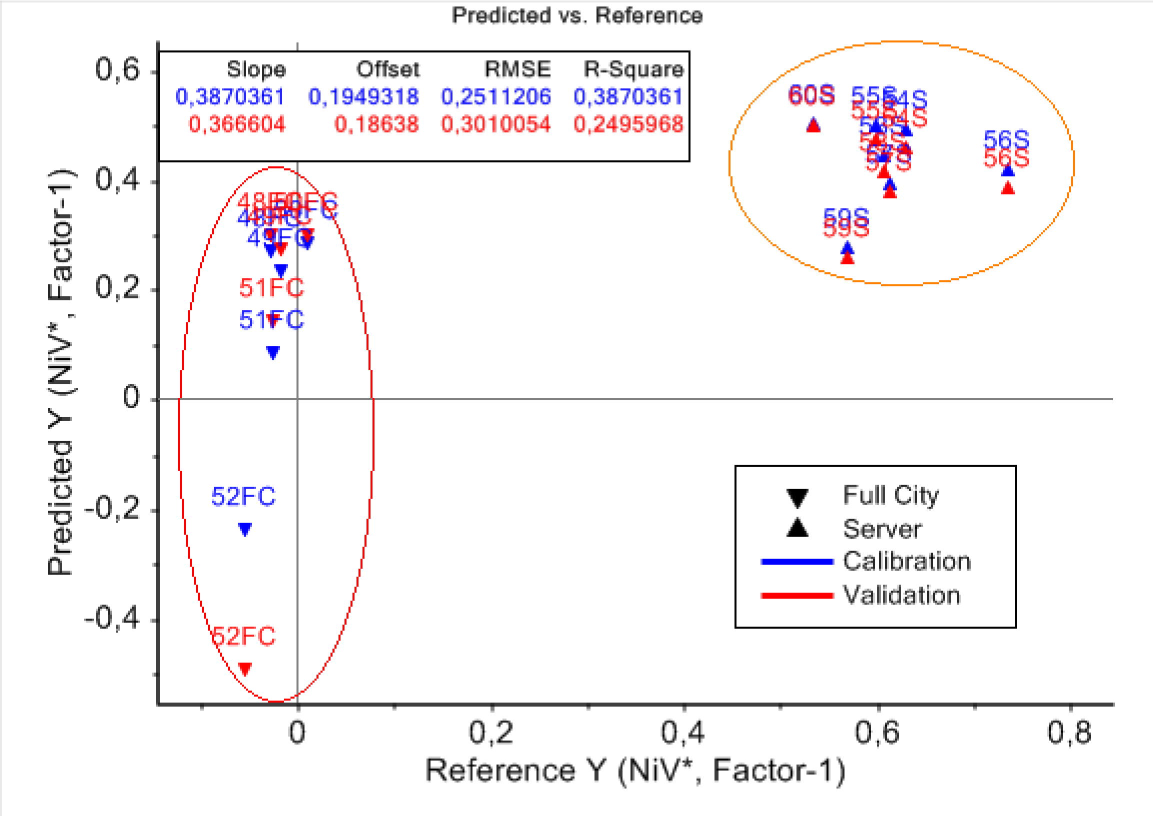


Image 4. 13 - PLS-R plot of metal ratios of samples from Full City and Server, predicted vs. reference plot of the VNi* ratio. Within the red circle are Full City samples and within the orange circle are Server samples.

As can be seen in image 4.13, the two oil spills are neatly separated by the NiV ratio. Even sample 52, which is weathered or contaminated stays with the other Full City samples on the left side of the plot.

4.4.2 PARTIAL LEAST SQUARES DISCRIMINANT ANALYSIS

The PLS-DA model was built to investigate the trends observed in the PCA plots. Visual inspection can be a powerful tool, but it lacks the numerical approach necessary for statistics.

4.4.2.a PLS-DA of non-NS crude oils

It has been pointed out that the non-NS crude oil group appears to be separated into two sub-groups. A PLS-DA of these variables can help identify if this is true or not. The non-NS crude group was split into two groups according to the previous PCA plots. Group A contains low levels of metals compared to group B, which contains relatively high levels of metal. This classification can be seen in table 4.13 below, and image 4.14 presents the PLS-DA model for the data.

Table 4.13 – Classification of the non-NS crude oil group used by PLS-DA

Non-NS crude oil	Samples
Group A -1 □	11, 12, 17, 19, 22
Group B + 1 ■	01, 05, 07, 26, 29, 39, 44, 45

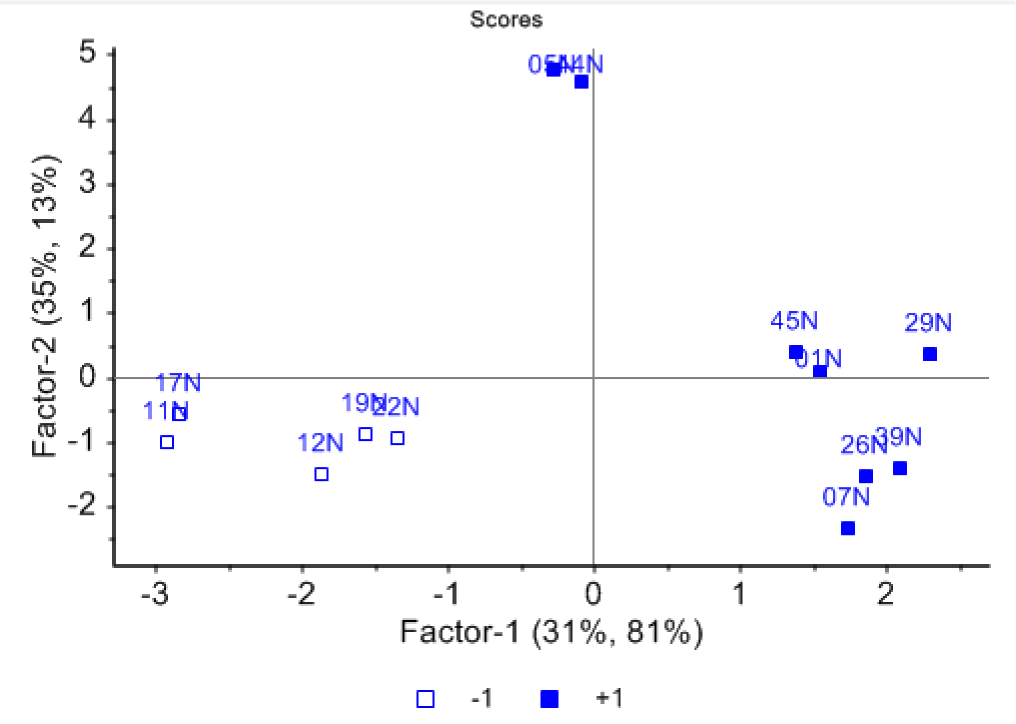


Image 4. 14 - PLS-DA scores of metal ratios of non-NS crude oils.

From image 4.14, there does appear to be a difference between the two sample groups. This can be confirmed by running a PLS prediction (image 4.15). According to this classification, samples < -0.5 are in group A, while samples > 0.5 are in group B.

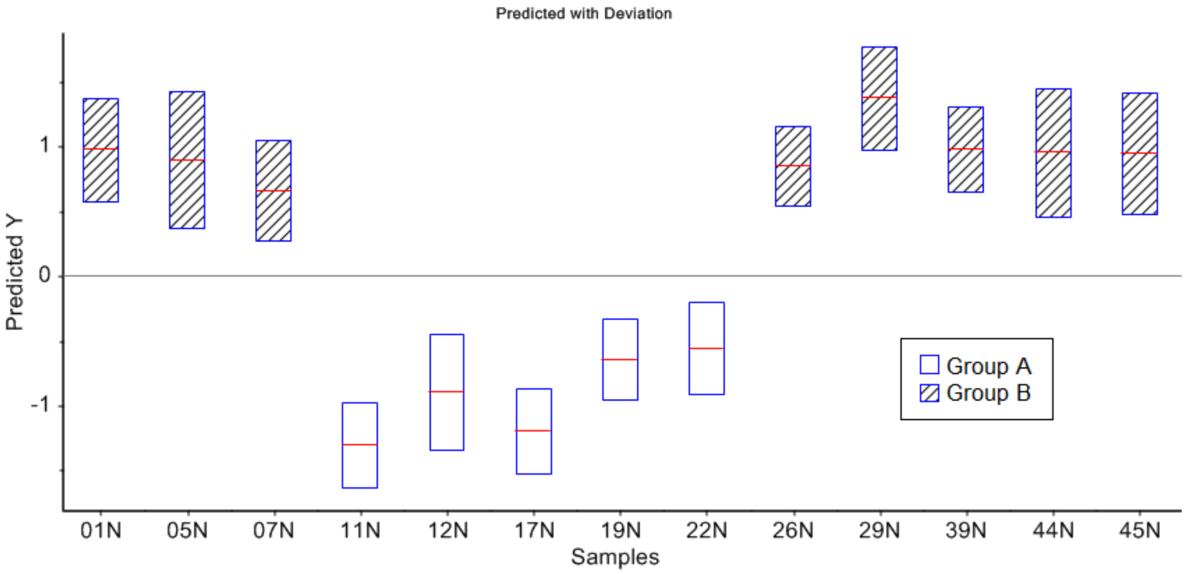


Image 4. 15 - PLS prediction with variance of non-NS crude oils. < -0.5 are in group A and samples > 0.5 are in group B. See table 4.13 for classification.

The same strong result was found when analysing these samples with the DR's, indicating that there are two subgroups within the non-NS crude oil group.

The same model was then applied to the other crude oils as well, providing the classification seen in image 4.16.

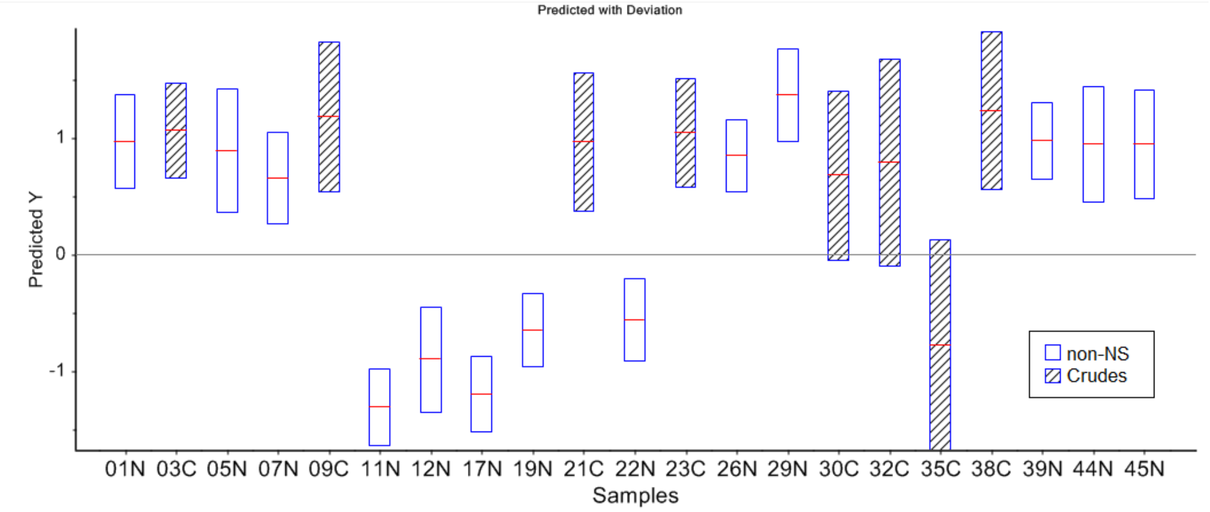


Image 4. 16 - PLS prediction with variance of non-NS crude oils and crude oils. < -0.5 are in group A and samples > 0.5 are in group B. The marked samples are from the class "crude oils".

As can be seen in image 4.16, only one of the crude oils fall into group A with low metal content, while the rest fall into group B with high metal content. The samples in the crude oil group could be from the NS, which contains oil primarily of marine origin.

4.4.2.b PLS-DA of weathered samples

Another good use of PLS-DA is the classification of unknown samples. A PLS was run of the weathered samples of known classification (non-NS crude, crude and bunker), classifying the two crude oil groups as +1 and the bunker fuels as -1. The result of this model can be seen in image 4.17.

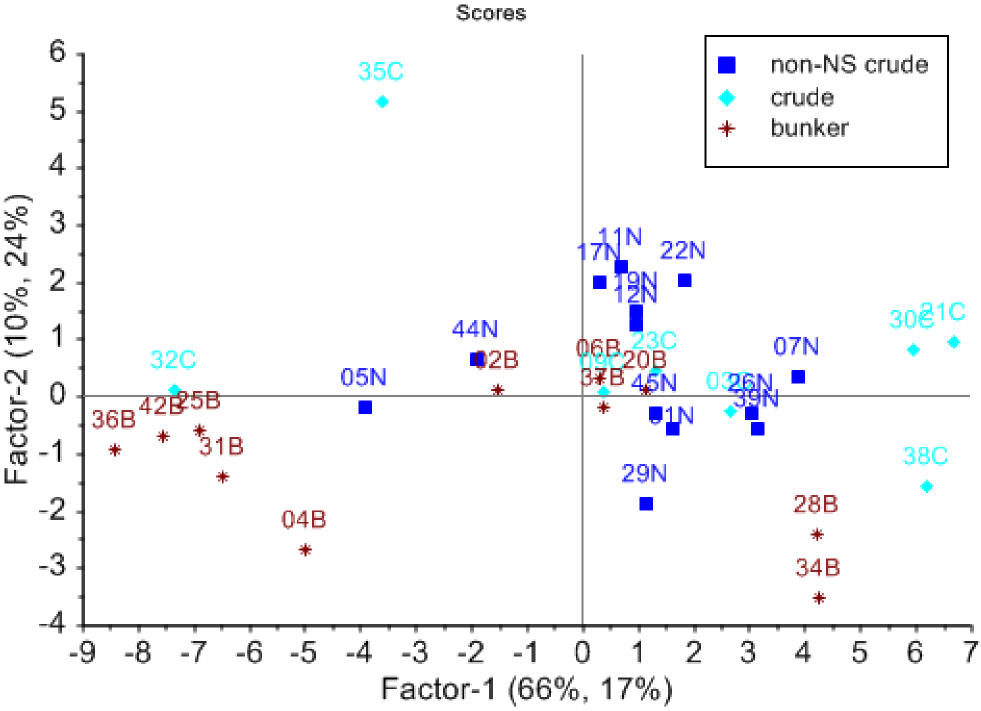


Image 4. 17 - PLS-DA scores of metal ratios of weathered samples of known classification.

This model was then used to predict all the weathered samples, including the unknown samples, seen in image 4.18.

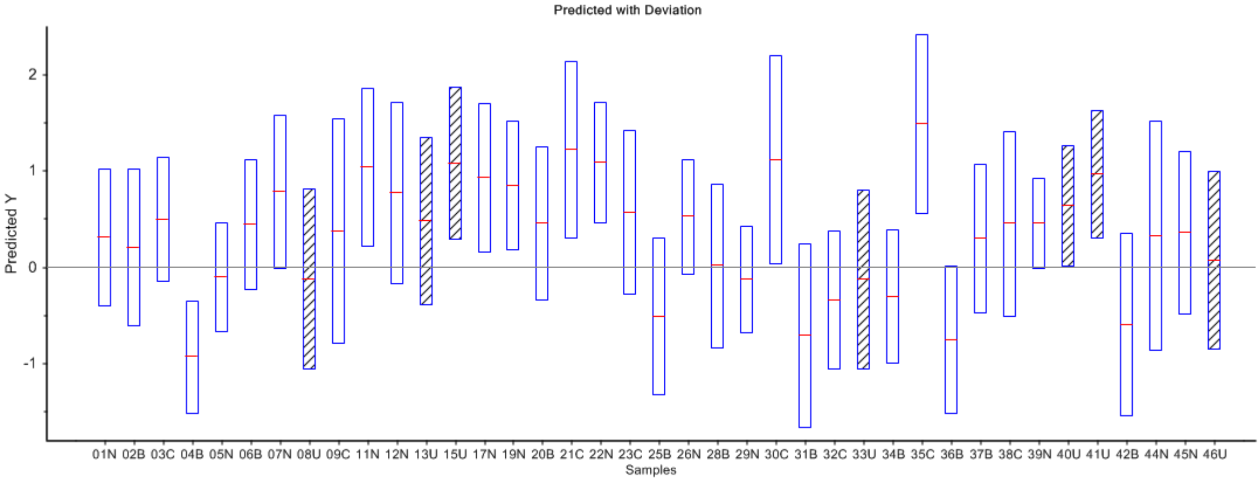


Image 4. 18 - PLS prediction with variance of non-NS crude oils from the model in image 4.16. < -0.5 are bunker oils and samples > 0.5 are crude oils. The marked samples are from the class “unknown oil”.

The model gives the unknown samples the values seen in table 4.14, classifying unknown samples 15, 40, 41 and almost 13 as crude oils.

Table 4.14 – Values provided to the unknown samples by the model in image 4.18. < -0.5 are bunker oils and samples > 0.5 are crude oils.

Sample	Predicted	Sample	Predicted
08	-0.1264	40	0.6331
13	0.4759	41	0.9570
15	1.0728	46	0.0659
33	-0.1318		

When the same model is run with DR's instead of metal ratios, a slightly different trend can be seen in image 4.19 and 4.20. This model provides the following values for the unknown samples (table 4.15).

Table 4.15 – Values provided to the unknown samples by the model in image 4.20. < -0.5 are bunker oils and samples > 0.5 are crude oils.

Sample	Predicted	Sample	Predicted
08	0.5152	40	0.5848
13	0.2515	41	0.4192
15	0.9234	46	0.3004
33	0.0889		

In this table, the unknown samples 08, 15 and 40 are classified as crude oils. This illustrates the difference between the data.

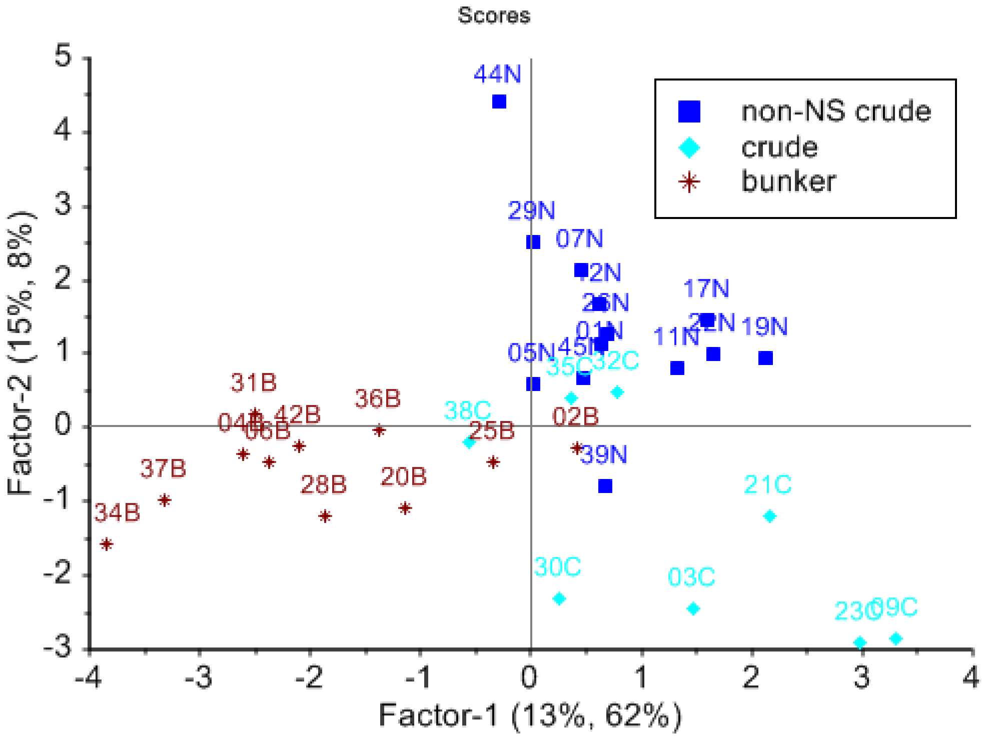


Image 4. 19 - PLS-DA of standardised biomarkers of weathered samples of known classification.

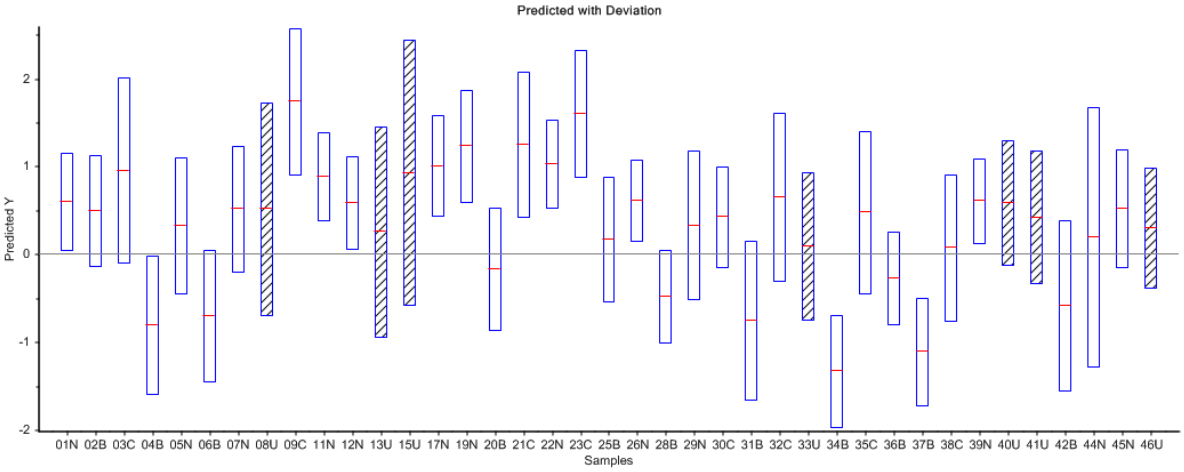


Image 4. 20 - PLS prediction with variance of non-NS crude oils from the model in image 4.19. < -0.5 are bunker oils and samples > 0.5 are crude oils. The marked samples are from the class “unknown oil”.

4.5 RARE EARTH ELEMENTS

The most common way to present REE's, is to normalise them against the average of a chondrite meteorite, specifically of the class C1 chondrite, and then inspect the pattern for differences. This has been very useful in geology, classification of minerals and petroleum geology, but is of limited value where samples have been heavily weathered, evaporated and would have had their REE concentrations increased to that respect. Even so, a chondrite normalised plot of the log transformed samples can be seen in image 4.21 below.

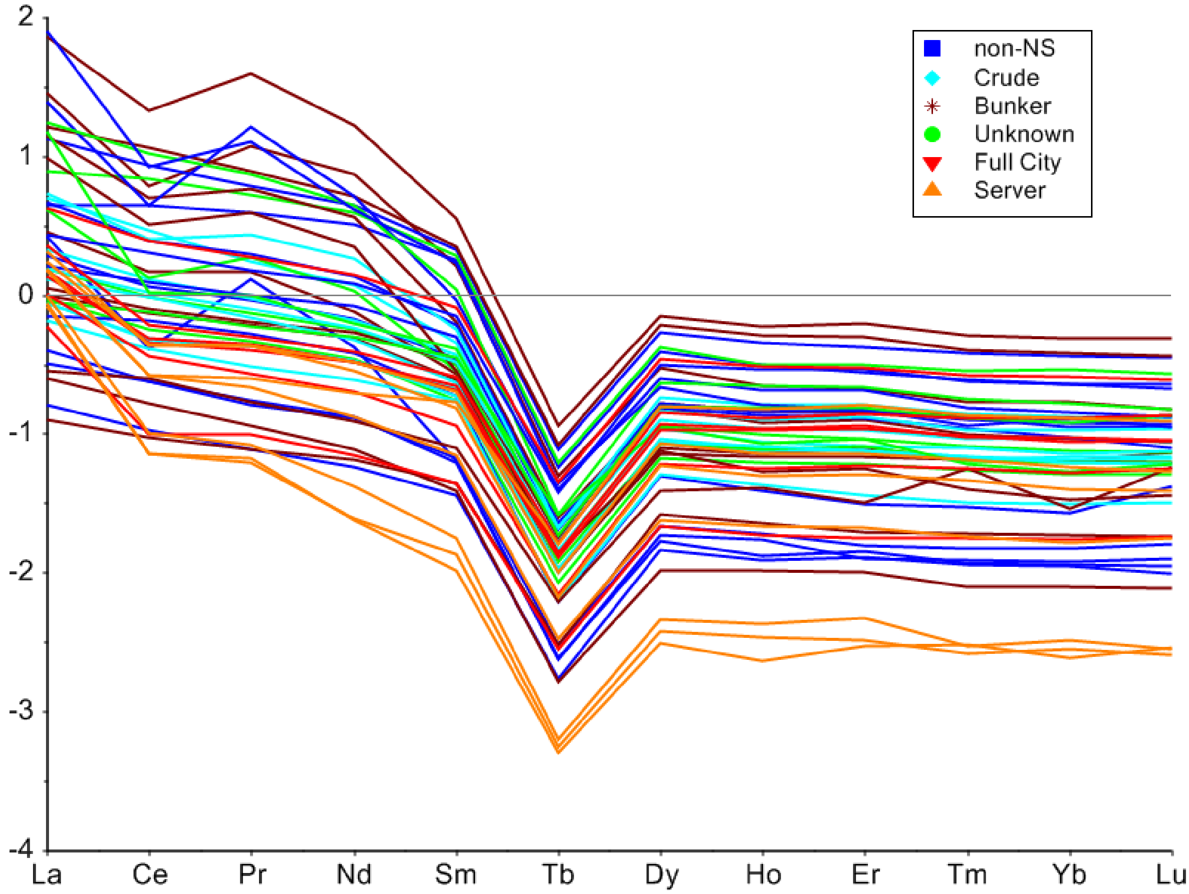


Image 4. 21 - Chondrite normalised line plot of log transformed REE measured by ICP-MS..

This image is quite messy and difficult to interpret. In general, the samples are all showing very similar trends with a few differing measurements. Such as terbium being greatly depleted compared to chondrite as well as all HREE's after that. It might be noticed that 3 of the server samples are standing out from the rest, but the trend is weak and this traditional presentation appears unable to illustrate the subtle differences found in the samples.

Before continuing with any MVA, the data was inspected by Kolmogorov-Smirnov tests of normality with a significance level of 5 %. REE's lanthanum, cerium, praseodymium, neodymium and samarium scored "Assumption of normality cannot be rejected" while terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium scored “Assumption of normality not supported”. In all cases, the differences were subtle, and an elevation of the significance level would have quickly pulled all under the threshold where assumption of normality could not be rejected. It is interesting, however, that all the elements which were rejected for normality were the HREE’s.

In light of this, PCA of standardised values was attempted (image 4.22). In this image, as with the line plot in image 4.21, the information is messy and confusing, and apart from the 3 Server samples on the top left corner, little clustering can be observed. PC1 explains a lot of variation (89 %), but it appears as if this is attributed mostly to concentration factors and noise. Beneath this large PC, there does seem to be some information, such as all the Full City samples plotting along the bottom half of the plot and all the crude oil samples gathering in the middle.

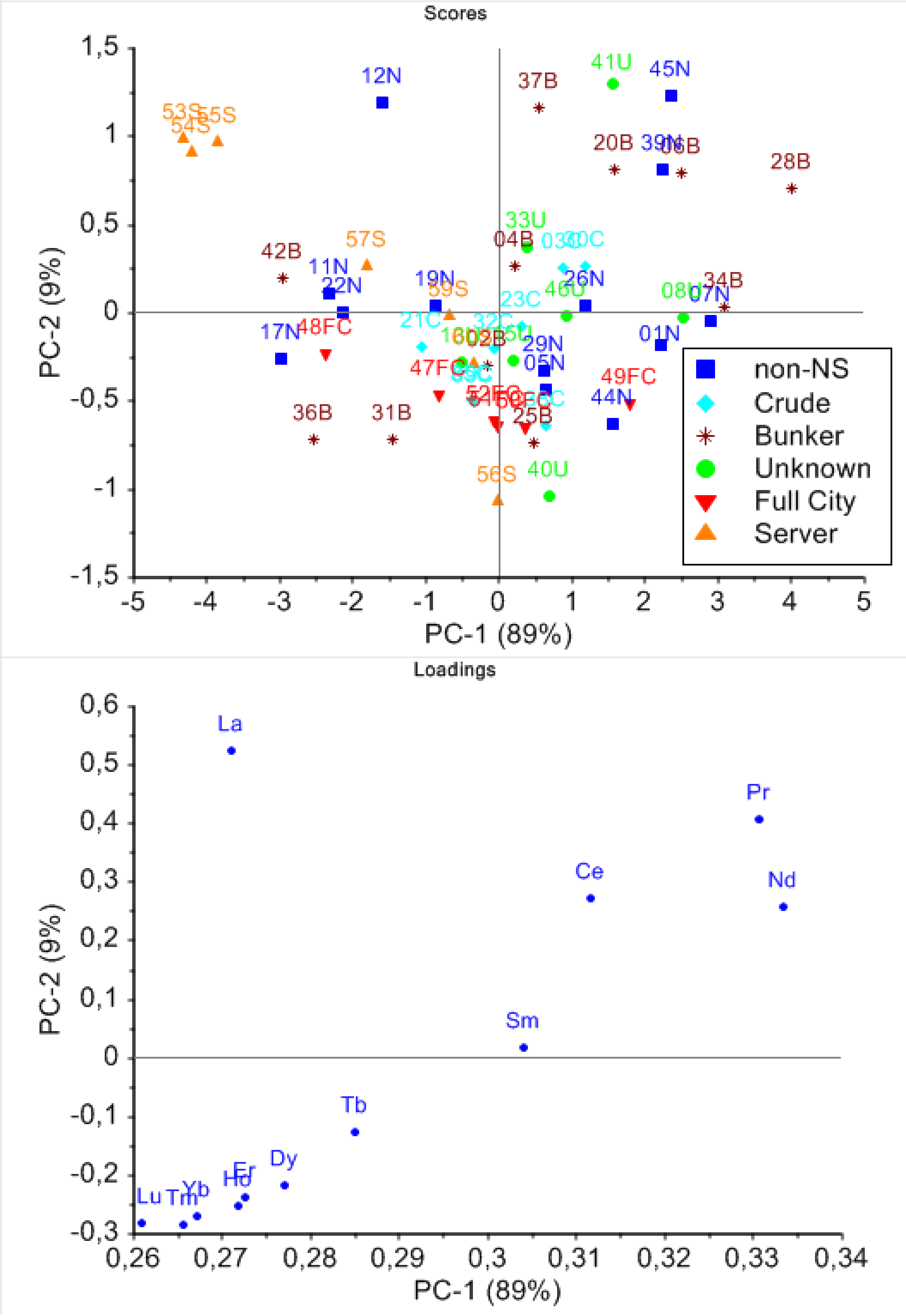


Image 4. 22 - PCA scores and loadings of standardised REE elements, PC1 and 2.

To explore this further, PC2 and PC3 can be seen in the following plot, image 4.23. In this plot, a separation between spill samples and weathered samples can be seen clearly along PC3, even with two outliers, sample 45 and 46. The Full City samples can be seen in a loose cluster on the left, but the Server samples are not so uniform.

One potentially interesting feature this plot exhibits, however, is a tighter cluster of crude oil samples than previously seen. In the previous plots, the crude oil group has always been showing clusters bigger, or of roughly equal size to the non-NS crude oil group. With the REE's it would appear as if the non-NS crude oil group are the least homogenous, while the crude oil group are actually more similar.

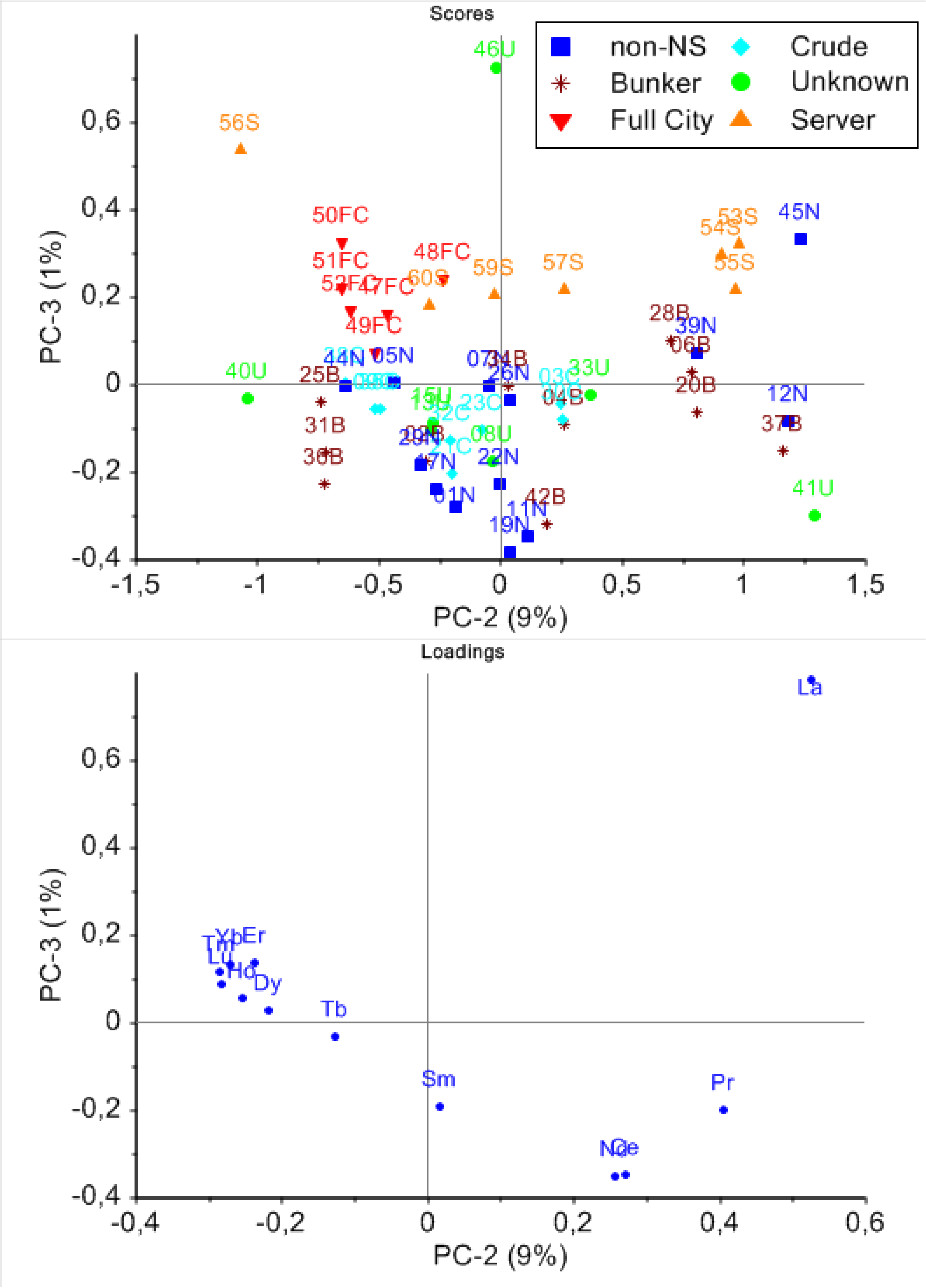


Image 4. 23 - PCA scores and loadings of standardised REE elements, PC2 and 3.

5. DISCUSSION

In this chapter, an attempt is made to discuss and interpret results and limitations from the study. Sources of error and uncertainty are given particular attention alongside the possible results. The basis for the later conclusion is primarily given in this chapter. There is great variety in the data set, with everything from heavily weathered oils assumed to be 10-50+ years old, through spill samples that have suffered less than a year of weathering. At only n=52, after having removed several samples (10, 14, 16, 18, 24, 27, 43, 58, and the fresh crude oils 61-80), little is left to try and draw conclusions from. It is acknowledged that the sample size is small, and can be treated only as indicative for possible results.

5.1 FIELD WORK

The field work in this study was optimised for organic analysis, which probably had a detrimental effect on the results from the metal analysis. Aluminium, for instance, could have been a very interesting metal to investigate, as it is the only metal not found naturally in oil which is added during refinery processes (table 2.2), all other metals can be found both naturally and added during refinery and processing. However, the use of aluminium containers during field work renders any aluminium results highly questionable and unreliable. The samples were also scraped off using spatulas made of stainless steel (iron and chromium oxide), possibly bringing along shavings of stone and sand, which might incriminate the results as well. Cross contamination from the sampling equipment was another factor, as the spatulas used to collect the samples were given no more cleaning except wiping them clean in between each sample.

Although more expensive, the use of sample glasses or jars rather than aluminium boxes could help alleviate this problem. The silicon from the glass will be incriminated later during sample workup, because quartz tubes have to be used in preference to Teflon, which oil samples etch through during the time in the Ultraclave along with the acid.

The samples from the field work themselves were highly weathered, old samples of oil. They would have spent possibly years at sea, equilibrating with the water column and adsorbing sediment particulates, before being deposited onto a rock at high seas and melted during sunny weather where they would've stayed indefinitely until discovery. The long lifetime of the weathered oils could possibly mean the underlying rock, although slow, might have had the possibility to desolvate minerals into the oil by an equilibrium constant.

Feathers, moss, fungi, small gravel and other matrix contaminants were often prevalent, and the far-reaching, complex system of ocean currents mean the oil could originate from anywhere in the world, as might have been illustrated by for instance sample 09 suddenly finding a quite good correlation in a sample from the Shetland Isles in the UK, both along the course of the North Atlantic current.

Other possible contaminants could happen far at sea, while the oil is still miscible. If several oil spills meet at sea, they could interact and mix, ruining the unique fingerprint of both oils in the process and leading to erroneous conclusions when the oil is assumed to originate from one single source. During the lab work, an effort was always made to sample from an assumed less contaminated centre of the oil sample if this was possible and then homogenised, but this method cannot identify if the oil sample itself was heterogeneous in source.

Another factor of consideration is the biodegradation of PAH's and other biomarkers. Although they have been found to be persistent in the environment, they are not indestructible; all constituents in oil will be degraded, given enough time (Wang and Stout, 2007). While this is not an issue during oil spills where the time from the spill to the sample is collected and analysed is usually no more than a couple years at most, weathered samples have been exposed to the forces of nature for a lot longer, a common estimator possibly being as much as 50 years.

No weathering experiment has been conducted for this large timespan yet, which means the robust biomarkers might be affected and cannot be trusted blindly. Especially sesquiterpane and naphthene ratios have been found to suffer from weathering effects, and were treated carefully. In certain cases, this could lead to uncertainty as to whether or not a biomarker was ever present in the sample, or if it has been weathered past the limit of detection. This would be especially important with peaks such as 30O, whose presence weighs heavily in the classification of oil.

5.2 SPILL AND FRESH CRUDE SAMPLES

The spill samples from Full City and Server had all been stored cold (4 ˚C) and dark since their arrival in 2009 and 2007, respectively. The samples were collected and stored in small glass jars.

Although these samples are expected to suffer matrix effects from adsorbing particulates from the water column and to some degree their area of deposition, this was expected to play a lesser role compared to the highly weathered samples from the field work. The samples were larger, had suffered less weathering and were sampled less than a year from the time of the accident. Factors which might serve as both identifiers and contaminants is the presence of metals from pipes, tanks and the ship in general, as well as mixing of various oil types, mixing of different oils in the same tanks, collection of sludge in the ship's hull and water washing.

For the fresh crude oils, although these are routinely stored in 1 L glass bottles, dark at 4 ˚C, they usually arrive in larger barrels or jerry cans. These containers would be expected to influence the metal content of the oil.

Sadly, the metal content of the fresh crude oils were far too low for the sample workup chosen for the ICP-MS analyses, and no reference sample set containing information about different crude oils could be gathered.

This could be remedied by using the 250 ˚C+ fraction of each oil, which was also available. These "controlled weathering" tests done in the lab are required for each oil in order to estimate how the oil might act in the event of an oil spill and provide an appropriate action plan. The biomarkers remain largely unaffected by these procedures, but the removal of lighter components would concentrate the heavy fraction, where most metals are expected to reside, and possibly push the metal content above the LOD where they can be estimated with more confidence.

In summary, all oils must be expected to adsorb particulates and minerals from the water column. This is a natural part of oil spill and weathering, and cannot be removed. For metal analyses to be applicable to the real world, they must be robust enough to reach a conclusion in spite of this.

5.3 CHEMICAL ANALYSES AND RAW DATA

The samples were treated differently in preparation for GC-FID/GC-MS and ICP-MS analyses. While GC-FID/GC-MS is concerned with the organic and volatile (within the parameters of the GC), the ICP-MS covers the inorganic metal analysis, providing a nuanced and complex image of each sample. In the case of the weathered samples and spill samples, these were primarily collected off rocks and areas with sand and kelp as possible contaminants. Bird feathers were most common from the spill samples. Contaminants are described in Appendix A, but were always removed as well as possible. Arising issues and specifics about samples are also introduced. Reliability of the results is a key issue in any study, and this is an important point touched upon several times throughout the text.

The main reason reliability is such an issue with this study, is the inherent uncertainty of the metal content, not the analysis itself. Oils are expected to take up suspended sediment particles in the water column, and sand and gravel from shores and rocks. Another issue is water washing, in which the metals already present in the oil are removed by rain or seawater at different rates, disturbing informative ratios. The third issue is specific to very weathered samples. When an oil sample contains small amounts of organic matter and biomarkers, it is uncertain what it contains instead, and whether this will have an impact on the metal concentrations or not.

5.3.1 GAS CHROMATOGRAPHY

The sample workup for GC-FID and GC-MS was identical, allowing the same extract to be used for both instruments. Reusable equipment such as spatulas were always cleaned with DCM and left to air dry between each sample, reducing the risk of cross contamination.

All the samples were filtered first with sodium sulphate to remove particulates and water, and later through a silica column to remove polar compounds, allowing for sharper peaks and reproducible results, but at the same time possibly removing interesting constituents in the sample. The chromatograms of n-alkane standards and DCM-blanks showed that the instruments were both stable and reliable for the duration of the analyses. Despite the equal treatment of samples and roughly equal amount of oil used for each sample, responses from the GC-FID could vary immensely. This indicates that looks and weight of a sample alone is not a good indicator of oil or biomarker content, especially with weathered samples.

The only exception to this were the samples 43 and 44 (Appendix E). Both these samples display a large contamination peak at the exact same retention time. Sample 43 was concluded as not oil, and whatever the sample did contain instead might have contaminated the following sample. No other sample displayed similar contamination peaks, and the samples were not rerun.

One interesting point on the GC-FID chromatograms, out of all chromatograms with very large UCM humps (02, 04, 06, 23, 25, 28, 31, 33, 34, 36, 38, 42, 46, Appendix E) and low/very low presence of hydrocarbon patterns, most of these oils were classified as bunker fuels. This could be a remnant of the extensive use of catalytic cracking in order to squeeze out as much valuable material as possible, but also that heavy tankers run on the heavy oil fractions left after most other products have been extracted.

An interesting sample as a continuation of that is sample 31. While displaying a huge UCM hump, when analysed by SIM by the GC-MS, the m/z 85 came out displaying large hydrocarbon peaks in two distinct groups often seen with lubricating oils. This might indicate contamination of the sample, or a large amount of heavy components in the oils which are not being analysed by the SIM.

An interesting observation was that high values of the biomarker 29ab often correlated with normal-high values of the biomarker 30O. The Pr/Ph ratios and derivations thereof were treated carefully and never allowed to influence the final conclusion as they were highly weathered and often not even detectable from the baseline in the weathered samples.

Other than visual inspection and interesting features, the GC-FID results provided little to the subsequent statistical analysis. Pr/Ph ratios and derivations thereof are included by COSIWeb, but considered too weathered and unreliable to be given any weight.

The initial classification is a subject of some controversy as well. Some cases, such as samples displaying high abundance of MA or retene could fairly easily be discerned as either bunker or crude oil, respectively. Other samples were a lot trickier, and several total revisions of the data was made before the result was satisfactory. Unknown samples were generally undesired as they provide little information to the statistical analysis, but are hard to avoid entirely. Unknown samples often ended this way based on vague hydrocarbon patterns, lack of retene, lack of MA and an indistinguishable MP pattern due to weathering.

It is, however, important to remember that the classification is a subjective assessment of the GC-FID and GC-MS chromatograms. Although the classifications appear rigid when nicely colour coded in the various MVA plots, they are actually the most prone to change and human error. It is sobering to mention that in a handful of the samples analysed by both Henriksen (2012) and the author, a different classification was reached (Appendix A).

5.3.2 INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

The sample workup used for oil samples in ICP-MS is not yet as established and standardised as its GC counterpart, which gives room for more uncertainties and possible contamination. Visible contaminants were removed and the samples were homogenised, but they were not filtered through sodium sulphate, which might have introduced unnecessary contamination into the analyses. Filtering through silica was determined too risky as there might have been adherence of metal-bearing polar components onto the column, although duplicates with and without silica workup should have been done to make sure.

The degree of "dryness" achieved by shaking the quartz tubes violently can also be debated, possibly carrying through metals from previous samples, even in small amounts.

As raw data, the ICP-MS results were not normally distributed and could not be used for PCA or PLS. The logarithmic transformation proved suitable for the data set. This not only normalised the data, but also removed instrument anomalies such as negative values. Limpert et al. (2001) argues that the lognormal distribution is showing up more often in nature, especially geology and environmental sciences, and might be the more common distribution pattern, as opposed to the more accepted normal distribution. Thus it is not unlikely that metals are distributed in various oil types after a lognormal pattern.

Because the information gained from the metal analyses are inherently uncertain, ratios might be an important factor in the development of a method. Measuring the concentration of a sample with any degree of accuracy is a lot more difficult than measuring the ratio of compound A to compound B in any solution. It is also a lot easier for an instrument to measure and report. Using ratios is a lot more stable and reliable compared to concentrations, especially when dealing with samples close to the LOD of the method. This also helps decrease the difference between results presented from different labs, instruments, analysts, seasons, etc. as has been seen in the successful adaptation of the COSIWeb database.

The problem with ratios, however, is the degree of weathering the samples have been exposed to during their lifetime. Extensive time spent at sea and exposure to rain and weather would have caused water washing and possible alteration of the ratios. Information about water washing was only found for the VNi* ratio. These two metals display very similar chemical properties and are found primarily in the same fractions of the oil, causing them to water wash at approximately the same rate, keeping the ratio stable (Lewan, 1984).

The other set of metals which is assumed to be reliable in spite of water washing are the REE's. Just as vanadium and nickel, the REE's display very similar chemical characteristics, even if they are often divided in the LREE's and HREE's (and sometimes MREE's), although some differences have been observed (Fu et al., 2010).

The same information could not be found about any of the other metals in the study. Using vanadium as the stable "baseline" to which most samples are compared helps alleviate the problem, but cannot fix it entirely, as vanadium might also water wash at different rates compared to any other metal in the oil except nickel. The problem is that there are no guarantees that, for instance, iron and vanadium water washes at the same rate when calculating their ratio. This introduces one of the largest uncertainties in the study and presents a potential area which needs further work.

Another issue was that the blanks showed variation and especially calcium, potassium and sodium had to be excluded because the baseline was not stable. In wolfram, there was also the dreaded "tailing" effect, caused by high concentration samples affecting the subsequent low concentration samples, rendering the results unreliable. The disturbing samples (09, 21, 23 and 38) had not shown high concentrations or otherwise deviating behaviour previously, indicating that there might be interesting information embedded there, but it is unclear if it is worth pursuing routinely at the risk of tailing effects in the data.

Although not as pronounced anywhere else, there is no guarantee that similar, but weaker, tailing effects have not happened with other samples and metals, but were not picked up because they were within the assumed "normal" range of blank samples.

This, and because low concentration samples should be analysed prior to high concentration samples, lead to further uncertainty tied to the results from the fresh crude oils. The fresh crude oils displayed the lowest concentrations in the entire study, but were analysed last of all in the instrument, making even the few fresh crude oil samples above the LOD questionable.

The reference material used in this study did not contain all the metals used in the analyses. Suitable reference material for metal analyses in oil is limited, and subsequent studies might have to work within these constraints or develop tools and reference material which addresses this issue.

The biggest uncertainty for metal analyses in oil does appear to be the prevalence of metals and minerals in nature, exposing any results to a lot more confounding factors compared to biomarkers. There are some biomarkers being made in nature (such as retene from combustion of wood), but the concentration is usually much, much lower than the concentration in oil.

5.4 MULTIVARIATE ANALYSIS

As the multivariate statistical analysis took up the most of the time in the study, it seems fair that they also demand most of the pages in the discussion chapter. MVA was used to visualise, exemplify, but in many cases also attempt to verify and investigate trends, certain features and classification in the oil samples.

The data in this study is of a qualitative and not quantitative nature. Even with the ICP-MS, which provides results in µg/g of the sample weight, the preferred data set is still processing that data into ratios due to the increased stability of ratios as opposed to concentration discussed previously, even with the dreaded water washing effect. Although the data matrix is occasionally used in its entirety of both DR's and metal ratios, the data is often explored in pieces, such as the REE's to explore trends which may have been too difficult to spot when analysing the data set as a whole.

5.4.1 DIAGNOSTIC RATIOS AND COSIWEB

One of the first things which spring to attention when inspecting the chromatograms and PCA plots for the standardised DR's is how sample 52 from the Full City oil spill is quite a lot different from the other spill samples from Full City and Server (47-60). The only explanation which could be deduced from the sample information is that 52 was sampled on the 19th of August, 12 days after any of the other samples had been taken. This could explain some of the differences observed in the plot, but does not seem enough to explain all of it. Especially when taking into consideration that COSIWeb did not match sample 52 with any of the other samples from Full City.

Interestingly, for the other samples from Full City, sample 52 was not among the 50 best correlated values calculated by COSIWeb at all. This could further indicate that sample 52 was exposed to strange and intensive weathering or more likely, had suffered contamination from some unknown source not mentioned in the report. It also serves as a reminder just how similar bunker fuels can be, especially when reduced to a few statistical numbers by a database. Visual inspection and a skilled analyst are still very important.

Another interesting sample from the Full City accident is sample 51, which was partially matched to sample 37, found on the island Kya. It does seem possible that sample 34 might be a remnant from the Full City accident, which would make the sample quite young compared to the average assumed age of weathered samples.

This, along with the other possible matches from the weathered oil samples, raises a couple of good points. Firstly, the use of an international database could significantly increase the knowledge of the scope of a spill. After all, most countries are only concerned about the samples found along their own borders. With a database like COSIWeb, correlation can be found and investigated for samples from all over the world, especially underlined in this study by several samples from the Shetland Isles correlating with samples off the Norwegian coast.

Secondly, because each lab is analysing their own samples, different labs do not have to run analyses twice over to acquire data, such as the correlation between Shetland and Norway above. A shared database and format makes interlaboratory and international cooperation a lot easier and more appealing for all parts, especially since the work load does not increase significantly. In an ideal setting, the analyst would upload the samples into COSIWeb in any case to compare the spill samples he or she has received. Discovering other correlating samples in the middle of the known spill samples would be an interesting bonus and quite possible lead to a more nuanced picture about the spill in question.

Lastly, for field trips such as the ones conducted by the course Marine Organic Environmental Chemistry, where weathered and unknown samples are collected, using a database such as COSIWeb might increase the knowledge about the samples which are being collected. Even if it is just a handful of samples in a collection of 100, any sample linked to a source by match or partial match would increase knowledge and would mean a few less samples labelled just “unknown”.

5.4.2 METAL VARIABLES

One of the most interesting, new features in this study has undoubtedly been the metal analysis. As is becoming the norm, more than the exception these days, it is not a problem to acquire new data, but rather how to present and interpret the data in question. This issue has demanded a lot of time and testing, and it is not even certain that the method and style presented is the best way to present the data.

5.4.2.a On the removal of metal variables

In the presentation of these results, several metals were removed from the sample set. This deserves particular comment, considering how it might otherwise give rise to some confusion.

When this study was first started, it was not known what to expect. Some information could be gleaned from the literature, but this was exclusively work with fresh crude oil samples or oil stored on tanks and in pipelines. No information about metal content in oil spilled to the environment was available. To this end, it was decided to analyse all the elements available to the ICP-MS instrument and remove uninteresting metals later. In this way, few assumptions had to be made before the data was available, which hopefully meant little information was lost.

Once the data was in, however, it was obvious that several metals were redundant, missing, or just plain uninformative, and could be removed. It was never the intention to work with the entire data set, but rather reduce it into a much more manageable and informative set of metals, akin to the reduction of available biomarker ratios into the 29 essential biomarkers seen in the COSIWeb database.

It was also a problem that the reference material available only contained 22 of the known metals found in oil. Without reference material, the remaining metals become uncertain and have to be treated with care. Interesting groups such as the REE's are missing entirely from the reference material, but might be saved by their own, internal reliability.

5.4.2.b On the metal ratios

Choosing the metal ratios to use and present in this study was one of the most challenging parts of this study. Where available, ratios suggested in the literature were used, along with isotope ratios.

For the remaining metals, it was determined to base all ratios on vanadium. It would make little difference whether vanadium, nickel or sulphur was used for this, as they are all stable and strongly correlating. The decision to use a single element as reference was done in order to have a stable reference point, but it does bring with it some issues. The first being that elements with different chemical properties from vanadium might be expected to water wash from the oil at a different ratio, and might thus skew the ratios.

The second issue is relating to using only vanadium in itself. This means most elements are presented as ratios related to vanadium alone and nothing else. The only ratios not using vanadium in the denominator were ratios found in literature (table 4.11). There could be a lot of underlying information between other elements of similar chemical properties, which would be dwarfed or ignored by these plots.

A good solution for this would have been to combine all the 64 elements and isotopes and work from there. This would, however, present 2016 unique combinations, not withdrawing the samples which were excluded, and then investigating each combination for its ability to explain interesting features in the data. This was beyond the scope of the study, and a reduced subset had to be chosen, at the risk of missing out important information.

To this end, it is acknowledged that the ratios are skewed toward vanadium and the risks that follow this decision. Vanadium is not expected to water wash from the oil to such a degree that it would be undetectable, especially because most of it is bound in organic molecules. While this is an asset for stability and reproducibility, it may be detrimental to ratios where the other metal is in a very different phase, for instance not bound by any organic molecule, but suspended in the oil as an inorganic salt. More studies on the speciation of elements in oil might be useful.

5.4.3 PRINCIPAL COMPONENT ANALYSIS

PCA analysis is the main workhorse in most MVA tool boxes, and is usually one of the first methods to be tested on the dataset after some basic statistical tests and assessment of normality. It can be used to detect outliers, skewness in the data, and discover important trends and correlations. It has been used extensively in this study in various shapes and forms.

5.4.3.a PCA of biomarkers

For the biomarkers, it is worth pointing out is the lack of normality in the data. This could be expected, considering the many peaks which are identified only by present/not present, but it does present a problem, because PCA assumes normality of the data.

Retene, for instance, is usually either not present or a strongly defined peak, with few alternatives anywhere between. Despite only 6/29 variables being considered normally distributed, according to the Kolmogorov-Smirnov test with a significance level of 5 %, PCA on biomarkers does provide valuable insight and has been very successful in previous studies (Faksness et al., 2009 and Henriksen, 2012 among others). The PCA analyses in this study, as well, have found a good degree of separation between the different groups.

When looking at the first PCA of the standardised biomarkers (image 4.1), there are some interesting trends. First are the spill samples from Server and Full City clustering to the left. Inspection of the loadings plot reveals correlation with MA, traditionally associated with bunker oils. The ratios of C18/Ph and C17/Pr can also be seen here, which is related to the freshness of the oil, these ratios were all very small or missing in the highly weathered samples.

Just as the COSIWeb database, Full City sample 52 was immediately identified as different by the model. Apart from the long distance from the source of the spill and delayed sampling time leading to prolonged weathering and the possibility of mixing with other substances, there is no obvious explanation as to why this sample should be different. Other samples (51) were found further from the spill, but sampled earlier in time, so distance cannot be the only factor. Also, the other spill samples from Server are more similar to Full City than sample 52, which could further indicate mixing of this sample with an unknown contaminant.

Although PC1 in the standardised PCA is clearly related to degree of weathering of the samples, it is also capable of separating the bunker oils from the crude oils. It is also interesting how PC2 is clearly separating the two classes of crude oils, which indicates that the two classes of crude oils really are different. Another interesting feature is how the non-NS crude oils appear to bunch together quite tightly, compared to the crude oil group. There could be several possible explanations for this, one might be that the different crude oils are more different, and could possibly be separated into even smaller groups.

This might illustrate the point made in the beginning of the results chapter; even if an oil is not in the group non-NS crude oils, it does not mean that it is an NS crude oil. It certainly could be, but might also be Canadian, Asian, Australian, or any other sort of oil where there was not a stratification of the water column at the time of the deposit (30G) or the source material was not of terrestrial origin (30O).

It is not obvious what the remaining PC's are explaining, but there is more information in the dataset. Even up to PC7, the various groups can still be identified as clusters. This indicates that there is a lot of useful, underlying information in the data, but might also indicate that not all information has been extracted from the components, even though seven should be more than enough for any sort of MVA.

5.4.3.b PCA of metals

By the first, log transformed PCA plots of the metal concentrations, it could be confirmed that there was information in the dataset. The problem now was to present or extract this data in the best possible way and identify the most essential variables to the study.

After standardisation of the log transformed variables, an interesting trend was observed. Strong dividing lines between Full City, Server and some of the other bunker fuels could be seen. This is interesting, because the biomarker analysis of the same samples bunched Full City and Server quite tightly together when analysed along with the weathered samples. The metals, on the other hand, are separating the two spills. This could be a useful feature if several oil spills have occurred in the same area, for instance a harbour or busy shipping bay. The important variables in this separation appears to be vanadium, nickel and sulphur, which is good news as these are the most abundant in oil and easy to measure. They have also been studied more extensively than any other metals in oil, and would be more defensible in a legal situation.

The influence of the two selenium isotopes in the plots is a surprising one, but could potentially be very helpful. Isotope ratios such as lead, selenium and cadmium would be a lot more stable than most other metal ratios presented in this study, as isotopes would be expected to water wash at the same ratios. There should be no difference in oil phase preference or organic molecules either, and so the isotope ratios are considered reliable and stable.

The correlation seen between vanadium, nickel and sulphur is in agreement with literature. This indicates that even extensive weathering and water washing of the samples has not been able to remove or ruin this information, which is assumed to be the three most important elements in the study.

5.4.3.c PCA of metal ratios

An interesting thing to notice when looking at the PCA of the metal ratios is how most of the metals seem to cluster in a group along with the crude oils. It is possible that the simple presence of certain metals could be a tell-tale indicator of whether or not oil is a crude or bunker fuel. This is because of the strict legislation put on oil refineries to remove sulphur in the oil before it is put out on the market. Removing the other metals is in the self-interest of the refineries, as several metals, especially lead and aluminium, would quickly poison and render their catalyst inactive. This effect could get muddled by heavy weathering though, as seen by some weathered bunker fuels making their way towards the metal cluster to the left on the PCA plot. Both evaporation of oil and adsorption of particulate matter from the surroundings might contribute to this effect.

Another thing to notice about the metal PCA plots is their seeming inability to differentiate the two classes of crude oils. This could be another argument in favour of how one of the most identifying factors about the metal analysis is whether or not the oil has been through a refinery, and had most of their metals removed.

5.4.4 PARTIAL LEAST SQUARES

Although interpretation of PLS data is not always as intuitive and straightforward as opposed to the simpler PCA data, PLS can be hugely informative in its own right. It does provide a whole lot of information in a very condensed way, and the issue is then often to interpret it, rather than acquire it.

5.4.4.a Partial Least Squares-Regression

In using the PC's rather than ratios from the biomarkers, the PLS-R model can be seen as approaching a principal component regression (PCR) in some ways. This hybridisation does not appear to have any detrimental or beneficial effects on the model as a whole, considering how the explanation power is only slightly increased in % compared to using standardised biomarkers.

One thing that might be of concern is the distribution of influence between the samples. There is a trend across the MVA analyses, that the spill samples exert less influence compared to the average, because they are more homogenous in nature. On the other hand, crude oil samples are often found on the opposite end of the influence scale due to their much higher variation. This could skew the model more towards trying to explain trends in the crude oil samples rather than the oil samples as a whole.

When it comes to one of the aims of this study, however, the PLS-R model is not providing convincing data. compared to the first, standardised biomarker ratio PCA (image 4.2), neither the PCA models of metal ratios or PLS-R models of combined ratios seem to perform better than the tight and relatively separated clusters found in the first and varimax DR model. In this sense, it is more interesting to look at a few, key metals as opposed to a suite of metals.

Where the metals appear to have some advantage, however, is in separating two different oil spill samples, such as Server and Full City. In this case, it was shown that the primary factor was the NiV* ratio. It was especially interesting to see that sample 52 did not present any confusion with regards to the classification, as this sample has shown signs of weathering and contamination.

With 19 days from oil spill to sampling, sample 52 displayed the longest time span from the Full City samples. 19 days is nothing compared to the longest time span for the Server sample though, with sample 60 having to wait 105 days from the time of the spill to the time of sampling (Appendix A). The model shows no problem in placing sample 60 in the tight cluster of the predicted vs reference plot (image 4.13), which is a further indication that sample 52 has suffered unknown contamination.

5.4.4.b Partial Least Squares-Discriminant Analysis

The most interesting feature observed by the PLS-DA model in this study, was its ability to separate crude oils and non-NS crude oils into two distinct groups based on high and low metal content. Literature reveals that low metal content in oil is typically associated with oils of terrestrial source material, and a theory is proposed that the difference between marine and terrestrial source material is what the model is separating. This could be of value in cases where biomarkers such as 30O are not providing sufficient information.

The other PLS-DA model was made to try to identify some of the unknown weathered samples in the study. For the two models, one for DR's and one for metal ratios, several of the unknown samples were classified as crude oils, but only two of these were classified as crude oils by both models. Under the assumption that DR's are optimised for oil analysis, it is concluded that the metal ratios perform less reliably compared to the DR model.

A drawback to this is that a PLS-DA classification is heavily reliant on good quality training data sets. The data set in this study was quite small, and some larger studies could be conducted to further investigate this theory. The model made with the data from the non-NS crude oils did classify the crude oil group as well, indicating that the model has explanation power.

5.5 INFLUENTIAL METAL RATIOS

In the study of these models, the MnFe* ratio has steadily emerged as an interesting and relevant ratio for the separation of groups, especially bunker oils. Manganese is added to petroleum fuels to improve combustion, suppress smoke and even to impede the formation of SO_3. This could be an explanation as to why this ratio is showing the ability to separate bunker oils from crude oils, but it is not immediately clear why the Mn* ratio is not showing a similar trend.

One possibility is that the presence of iron in oil handling equipment could have an effect on the ratio after the oil has been through the refinery. Vanadium, on the other hand, might be suffering losses during removal of metals from the oil. And while nickel and vanadium are removed at approximately the same rate, the same need not be true for manganese, especially if added to the petroleum after refining.

NiV* was also decisive in the separation of Full City and Server, but it is unclear if this was a "lucky coincidence" only relevant to these two oil spills, or if it could be applied to oil spills in general. As with biomarkers, this ratio would struggle when oils are mixed, and this might reduce the usefulness in important areas, such as harbours, where oil spills of various sizes would be expected to occur with some regularity. The NiV* ratio is one of the most well-known and studied ratios in oil and it is encouraging to see results, even though more cases are needed to fully assess its value as a tool in the oil spill fingerprinting toolbox.

Next on the list is the VS* ratio, another classic ratio from previous investigation of oils. This ratio, again, appear to primarily help separate bunker oils from crude oils. The strict legislation on desulphurisation of fuels, especially marine fuels, might be an explanation for this.

In the PCA plot of standardised metal ratios (image 4.8), the UPb* ratio is less dominating indicator for bunker fuels along with the Mo* ratio. These trends are somewhat dwarfed in the subsequent models, but can still be seen in the PLS-R of metal ratios and biomarker PC's (image 4.11).

Another encouraging thing about the metals in these ratios is that they can all, except for uranium, be found in the reference material Conostan. Lack of reference material is a serious drawback and can have a detrimental effect on the reliability of any results. If already-available reference materials can be used, this would lower the bar for most labs looking to implement some metal analysis into their oil analysis. All of these metals except for uranium were also found in the oils in concentrations larger than 1µg/g, which is encouraging with respect to using other instruments which may be less sensitive and display higher LOD's.

5.6 RARE EARTH ELEMENTS

One of the first interesting things about the REE's is the division of normality when the Kolmogorov-Smirnov test was performed. Looking at the CI normalised plot (image 4.21), these elements are the most depleted in the samples as well. After inspecting the raw data, it becomes clear that this is not an issue related to low concentrations and the sample LOD, as the samples are, on average, two orders of magnitude larger than the LOD and quite reliable.

One possible explanation might be that the small chemical differences between LREE's and HREE's make themselves more evident over time. In the study by Zhang et al. (2009) it was theorized that their results could be due to HREE's showing stronger affinity towards organic matter compared to LREE's, which is interesting.

In the loadings plot of image 4.22, there is clearly a line in the HREE's going from lutetium (71), though thulium (69), ytterbium (70), holmium (67), erbium (68), dysprosium (66) and finally, terbium (65), before the line seems to disintegrate slightly along with the LREE's. The numbers in the parentheses are the respective atomic numbers. It is not clear why this thulium before ytterbium and holmium before erbium would occur, but it is curious to note that both thulium and holmium have an odd number of f-electrons. And if PC1 is mostly concentration related, this could further illustrate the observations of Zhang et al. (2009), who noted that REE's were enhanced or depleted, depending on whether or not they had odd or even numbers of f-electrons in their outer shell.

In light of this, it would appear as if these results are contrary to the results on Zhang et al. (2009). If the HREE's show stronger affinity towards organic matter, why are they the most heavily depleted in all the oil samples compared to chondrite? One reason differences may be observed is that the study by Zhang et al. (2009) did not normalise against chondrite, but rather a background of mudstone in the area to spot differences specific to their reservoirs.

Another possible explanation could be related to atomic radii of the elements. The size of the elements decrease from the lightest to the heaviest REE, and since the depletion is so obvious in the HREE's this could be part of the reason. It does however not explain the extreme depletion seen in terbium.

One issue with regards to the REE's is how they mainly seem to separate the fresher spill samples Full City and Server from the weathered samples in general. The weathered bunker samples are still part of the weathered oils. This might indicate that the separation seen in the PCA (image 4.22) could be due to weathering effects. This would not be very useful in a spill related incident, especially considering how only one of the spills (Full City) is clustering, while Server is widely spread out.

Even though some information could be gathered from the REE's, it would seem they are not quite suitable for oil spill identification.

6. CONCLUSION

The aim of this study was to investigate the development and viability of ICP-MS analyses of oil samples, primarily with regards to oil spills. Laboratory work was conducted in order to provide a dataset with both GC-FID-SIM biomarker data and ICP-MS trace metal data for the same oils. Most of these oils were heavily weathered oils from the outskirts of the Trøndelag coast.

PCA was performed on both datasets to gain insight and information about the data at hand, and to compare the classification done by biomarkers and trace metals separately. This visual representation was also useful in potentially identifying unknown oil samples. There were in total 46 unknown, weathered samples in this study. Of these, 14 were classified as non-NS crude oils, 9 as crude oils, 11 as bunker oils and 7 as unknown oil. Several of the unknown oils were later classified as crude oils by PLS-DA. In addition 5 samples were not oil; these could be other materials such as plastic, rubber, coal or organic material.

The database COSIWeb was used to analyse and compare the different samples. By the help of correlation coefficients, 5 weathered bunker oils were concluded as "probable match" to oils from outside this study. One was a possible remnant from the Full City accident in Norway, while another had a match in the Shetland Isles of Great Britain, indicating that oils traverse substantial distances overseas.

On its own, trace metal analyses were found to perform well, but not as well as the traditional biomarkers. A PLS-DA model was successfully used to separate two classes of crude oil containing high and low metal content. A theory is proposed that this is separating oils of marine and terrestrial source material, respectively. A second PLS-DA model was made to identify unknown weathered samples as either crude or bunker, where the biomarker model performed better than the metal ratio model

In the case of the two spills, Full City and Server, the metal ratio Ni/V was highly successful in separating the two, and could provide useful information as part of an oil spill tool box.

The metal ratios Mn/Fe, Ni/V, V/S and U/Pb were found to be the most influential variables, followed by less influential but still relevant ratios such as Fe/(Fe+V), Sn/(Sn+V), Mo/(Mo+Cr) and Sr/(Sr+V).

REE's, while capable of separating oil spill samples from weathered samples, were not found to be relevant in the investigation of oil spill classification conducted in this study. For the other metals, they are identifying factors in the sense that they may be able to tell if an oil has been through desulphurisation and removal of metals and thus through a refinery.

In summary, a full scan of trace metals in oils by ICP-MS does not appear to be feasible, but a small suite of metal ratios, especially Ni/V, Mn/Fe and V/S could be a very helpful addition to the established biomarker method.

7. FURTHER WORK

This study has demonstrated that there is information about source and type in trace metals in oil samples from weathered oils and accidents. It could be interesting to look at larger, but more specific data sets, such as different crude oils or several different spill samples.

The issue with reliability based on suspicion of water washing of different metals in the oil is a problem which could be really interesting to investigate further. Some of the noise in the models might be due to information getting ruined by substantial weathering, and if this is investigated, methods could be put in place to mitigate such effects.

It would also be valuable to acquire more information about speciation of elements in oil, such as manganese, as this is only available for the most important elements today (sulphur, nickel, vanadium). The PLS-DA model, while promising, could benefit from a bigger study to assess its reliability with a larger and more varied dataset.

There are several aspects of this study which has not been investigated fully due to time restraints, and a lot of information could still be hidden in the trace metal dataset. Especially ratios not related to vanadium, nickel or sulphur would have been dwarfed by this study and present a large potential for further studies.

In further work, it is recommended to investigate the effect of filtration during workup, both sodium sulphate, silica and others, and especially if the 250 ˚C+ fraction of crude oils is more suitable for metal analysis compared to fresh crude oil. The classification ability demonstrated by the Ni/V ratio is also interesting, and is being investigated by several others already.

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APPENDICES

Appendix A: Description of the samples

Table 1: Description of selected samples from KJ3050, 2011. Star denotes samples which have been analysed in previous studies.

Msc ID	SINTEF ID	Field ID	Odour	Description	Prev. Class.	Classification	GPS coords.	Island	Information
KV0001	2012-0096	AS02*	Old oil	Bendable, slightly soft	non-NS crude	non-NS crude	N63o50,574 E008o27,105	Sula	Hard/old outside, sticky inside. Some gravel
KV0002	2012-0099	AS06*	Oil	Soft, bendable	Bunker	Bunker	N63o50,670 E008o27,053	Sula	Feathers in matrix
KV0003	2012-0101	AS08*	Oil	Sticky, bendable, slightly soft	North Sea crude	crude	N63o50,696 E008o27,052	Sula	Small, hard lump
KV0004	2012-0103	BS01*	Oil	Bendable, very sticky	non-NS crude	Bunker	N63o50,619 E008o27,106	Sula	Some matrix contaminant
KV0005	2012-0105	BS03*	Oil	Soft, sticky	Bunker	non-NS crude	N63o50,624 E008o27,129	Sula	Hard, shiny
KV0006	2012-0107	BS05*	Forest, oil	Soft, sticky, bendable	non-NS crude	Bunker	N63o50,549 E008o27,146	Sula	Hard, matte. Some contaminants
KV0007	2012-0110	BK01*	Strong oil-smell	shiny, sticky, rubbery	non-NS crude	non-NS crude	N64o01,963 E009o09,382	Kunna	Particles/contaminants in matrix
KV0008	2012-0112	BK02*	Not distinct	Shiny, soft	Unclassified	Unknown	N64o01,963 E009o09,382	Kunna	Hard/old outside, soft inside
KV0009	2012-0114	BK04*	Strong oil-smell	Shiny and sticky	North Sea crude	crude	N64o01,969 E009o09,374	Kunna	Hard
KV0010	2012-0115	BK05*	Slight oil-smell	Porous, not shiny, not dense	Bunker	not oil	N64o01,969 E009o09,373	Kunna	Not oil, more reminiscent of black sponge
KV0011	2012-0117	BK07*	Slight oil-smell	Not shiny, slightly sticky	non-NS crude	non-NS crude	N64o01,990 E009o09,367	Kunna	Soft, refuses to dissolve properly
KV0012	2012-0122	BSK02*	Yes, but not strongly	soft	non-NS crude	non-NS crude	N64o02,212 E009o08,138	Storkalven	Soft, refuses to dissolve properly
KV0013	2012-0126	BSK06*	Weakly	Rubbery inside	Bunker	Unknown	N64o02,204 E009o08,170	Storkalven	Semi-solid, sticky
KV0014	2012-0128	BSK08*	Not distinct	Dense and hard inside	Unclassified	not oil	N64o02,202 E009o08,200	Storkalven	Hard, shiny "crystalline", solid
KV0015	2012-0131	BSK12*	Not distinct	Rubbery, soft, sticky, dense	North Sea crude	Unknown	N64o02,209 E009o08,206	Storkalven	Hard outside, soft inside, does not dissolve properly. On the small side
KV0016	2012-0136	BSK16*	Yes, but not strongly	Dense, slightly hard inside	Unclassified	non-NS crude	N64o02,218 E009o08,365	Storkalven	Does not dissolve properly. Large sample size

KV0017	2012-0143	AK20*	No oil-smell	Tarball. Hard and sticky inside	non-NS crude	non-NS crude	N64o02,482 E009o09,673	Kunna	Soft, refuses to dissolve properly
KV0018	2012-0147	AK01*	Oily smell	A flat sample. Soft and sticky inside	North Sea crude	crude	N64o02,522 E009o10,019	Kunna	Feathers/contaminants in matrix
KV0019	2012-0150	AK06*	Oily smell	Tarball. Semi-solid and sticky inside	non-NS crude	non-NS crude	N64o02,533 E009o10,024	Kunna	Soft, refuses to dissolve properly
KV0020	2012-0152	AK08*	Oily smell	Flat and small sample. Hard and sticky inside	Bunker	Bunker	N64o02,548 E009o10,042	Kunna	Soft, refuses to dissolve properly
KV0021	2012-0153	AK09*	Oily smell	Irregular shape. Sticky and solid	North Sea crude	crude	N64o02,548 E009o10,042	Kunna	Soft, refuses to dissolve properly
KV0022	2012-0161	AK17*	Slight oil-smell	A piece of a tarball. Hard and sticky inside	non-NS crude	non-NS crude	N64o02,482 E009o09,673	Kunna	Soft, refuses to dissolve properly
KV0023	2012-0164	AVK02*	Slight oil-smell	Thin layer of oil. Sticky inside	North Sea crude	crude	N64o02,377 E009o07,730	Vesterkalven	Sticky, fair bit of matrix
KV0024	2012-0172	AVK10*	Slight oil-smell	Tarball 3 cm diameter. Soft and sticky inside	North Sea crude	not oil	N64o02,352 E009o07,709	Vesterkalven	Soft, refuses to dissolve properly
KV0025	2012-0175	AVK15*	Slight oil-smell	Flaky, 1x2 cm. Shiny and sticky inside	Bunker	Bunker	N64o02,336 E009o07,695	Vesterkalven	Hard and shiny
KV0026	2012-0178	AVK18*	No	6x3 cm. Soft and sticky inside	non-NS crude	non-NS crude	N64o02,298 E009o07,648	Vesterkalven	Lots of matrix contaminants
KV0027	2012-0179	AVK19*	Oil	Liquid, found in a lubricate oil container	N/A	not oil	N64o02,298 E009o07,648	Vesterkalven	Yellow liquid, will not dissolve in DCM, two clear phases

Table 2: Description of selected samples from KJ3050, 2012. Star denotes samples which have been analysed in previous studies

Msc ID	SINTEF ID	Field ID	Odour (1-5)	Stickyness (1-5)	Sample size	Prev. Class.	Classification	GPS coords.	Island	Information
KV0028	2012-0248	1A1*	2	2	15x10	Bunker	Bunker	N63o46,368 E008o18,691	Kya	A fair bit of matrix (contaminants)
KV0029	2012-0249	1A2	3	3	15x15	N/A	non-NS crude	N63o46,367 E008o18,691	Kya	A fair bit of matrix (contaminants)
KV0030	2012-0251	1A4*	2	3	5x8	North Sea crude	crude	N63o46,389 E008o18,665	Kya	Lots of contaminants
KV0031	2012-0256	1A9*	5	5	20x30	Bunker	Bunker	N63o46,492 E008o18,626	Kya	Semi-liquid, smooth
KV0032	2012-0258	1A11	3	1	150(?)	N/A	crude	N63o46,397 E008o18,548	Kya	Hard/sticky
KV0033	2012-0260	1A13	2	1	7x4	N/A	Unknown	N63o46,323 E008o18,469	Kya	Brittle "flakes", hard/sticky
KV0034	2012-0262	1A15	4	3	13x7	N/A	Bunker	N63o46,313 E008o18,517	Kya	"Grainy" texture
KV0035	2012-0267	1A20*	5	0	10x15	North Sea crude	crude	N63o46,264 E008o18,487	Kya	Big lump, quite solid
KV0036	2012-0269	1A22*	5+	2	70x8	Bunker	Bunker	N63o46,250 E008o18,509	Kya	Hard, weathered lid, liquid inside
KV0037	2012-0272	1B3*	1	2	10x8	Bunker	Bunker	N63o41,322 E008o20,473	Frøya (Kjervågsundet)	"Secretes" oil (or water?) when you take a sample
KV0038	2012-0273	1B4	1	5	8x5,5	N/A	crude	N63o41,329 E008o20,503	Frøya (Kjervågsundet)	Sticky, stubborn, hard.
KV0039	2012-0276	1B7*	3	5	19x111	North Sea crude	non-NS crude	N63o41,299 E008o19,971	Frøya (Kjervågsundet)	Bird feathers, sticky, "stubborn" soft
KV0040	2012-0278	1B9	2	3	12x10	N/A	Unknown	N63o41,308 E008o20,052	Frøya (Kjervågsundet)	Hard, slightly white on top, contaminants
KV0041	2012-0290	A05*	2	4	12x15x1	North sea crude	Unknown	N63o46,423 E008o18,804	Kya	Hard, white one top (fungi?)
KV0042	2012-0295	A10	0	0	3x3	N/A	Bunker	N63o46,440 E008o18,801	Kya	Hard and shiny, but sticky. On the small side
KV0043	2012-0301	A16	0	0	7x30	N/A	not oil	N63o46,450 E008o18,745	Kya	Not oil, Thin film, full of grass, not sticky
KV0044	2012-0309	B24	0	0	2x3	N/A	non-NS crude	N63o41,470 E008o20,386	Frøya (Kjervågsundet)	Hard, thin, slightly sticky and "stubborn". Small sample
KV0045	2012-0314	B29*	1	0	5x5	non-NS crude	non-NS crude	N63o41,480 E008o20,676	Frøya (Kjervågsundet)	Sticky with weathered "lid"

KV0046	2012-0316	B31*	1	4	5x10	North sea crude	Unknown	N63o41,446 E008o20,658	Frøya (Kjervågsundet)	Bird feathers, sticky

Table 3: Description of selected spill samples from Full City and Server

Msc ID	SINTEF ID	Location	Date of sampling	Distance from wreck (Kamalia, 2011)	Accident	Information
KV0047	2009-0485	Krogshavn	31-Jul	3.3 km	Full City	Krogshavn, ref.1 "20 L with smooth emulsion pumped up from the sea in Krogshavn"
KV0048	2009-0579	Såstein	6-Aug	N/A	Full City	Såstein, ref. 2. "Oil from bay within havarist"
KV0049	2009-0491	Nevlungavn, Ødegårdsfjord	6-Aug	9.8 km	Full City	Steinvik, match ref. 2 "1-15 mm thick, taken in Steinvik in Ødegårdsfjord, Nevlunghavn"
KV0050	2009-0493	Langesund bad	7-Aug	3.7 km	Full City	Langesund, match ref 1 "Langesund bad, 1 mm. Krogshavn."
KV0051	2009-0486	Landøy / Mandal	3-Aug	190 km	Full City	Match ref. 2, NM ref. 1 "Oil with traces of free water"
KV0052	2009-0622	Lyngholmane, Lillesand	19-Aug	115 km	Full City	Partial match ref. 2, NM ref. 1
KV0053	2007-0023			N/A	Server	Reference, "Sample from Tank 3"
KV0054	2007-0012		12-Jan	N/A	Server	Reference, "Emulsion from skimmer head on board KV Eigun"
KV0055	2007-0010		14-Jan	N/A	Server	Match, "Emulsion, taken from the sea by KV Ålesund"
KV0056	2007-0063		2-Feb	180 km	Server	Match, "Oil sample, Kvamsøy, Sande county"
KV0057	2007-0025		18-Jan	165 km	Server	NM CEN, Match multivariat, "Oil sample from sandy shore, Selje county"
KV0058	2007-0016		14-Jan	N/A	Server	Match, "Emulsion from crack in the rocks. Only patchwise oil in the area around the crack."
KV0059	2007-0064		31-Jan	N/A (far, far off)	Server	Match, "Oil sample, Stongholmvikjo, Bømle county"
KV0060	2007-0282		25-Apr	125 km	Server	M SINTEF, PCA and Scaled PLS-DA, NM unscaled PCA, "Oil sample, Vetvika, Bremanger county, Nordfjord"

Table 4: Description of selected fresh crude oils

Msc ID	SINTEF ID	Name	Information
KV0061	2010-0262	Ringhorne	Black, liquid
KV0062	2007-0426	Draugen	Black, liquid
KV0063	2009-0239	Kvitebjørn kondensat	Light yellow, see-through liquid
KV0064	2010-0327	Luno	Black, "heavier" liquid
KV0065	2008-0282	Alvheim kameleon	Black, liquid
KV0066	2007-0530	Alvheim konsensat	Black, liquid
KV0067	2006-0256	Kristin kondensat	Red, see-through liquid
KV0068	2009-0548	Norne Stære	Black, liquid
KV0069	2009-0552	Norne Alve	Near blank, slightly yellow, light liquid
KV0070	2011-0017	Trym	Light orange, sligthly opaque liquid
KV0071	2010-0351	Jordbær	Black, liquid
KV0072	2008-0500	Peregrino	Black, heavy, sticky, high viscosity
KV0073	2011-0421	Morvin	Black, heavy liquid
KV0074	2008-0099	Blane	Black, heavy liquid
KV0075	2007-0288	Alvheim	Black medium liquid
KV0076	2011-0431	Clair	Black, medium liquid
KV0077	2009-0547	Norne Svale	Black, liquid
KV0078	2010-0509	Caurus	Orange/red, slightly opaque, liquid
KV0079	2009-0284	Kobbe	Black, liquid
KV0080	2008-0045	Ormen Lange kondensat	Blank, see-through, light liquid

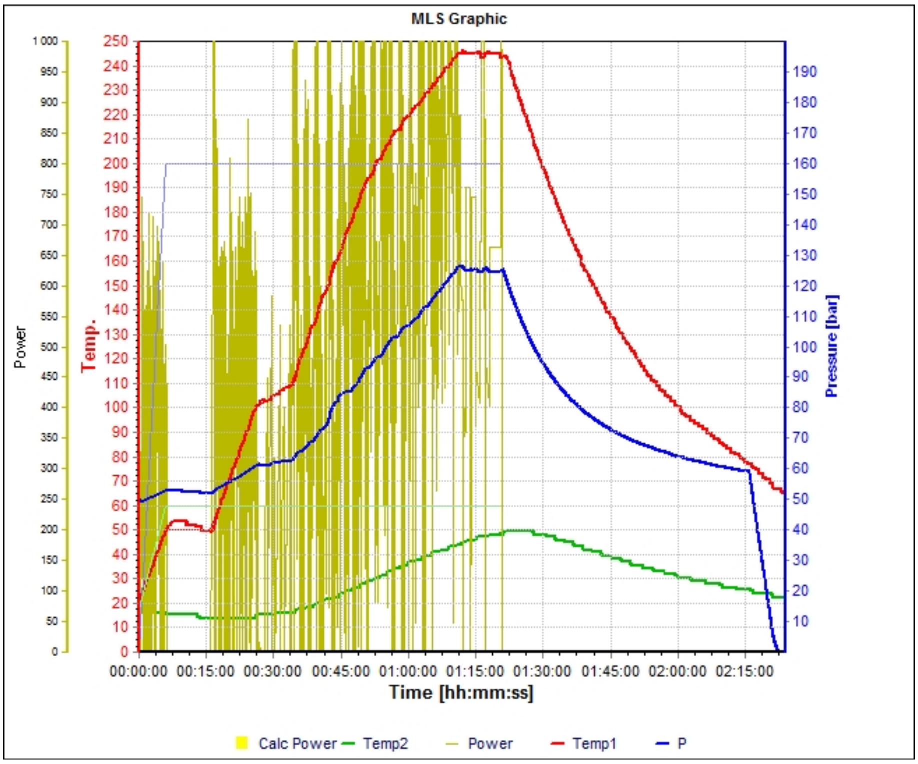
MLS Microwave Report

Application: ultraCLAVE

Report 25.10.2013 15:22:04 **Operator:** Administrator

Filename: M:\A\2013\PROJECTS NOT FINNISHED\KJEMI\MASTER\Kristine Vike - Oljeprøver\773-1-40-quarts-091013-Kristine-Vike-pnr73-80-Faksnes1-2.dpr

MLS Milestone
www.milestonesrl.com



Parameter

[illegible]

```
:Stand[illegible]
Create[illegible]:Administrator
Microwave power :pulse
Load pressure   :50.0 bar
Release temp.   :78.0 °C
Release pressure:10.0 bar/min
Cooling         :OFF
Auto open       :OFF
Cooling on Temp.:30.0 °C
Ground load     :300 30 2
Ventilation time:01:03:03
```

Remark:

Snr 773 vails 1-20 quarts 091013
Prosedyre ca 150 mg prove tilsettes 6 ml 50%v/v HNO3, dekomponeres i henhold til viste temperaturprofil, fortynnes sa til 60 ml som gir 0.6 M HNO3.
Prosjekt, masteroppgave Kristine Vike 80 oljeprover pnr 1-80, idag 73-89
samt 2 prover for Liv-Guri Faksness.

MW Program

Step	Time [hh:mm:ss]	Temp 1 [°C]	Temp 2 [°C]	Press [bar]	Engery [Watt]
1	00:06:00	50	60	160	1 000
2	00:10:00	50	60	160	1 000
3	00:10:00	100	60	160	1 000
4	00:08:00	110	60	160	1 000
5	00:16:00	190	60	160	1 000
6	00:06:00	210	60	160	1 000
7	00:15:00	245	60	160	1 000
8	00:10:00	245	60	160	1 000

Appendix C: Compounds analysed by GC-MS and used in CosiWeb

Table 5: Abbreviations used by CosiWeb and throughout this study(Wang and Stout, 2007; CEN, 2012).

Abbreviation	Name	Ion mass (m/z)
C16	C16 Alkanes	85 + GC-MS
C17	C17 Alkanes	85 + GC-MS
C18	C18 Alkanes	85 + GC-MS
Nor	Norhopane	85 + GC-MS
Pr	Pristane	85 + GC-MS
Ph	Phytane	85 + GC-MS
C23Tr	C23 Tricyclic diterpane	191
C24Tr	C24 Tricyclic diterpane	191
C25Tr	C25 Tricyclic diterpane	191
Tr28A	C28 Tricyclic terpane (A)	191
Tr29A	C29 Tricyclic terpane (A)	191
Ts	18α(H)-22,29,30-Trisnorhopane	191
Tm	17α(H)-22,29,30-Trisnorhopane	191
25nor	17α(H),21β(H)-25-Norhopane	191
28ab	17α(H),21β(H)-28,30-Bisnorhopane	191
29ab	17α(H),21β(H)-30-Norhopane	191
30O	18α(H) and 18β(H)-Oleanane	191
Hop	17α(H),21β(H)-Hopane	191

31abS	17α(H),21β(H), 22S-Homohopane	191 + 205
31abR	17α(H),21β(H), 22R-Homohopane	191
30G	Gammacerane	191
27dbS	13β(H),17α(), 20S-Cholestane (Diasterane)	217
27dbR	13β(H),17α(), 20R-Cholestane (Diasterane)	217
28aaR	24-methyl-5α(H),14α(H),17α(H), 20R-Cholestane	217
29aaS	24-ethyl-5α(H),14α(H),17α(H), 20S-Cholestane	217
29aaR	24-ethyl-5α(H),14α(H),17α(H), 20R-Cholestane	217
27bb	5α(H),14β(H),17β(H), 20R/S-Cholestane	218
28bb	24-methyl-5α(H),14β(H),17β(H), 20R/S-Cholestane	218
29bb	24-ethyl-5α(H),14β(H),17β(H), 20R/S-Cholestane	218
TASC26	C26, 20S-Triaromatic sterane	231
TASC27	C27, 20S-Triaromatic sterane	231
TASC28	C28, 20S-Triaromatic sterane	231
TARC27	C27, 20R-Triaromatic sterane	231
TARC28	C28, 20R-Triaromatic sterane	231
Retene	Retene	234
Tm-Phen	Tetra-methyl-phenantrene	234
BNT	Benzo[b]naptho(1,2-d)thiophene	234
2MF	2-Methylfluorantene	216
B(a)F	Benzo(a)Fluorene	216
B(b+c)F	Benzo(b+c)Fluorene	216
2MPy	2-Methylpyrene	216
4MPy	4-Methylpyrene	216

1MPy	1-Methylpyrene	216
4MD	4-Methyldibenzothiophene	198
2,3MD	2,3-Metyldibenzothiophene	198
1MD	1-Methyldibenzothiophene	198
3MP	3-Methylphenantrene	192
2MP	2-Methylphenantrene	192
MA	Methylanthracene	192
9/4MP	9/4-Methylphenantrene	192
1MP	1-Methylphenantrene	192
TMDBT	Tetra-mehyl-Dibenzothiophene	240

Table 6: The 29 biomarker ratios used by CosiWeb(Wang and Stout, 2007; CEN, 2012).

GC-FID:		
Ratio	Abbreviation	
C17/Pr	C17/Pr	FID
C18/Ph	C18/Ph	FID
Pr/Ph	Pr/Ph	FID
GC-MS:		
Ratio	Abbreviation	M/z
Ts/Hop	Ts	191
Tm/Hop	Tm	191
28ab/Hop	28ab	191
29ab/Hop	29ab	191
30O/Hop	30O	191
31abS/Hop	31abS	191
30G/Hop	30G	191
27dbR/27dbS	27dbR	217
27bb/29bb	27bb	218
TASC26/TARC26+TASC27	TASC26	231
TASC28/TARC26+TASC27	TASC28	231
TARC27/TARC26+TASC27	TARC27	231
TARC28/TARC26+TASC27	TARC28	231
C17/Pr	C17/Pr	85
C18/Ph	C18/Ph	85

Pr/Ph	Pr/Ph	85
2MP/1MP	2MP	192
MA/1MP	MA	192
4MD/1MD	4MD	198
2MF/4MPy	2MF	216
B(a)F/4MPy	B(a)F	216
B(b+c)F/4MPy	B(b+c)F	216
2MPy/4MPy	2MPy	216
1MPy/4MPy	1MPy	216
Retene/Tm-Phe	Retene	234
BNT/Tm-Phe	BNT	234

Appendix D: Instrumental-Limit of detection(I-LOD) and Practical-Limit of detection(P-LOD)

Table 6: ICP-MS limits of detection for each element used in this study. Yellow highlights indicates whether I-LOD or P-LOD was used in each case.

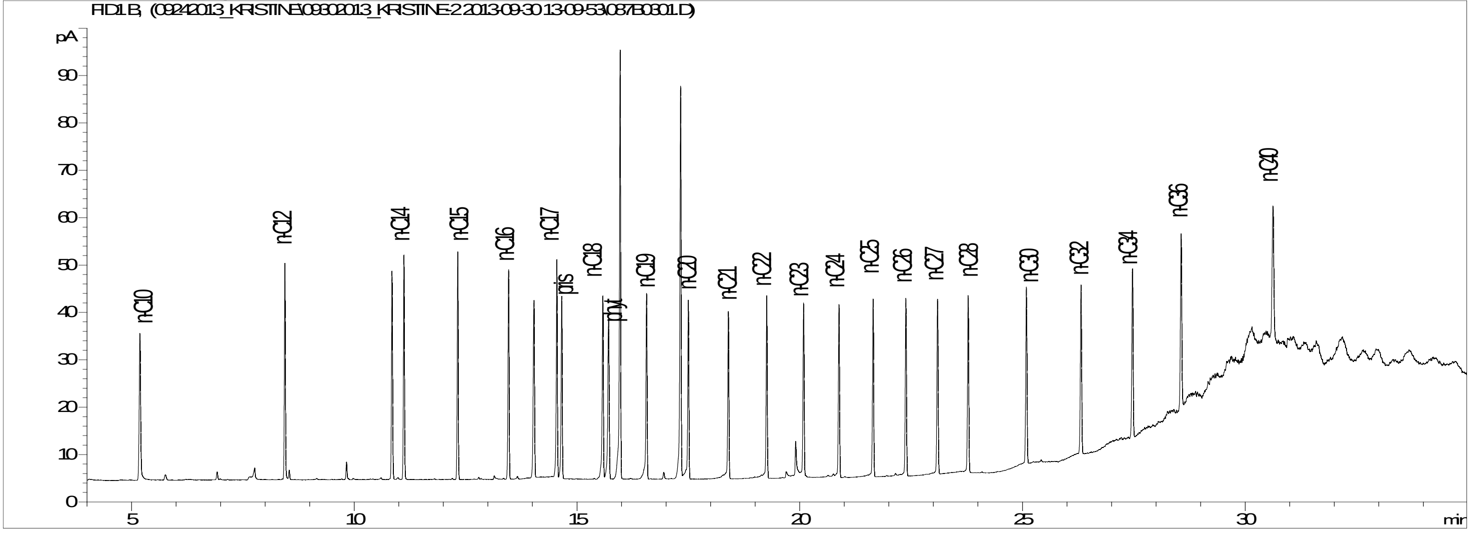
Lr, Mr, Hr = Low, Medium and High Resolution				IDL-25%	I-LOD		P-LOD
Sign	**Isotope**	**Element**	**Resolution**	**µg/l**	**µg/g**	**3*std**	**µg/g**
Al	27	Aluminium	Mr	0.2000	0.060000	10.2294	3.068832
Sb	121	Antimony	Mr	0.0020	0.000600	0.0034	0.001028
As	75	Arsenic	Hr	0.0250	0.007500	0.0021	0.000640
Ba	137	Barium	Mr	0.0130	0.003900	0.0213	0.006399
Be	9	Beryllium	Lr	0.0020	0.000600	0.0021	0.000629
Be	9	Beryllium	Mr	0.0080	0.002400	0.0011	0.000316
B	11	Boron	Lr	0.0500	0.015000	0.2587	0.077620
Cd	111	Cadmium	Lr	0.0020	0.000600	0.0039	0.001183
Cd	114	Cadmium	Lr	0.0020	0.000600	0.0026	0.000787
Ca	44	Calcium	Mr	2.0000	0.600000	87.3757	26.212712
Ce	140	Cerium	Lr	0.0002	0.000060	0.0028	0.000852
Cs	133	Cesium	Lr	0.0005	0.000150	0.0040	0.001196
Cr	52	Chromium	Mr	0.0050	0.001500	0.1000	0.029987
Co	59	Cobalt	Mr	0.0040	0.001200	0.0020	0.000609
Cu	63	Copper	Mr	0.0300	0.009000	0.0593	0.017804
Dy	163	Dysprosium	Mr	0.0020	0.000600	0.0006	0.000182
Er	166	Erbium	Lr	0.0003	0.000090	0.0003	0.000090
Ga	69	Gallium	Mr	0.0070	0.002100	0.0067	0.002012
Ge	72	Germanium	Hr	0.0200	0.006000	0.0043	0.001299
Au	197	Gold	Lr	0.0002	0.000060	0.0004	0.000124
Hf	178	Hafnium	Lr	0.0010	0.000300	0.0005	0.000138
Ho	165	Holmium	Lr	0.0002	0.000060	0.0002	0.000056

In	115	Indium	Lr	0.0005	0.000150	0.0005	0.000151
Fe	56	Iron	Mr	0.0200	0.006000	2.5912	0.777353
Ir	193	Iridium	Lr	0.0005	0.000150	0.0001	0.000043
La	139	Lantan	Mr	0.0020	0.000600	0.0021	0.000624
Pb	208	Lead	Lr	0.0020	0.000600	0.0232	0.006951
Li	7	Lithium	Mr	0.0300	0.009000	0.0125	0.003757
Lu	175	Lutetium	Lr	0.0002	0.000060	0.0001	0.000030
Mg	24	Magnesium	Mr	0.1000	0.030000	1.0093	0.302784
Mn	55	Manganese	Mr	0.0060	0.001800	0.0471	0.014139
Hg	202	Mercury	Lr	0.0010	0.000300	0.0017	0.000524
Mo	98	Molybdenum	Mr	0.0200	0.006000	0.0296	0.008888
Nd	146	Neodymium	Lr	0.0002	0.000060	0.0018	0.000534
Ni	60	Nikkel-60	Mr	0.0150	0.004500	0.0584	0.017527
Nb	93	Niobium	Hr	0.0250	0.007500	0.0162	0.004852
P	31	Phosphor	Mr	0.4000	0.120000	0.9938	0.298136
Pt	195	Platinum	Lr	0.0010	0.000300	0.0001	0.000044
K	39	Potassium	Hr	5.0000	1.500000	3.3822	1.014671
Pr	141	Praseodymium	Lr	0.0003	0.000090	0.0004	0.000109
Rb	85	Rubidium	Mr	0.0120	0.003600	0.0729	0.021881
Sm	147	Samarium	Lr	0.0005	0.000150	0.0007	0.000206
Sc	45	Scandium	Mr	0.0040	0.001200	0.0004	0.000130
Se	78	Selenium	Hr	0.1500	0.045000	0.0529	0.015875
Se	82	Selenium	Lr	0.0500	0.015000	0.0268	0.008031
Si	30	Silisium	Mr	4.0000	1.200000	235.9465	70.783943
Ag	109	Silver	Mr	0.0200	0.006000	0.0027	0.000815
Na	23	Sodium	Mr	10.0000	3.000000	7.9916	2.397485
Sr	88	Strontium	Mr	0.0250	0.007500	0.1370	0.041103
S	34	Sulphur	Mr	20.0000	6.000000	86.3247	25.897403

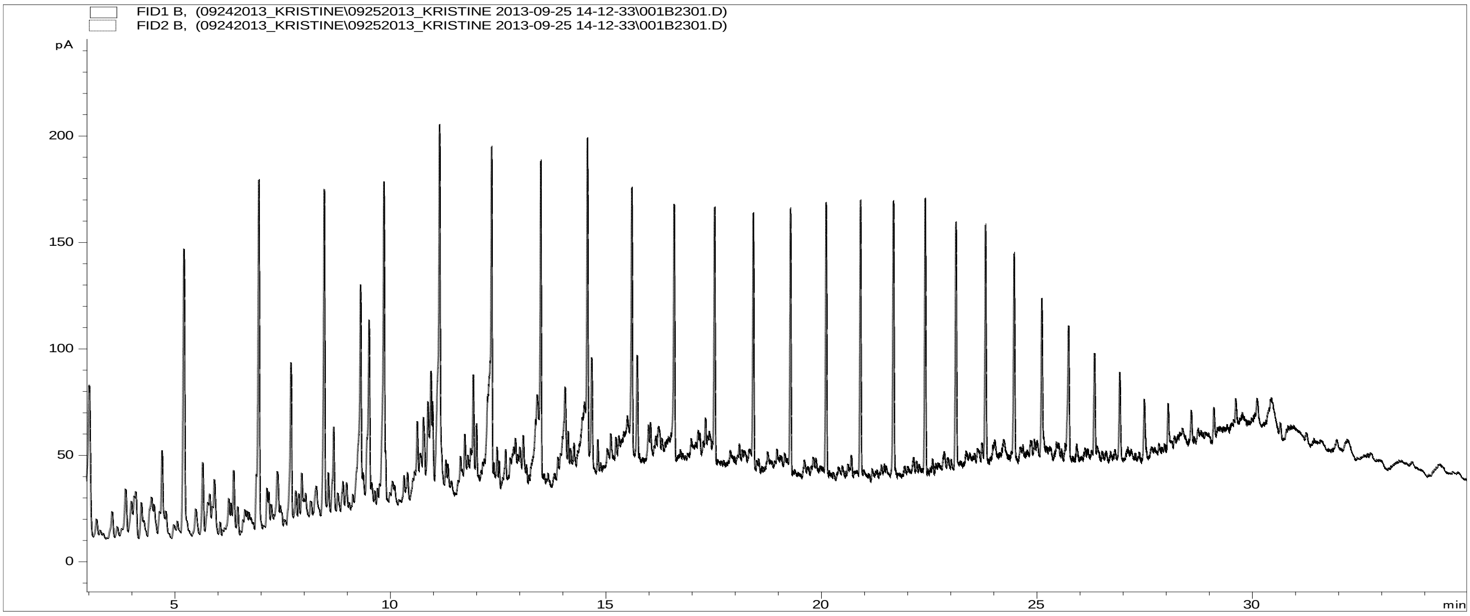
Ta	181	Tantalum	Lr	0.0002	0.000060	0.0037	0.001111
Tb	159	Terbium	Lr	0.0002	0.000060	0.0001	0.000028
Tl	205	Thallium	Lr	0.0003	0.000075	0.0009	0.000270
Th	232	Thorium	Lr	0.0005	0.000150	0.0007	0.000213
Tm	169	Thulium	Lr	0.0005	0.000150	0.0001	0.000017
Sn	118	Tin	Lr	0.0010	0.000300	0.1821	0.054643
Ti	47	Titanium	Mr	0.0200	0.006000	0.8839	0.265167
U	238	Uranium	Lr	0.0003	0.000075	0.0009	0.000266
V	51	Vanadium	Mr	0.0030	0.000900	0.0464	0.013928
W	182	Wolfram	Lr	0.0010	0.000300	0.1980	0.059400
Yb	172	Ytterbium	Lr	0.0004	0.000120	0.0004	0.000132
Y	89	Yttrium	Lr	0.0004	0.000120	0.0053	0.001575
Zn	66	Zink-66	Mr	0.0250	0.007500	1.5687	0.470602
Zr	90	Zirkonium	Lr	0.0005	0.000150	0.0195	0.005838

Appendix E: GC-FID chromatograms for all the samples

N-alkan std 0.5µg/L, CCV A448:



Sintef-mix:



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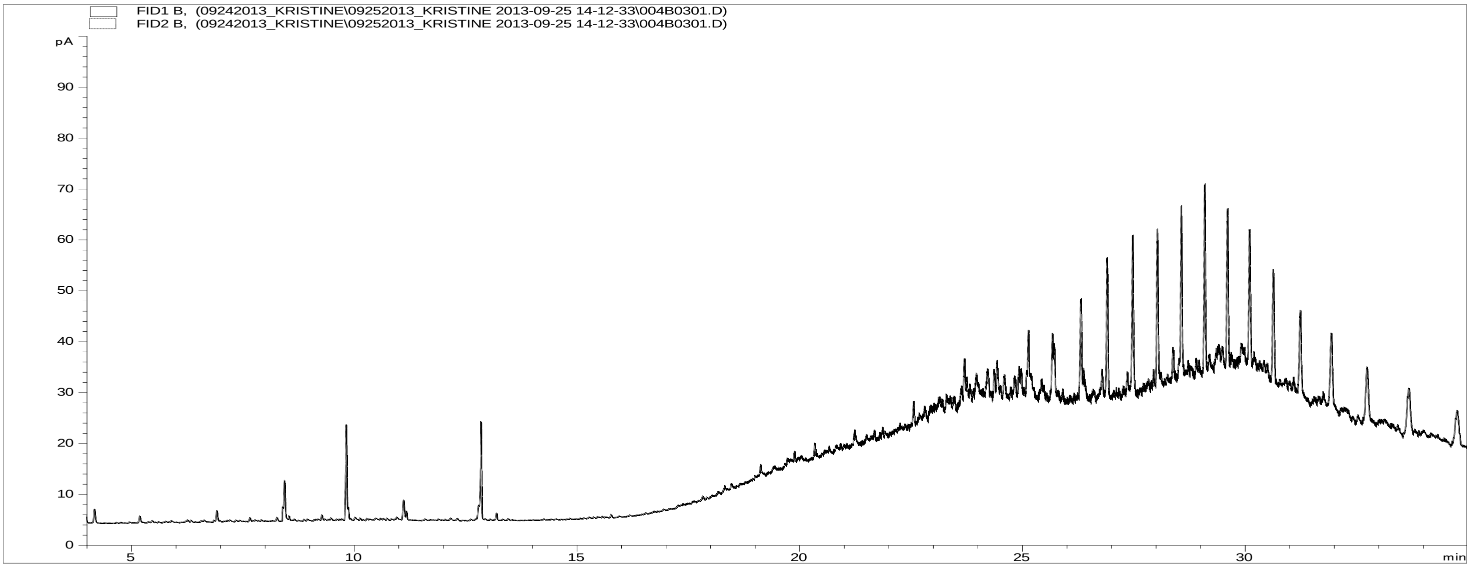

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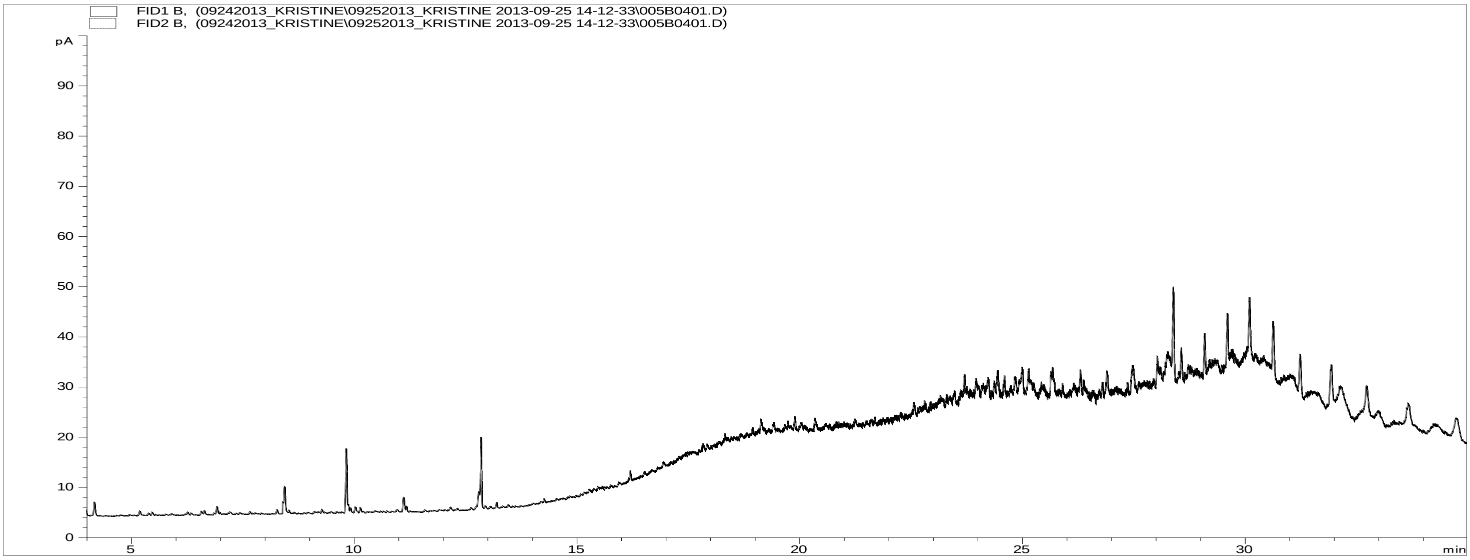

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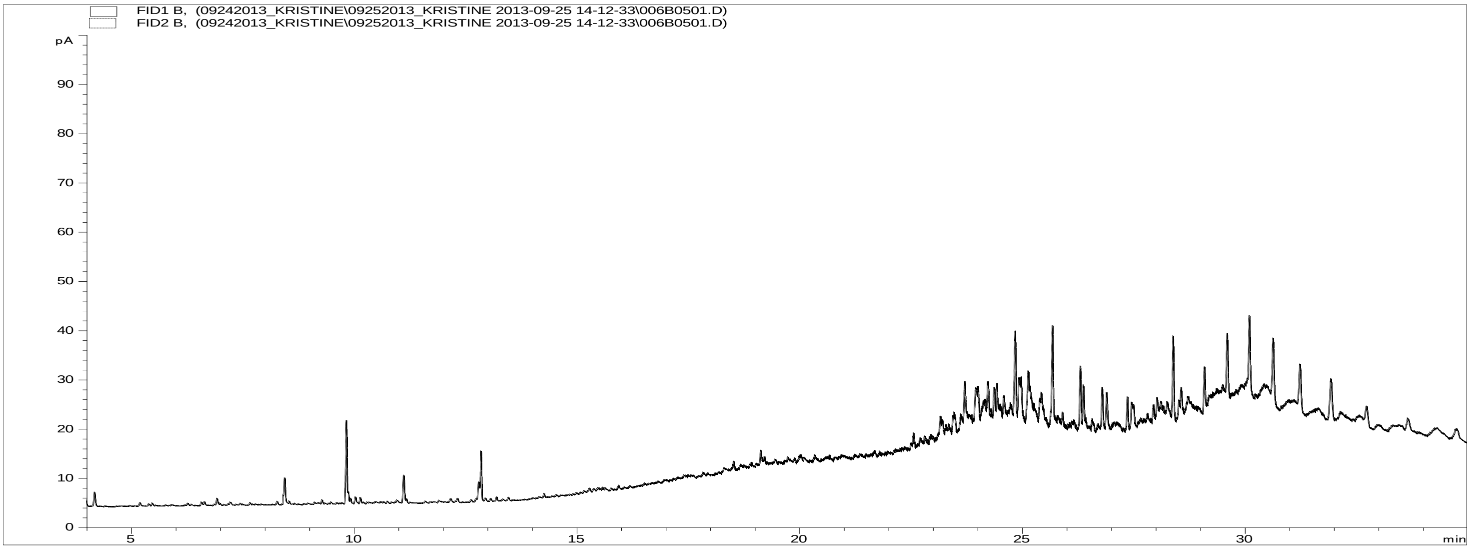

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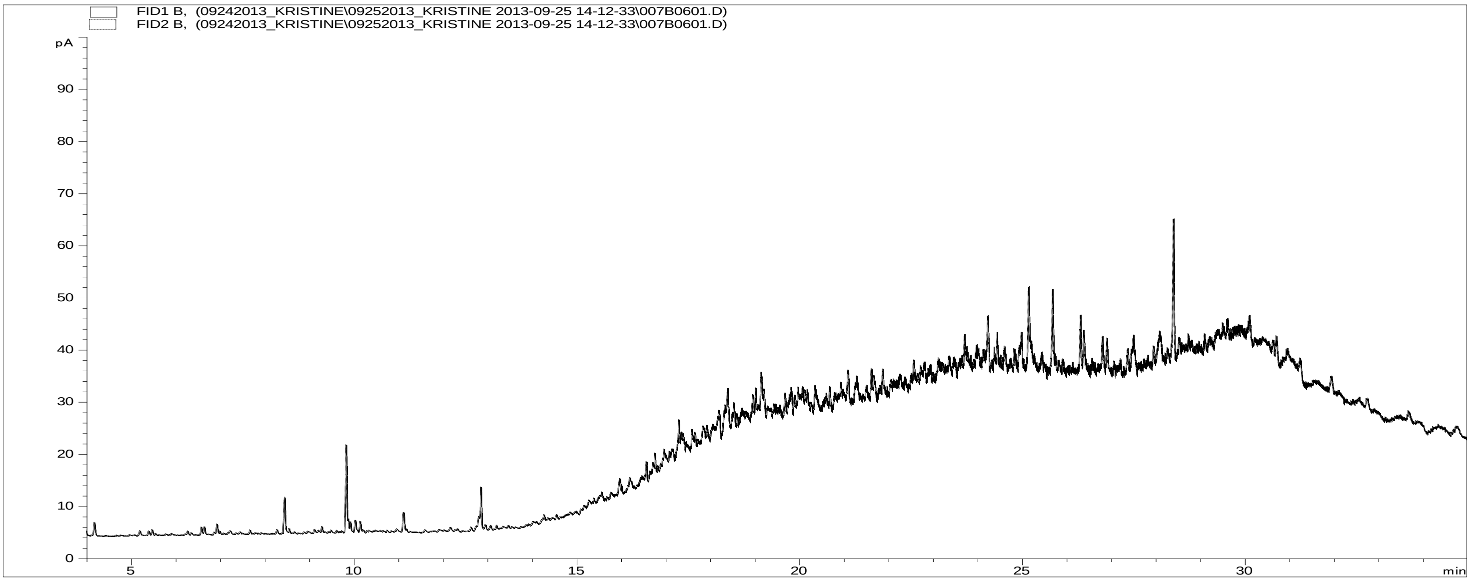

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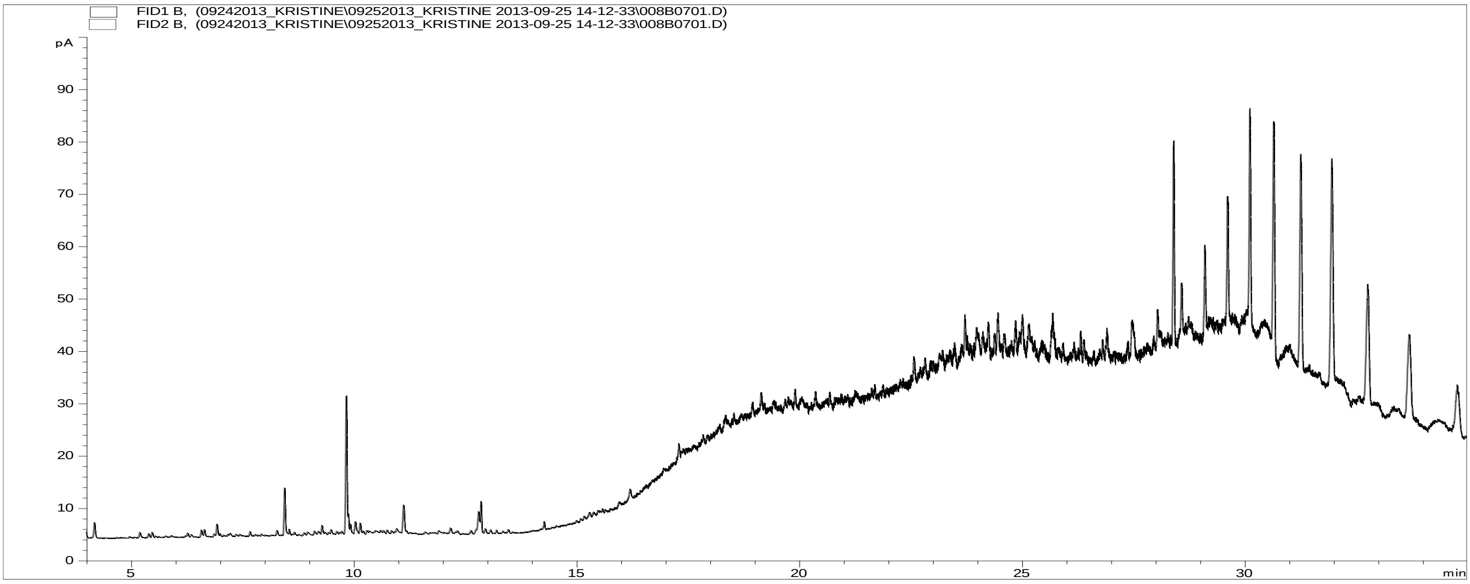

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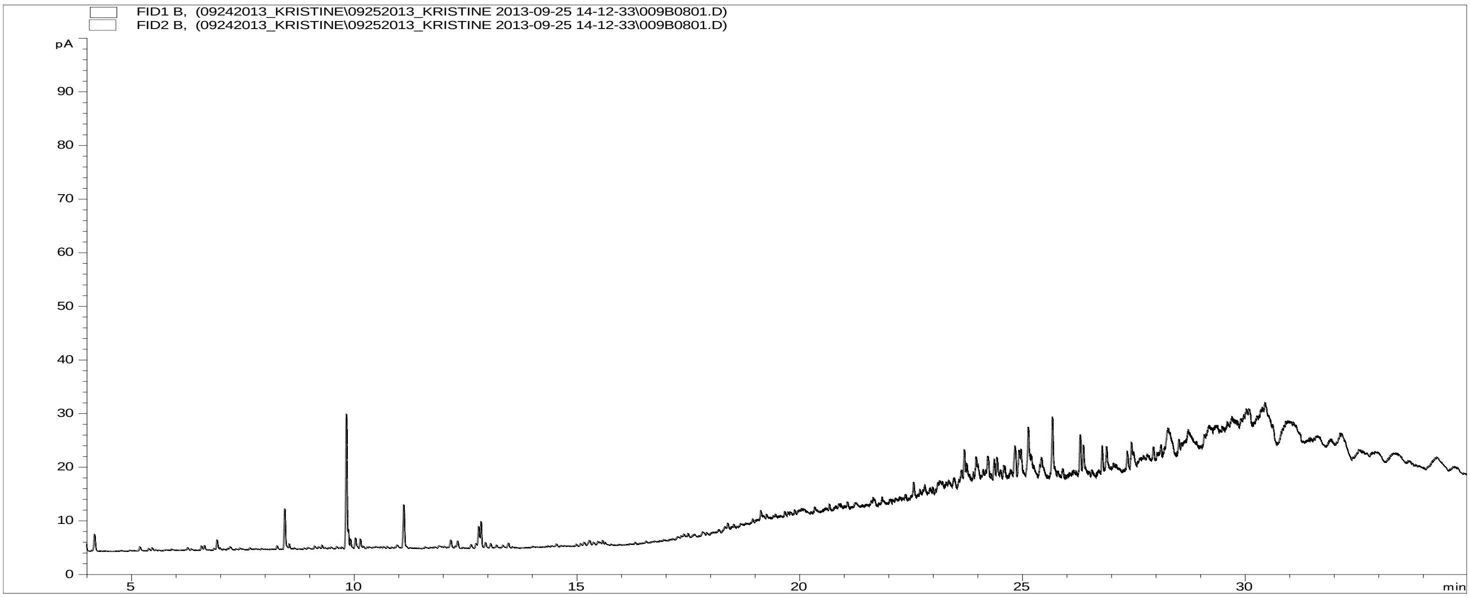

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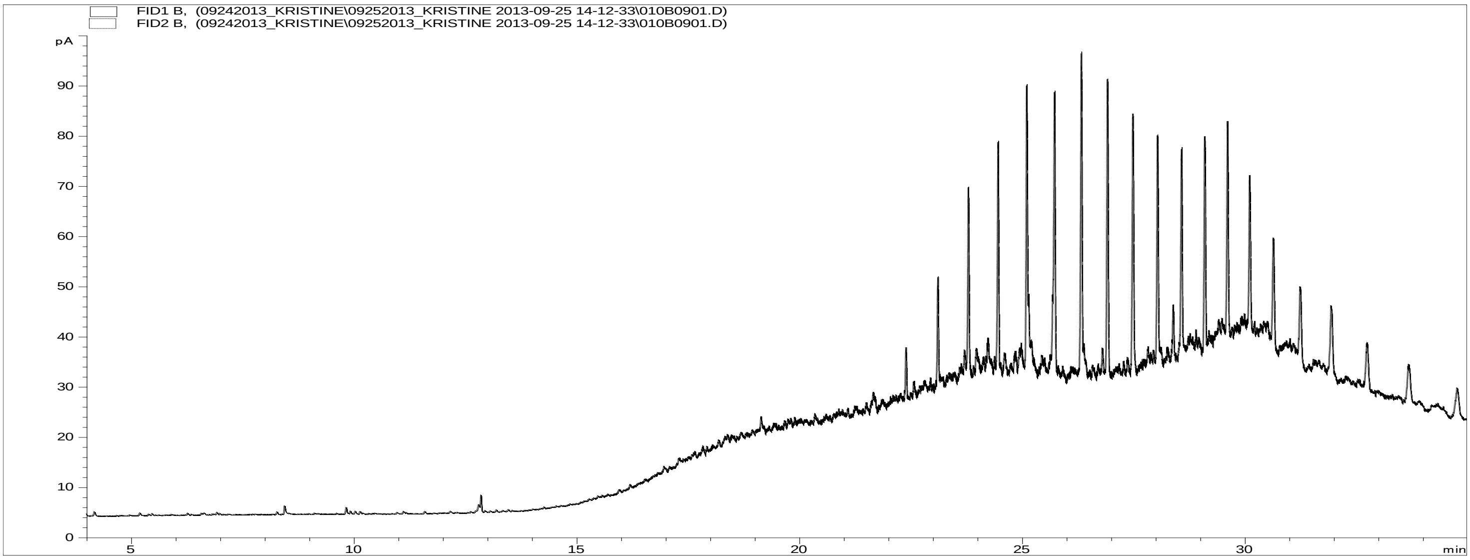

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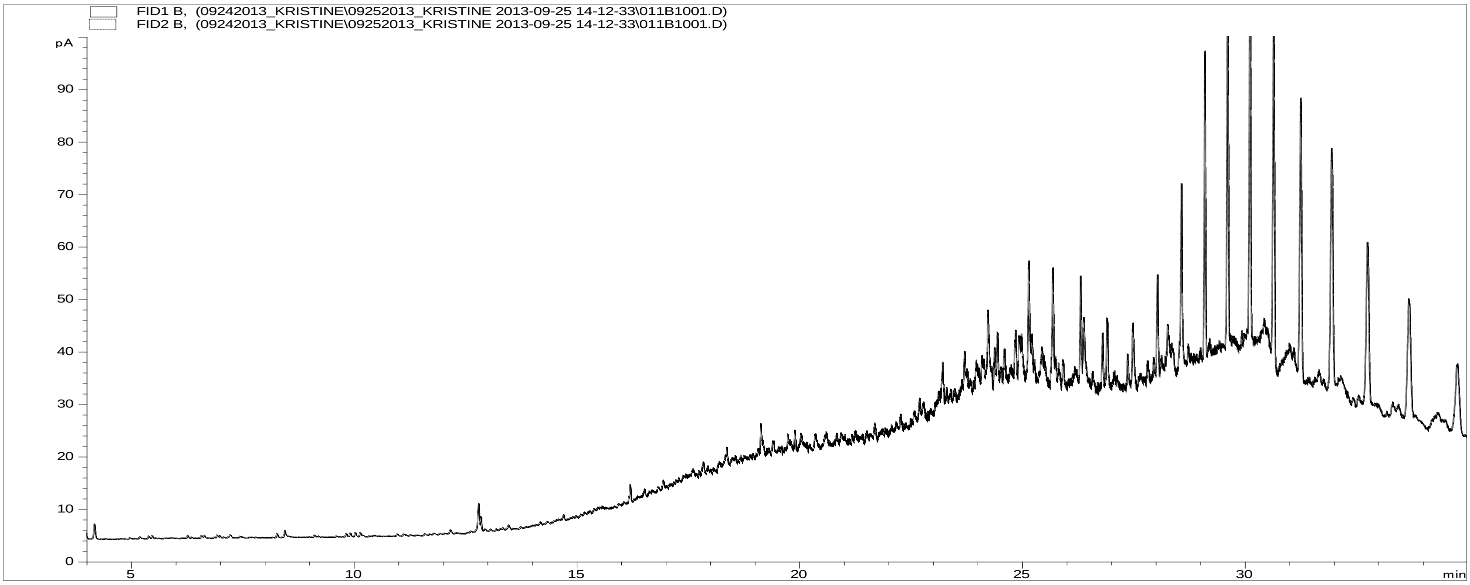

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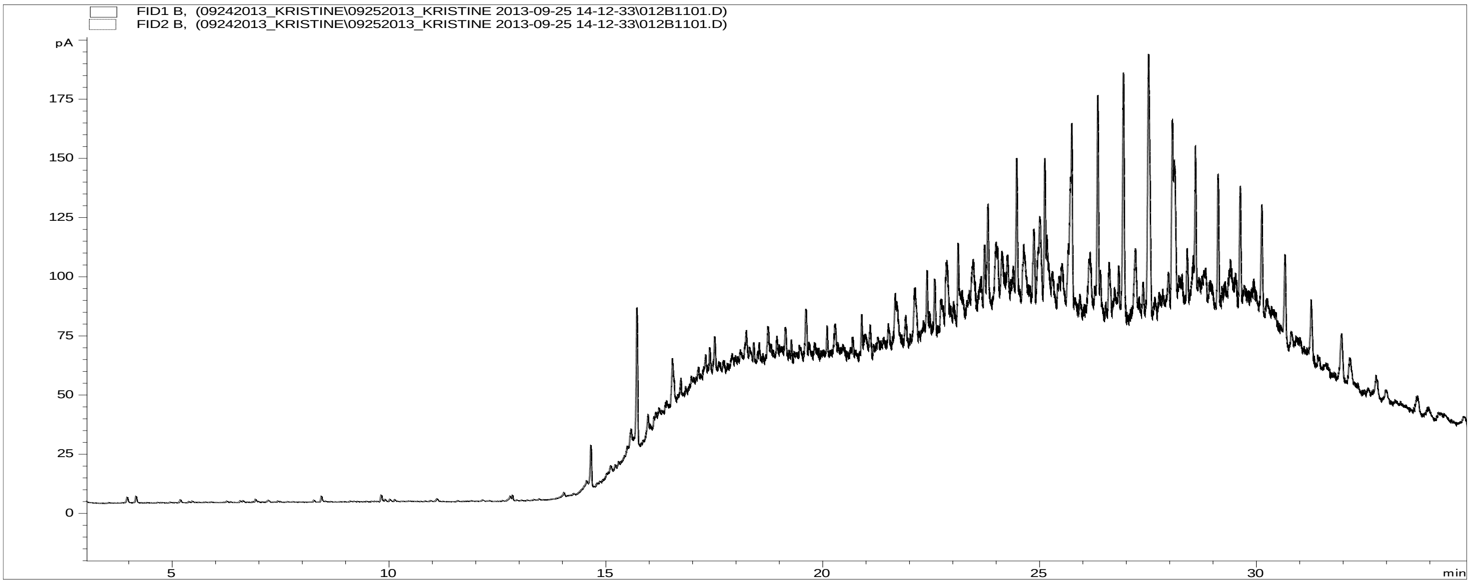

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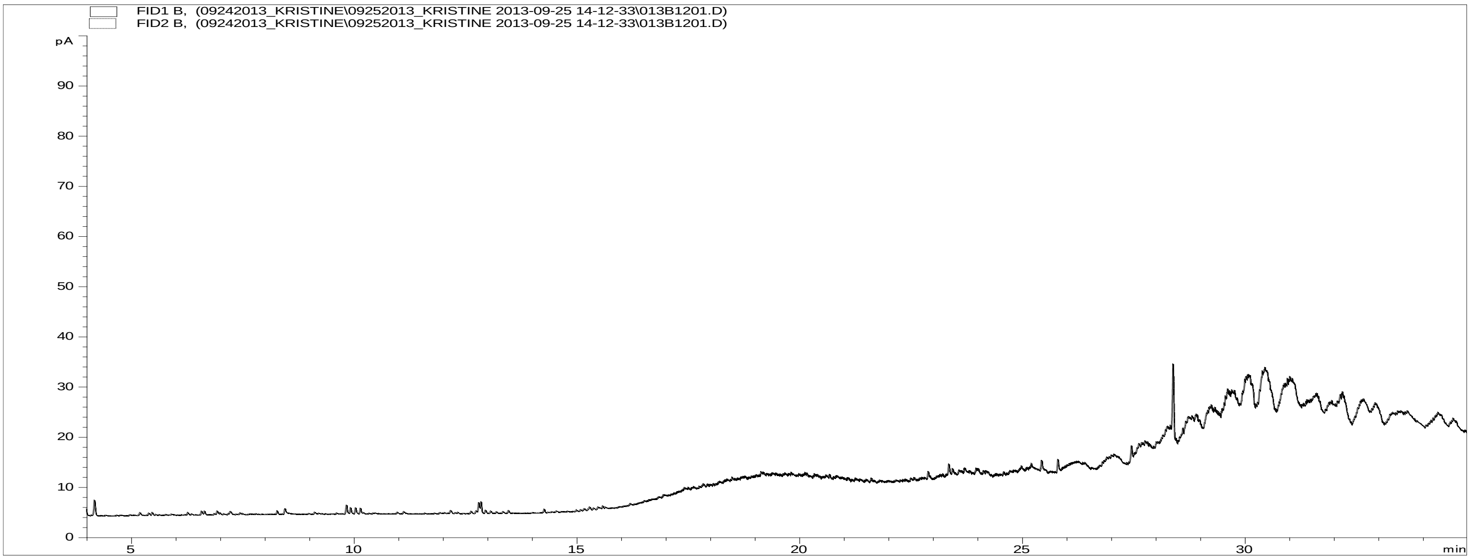

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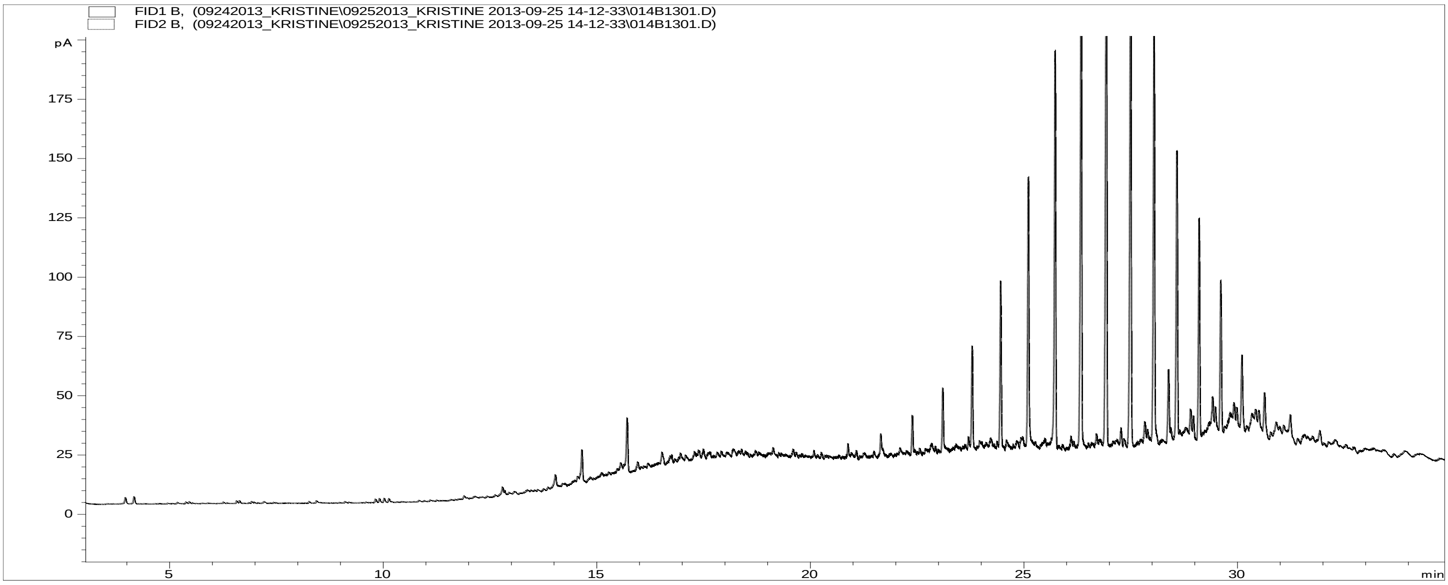

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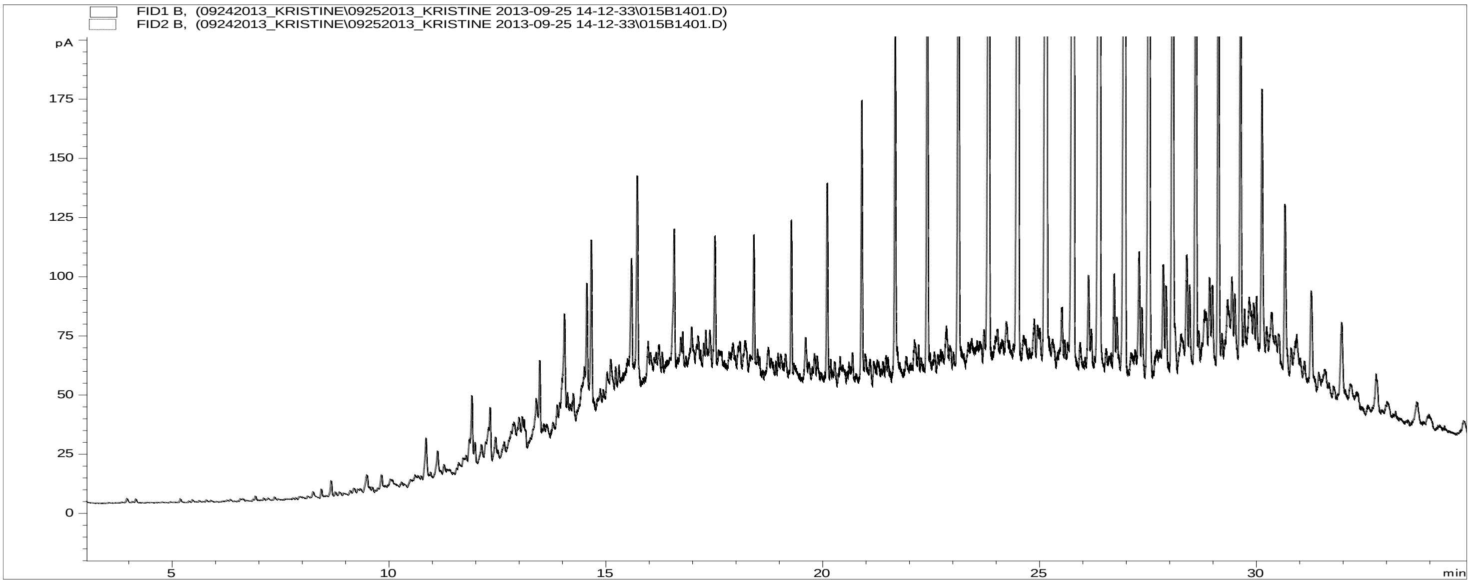

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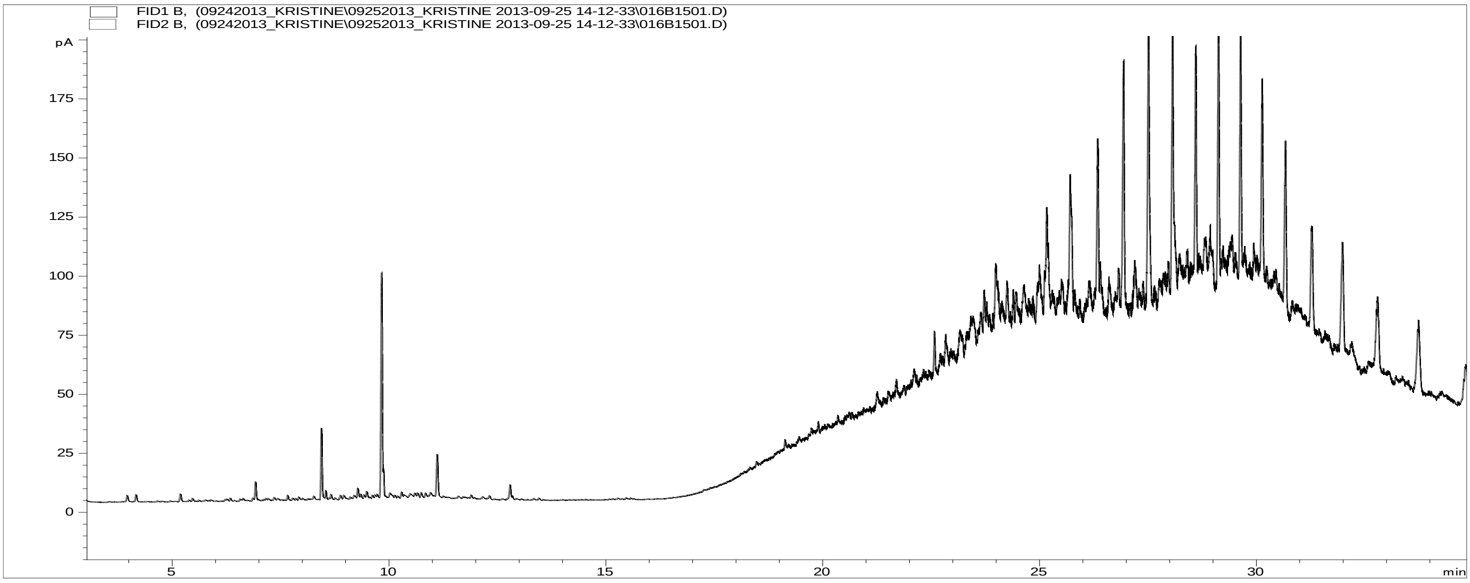

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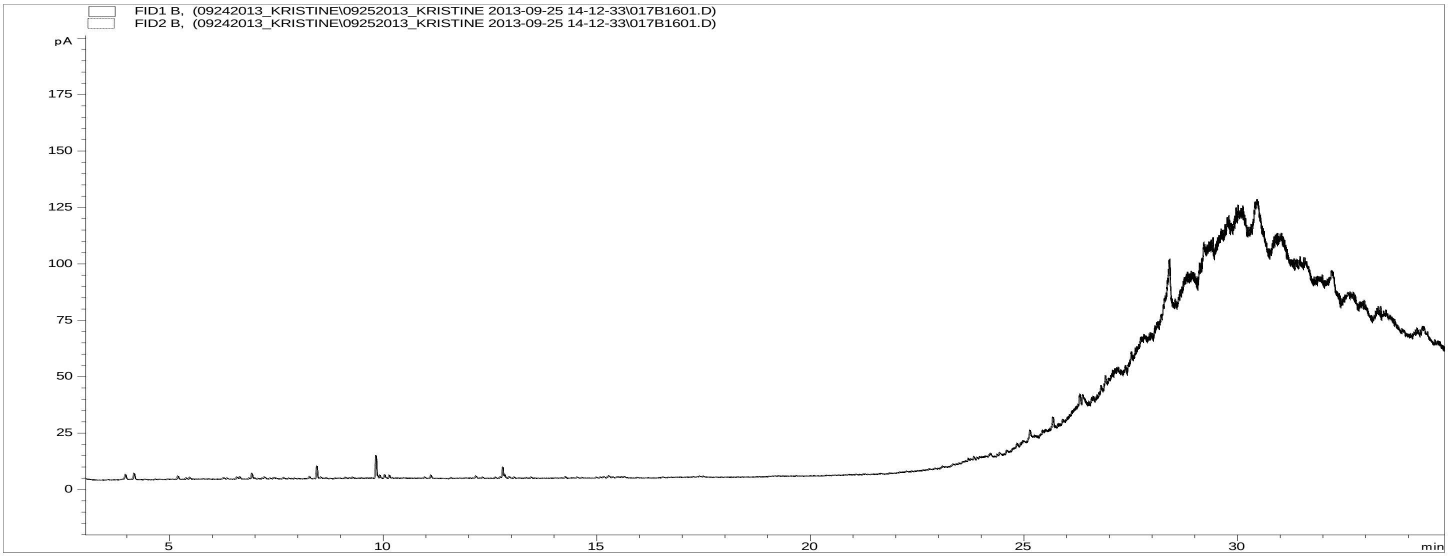

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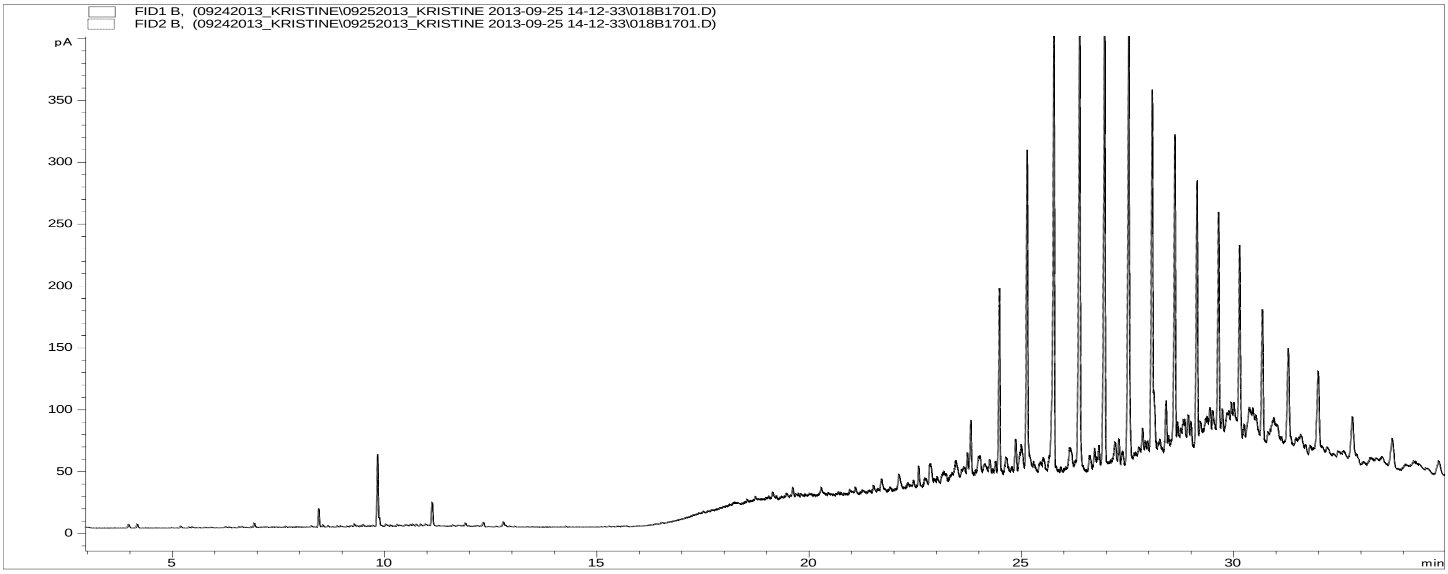

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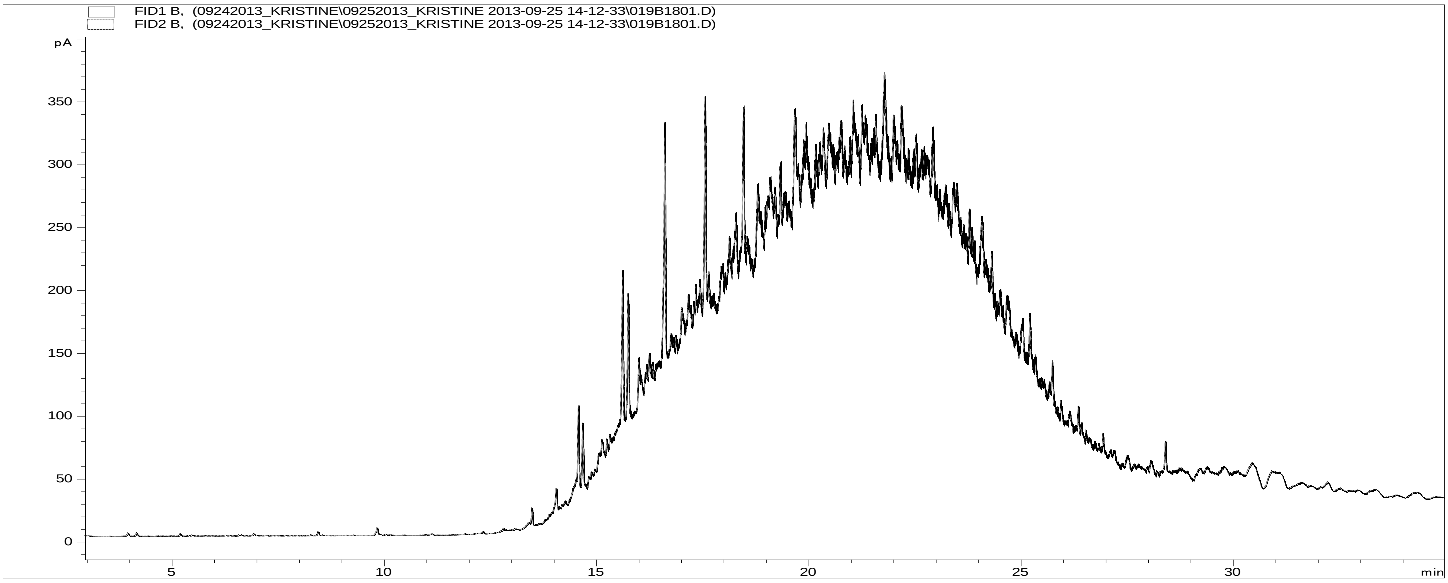

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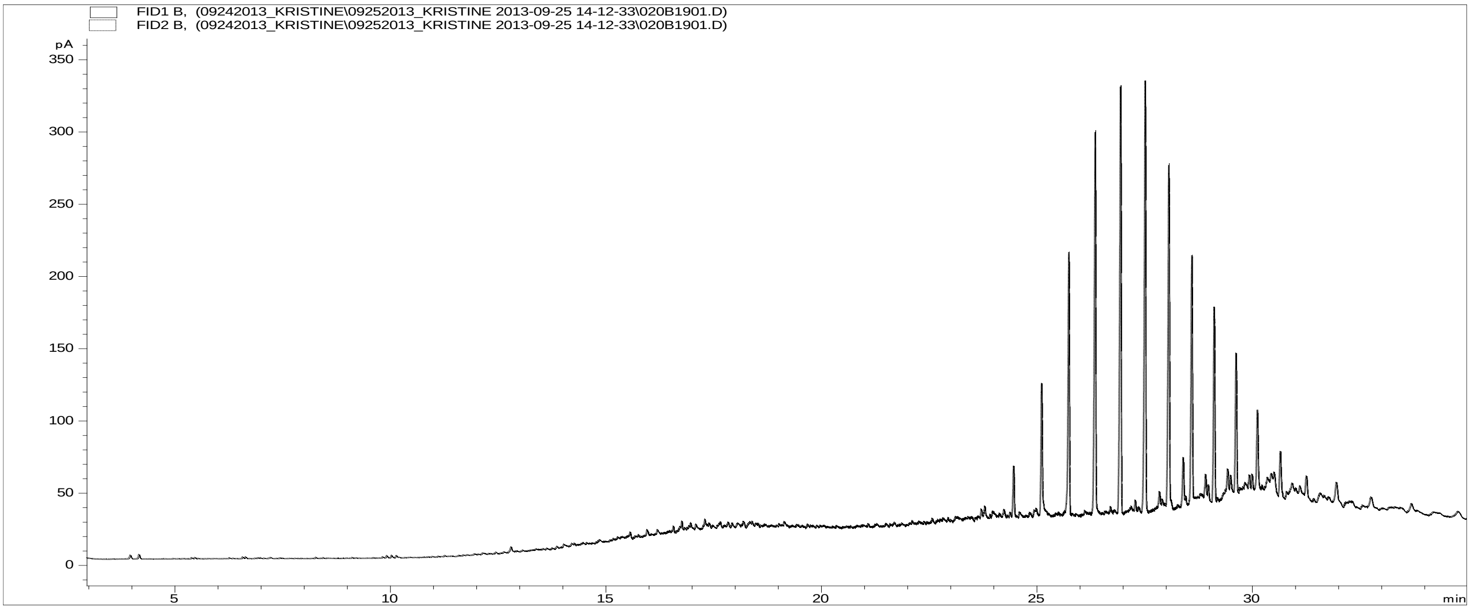

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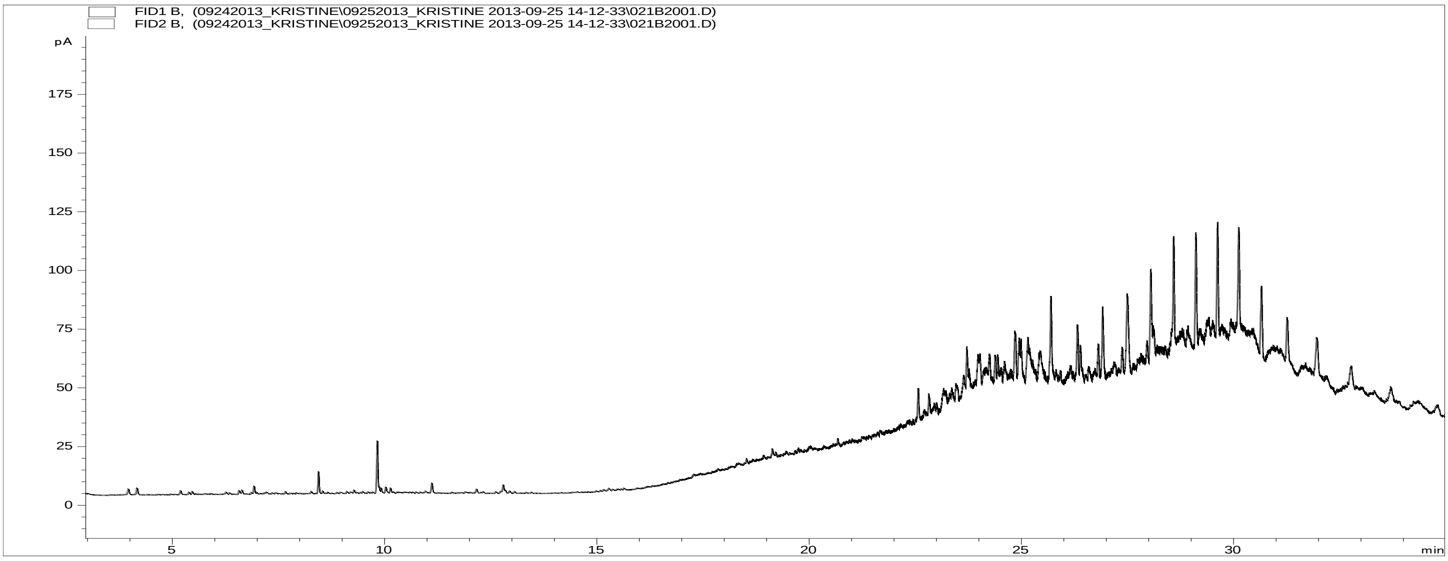

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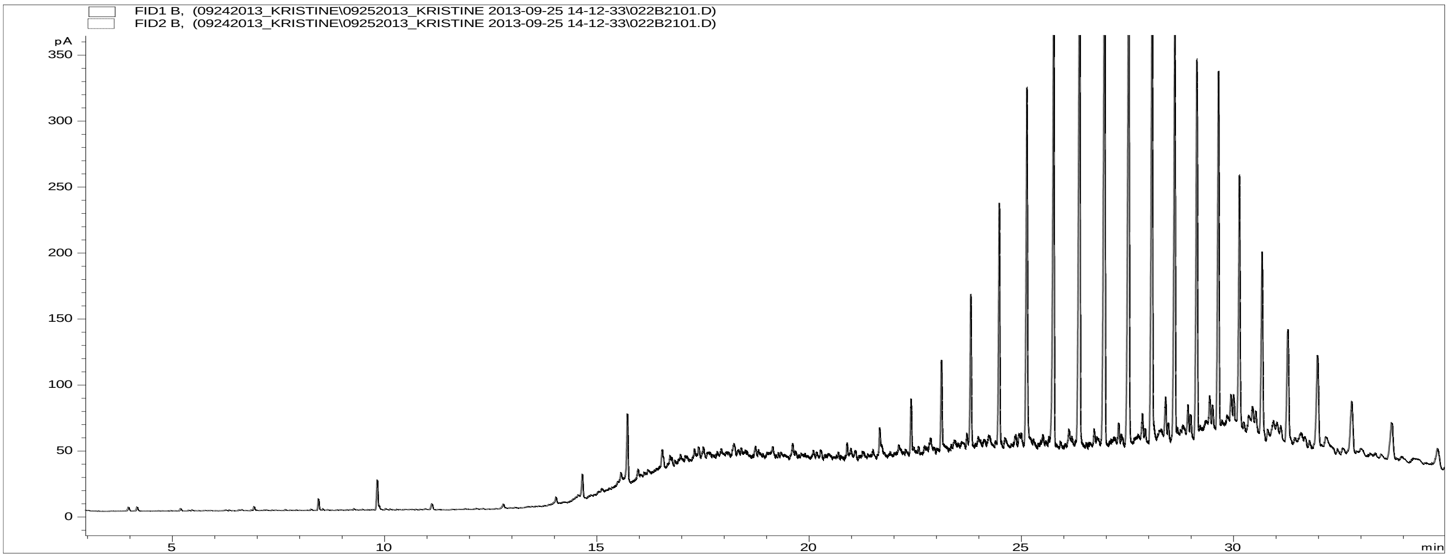

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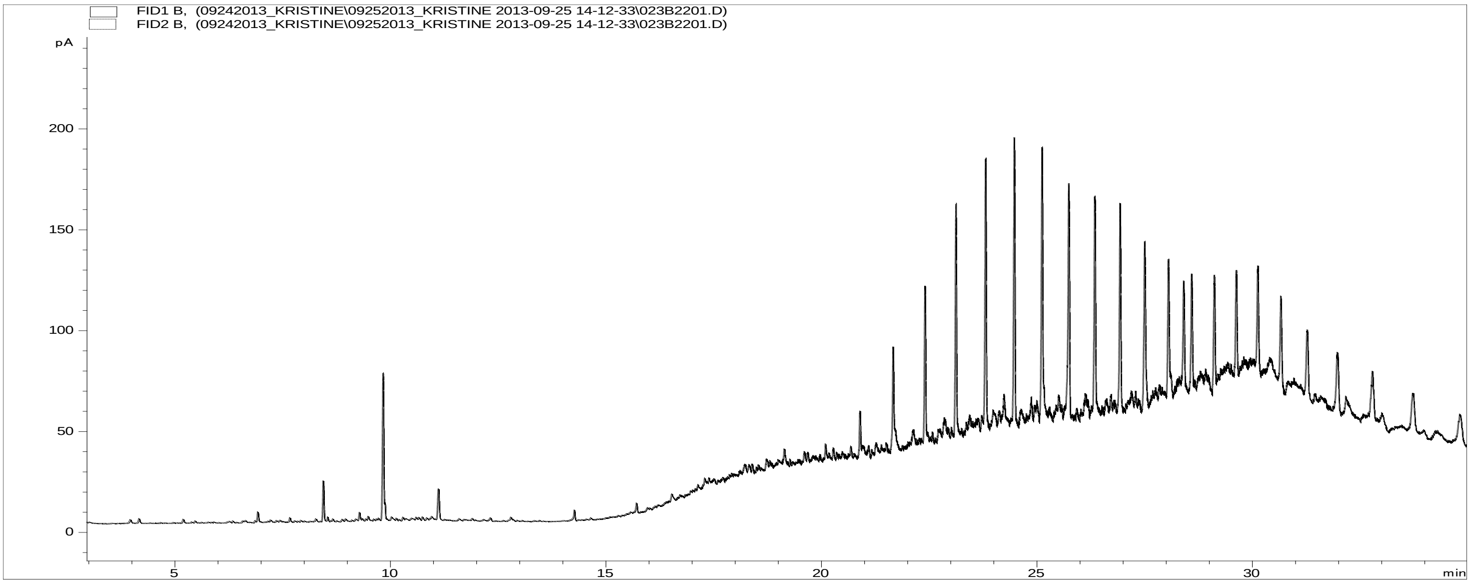

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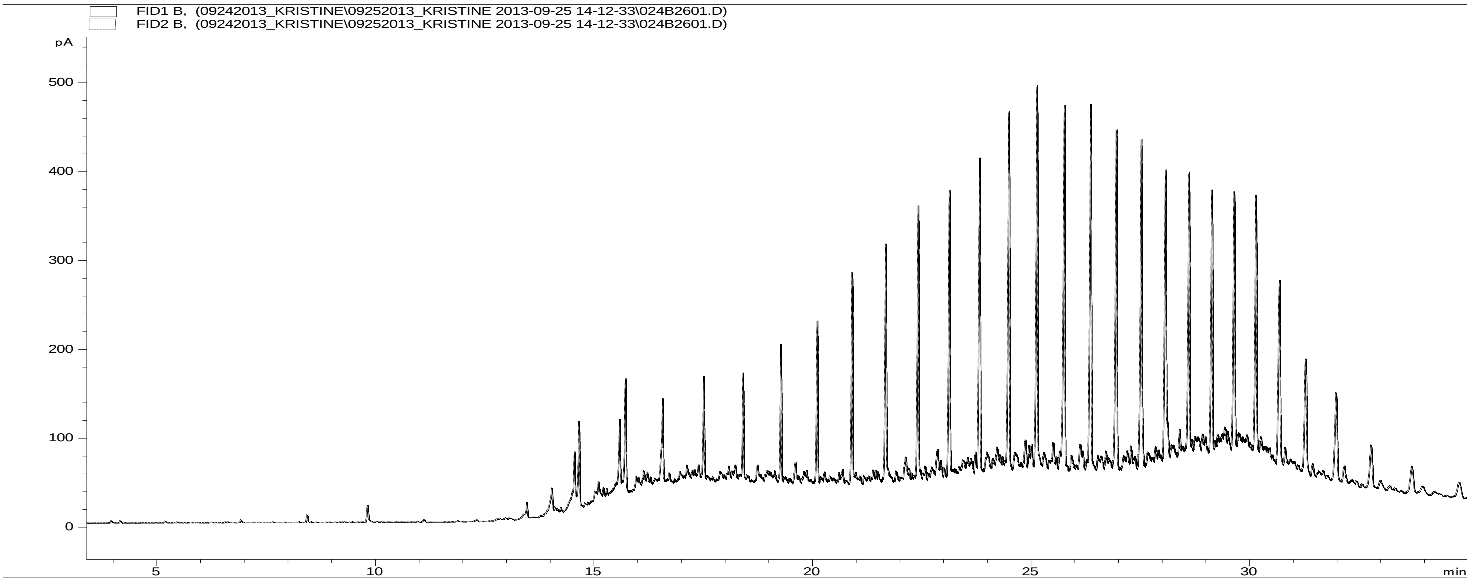

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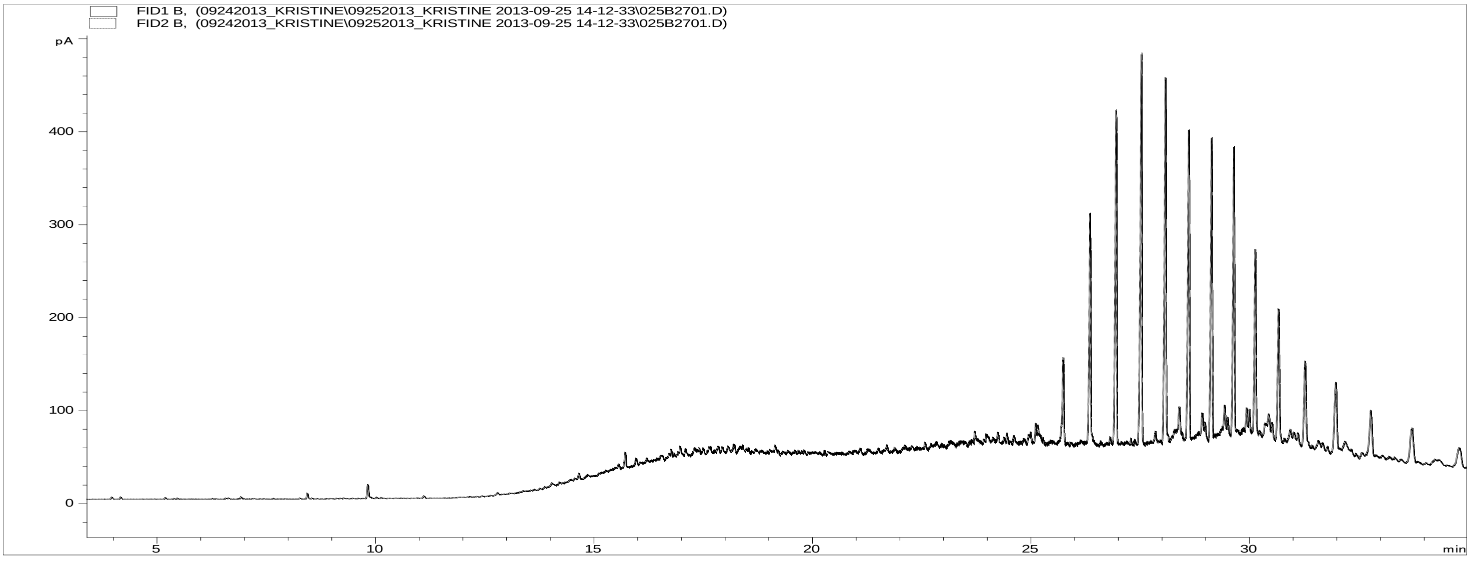

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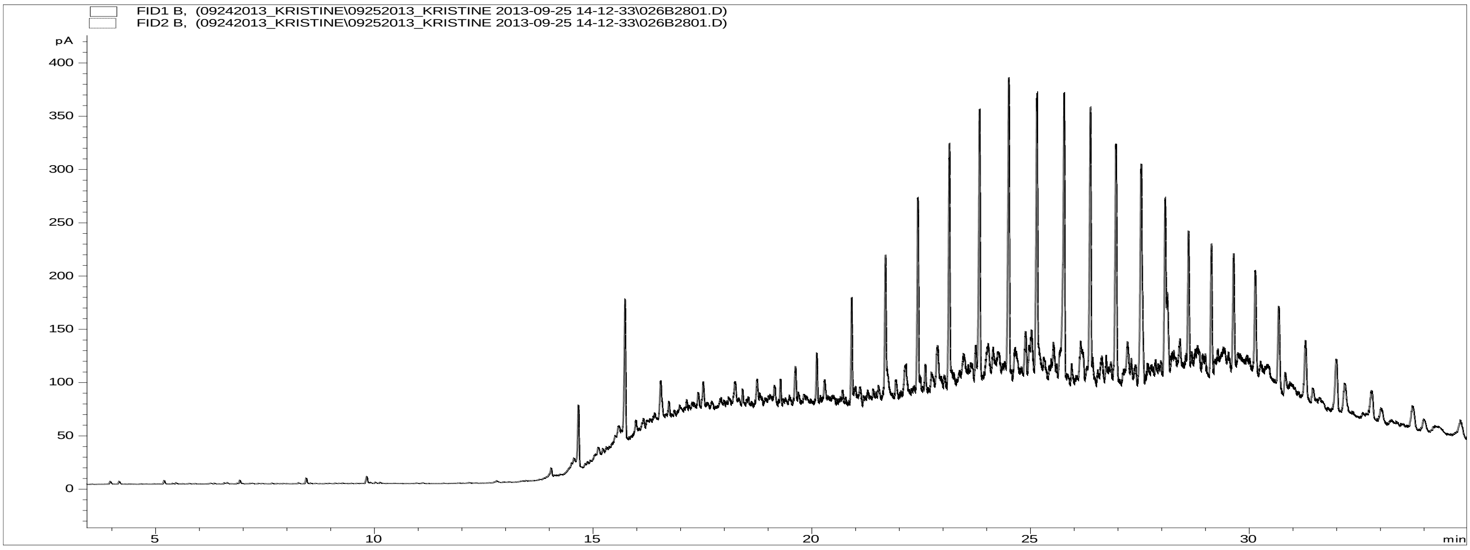

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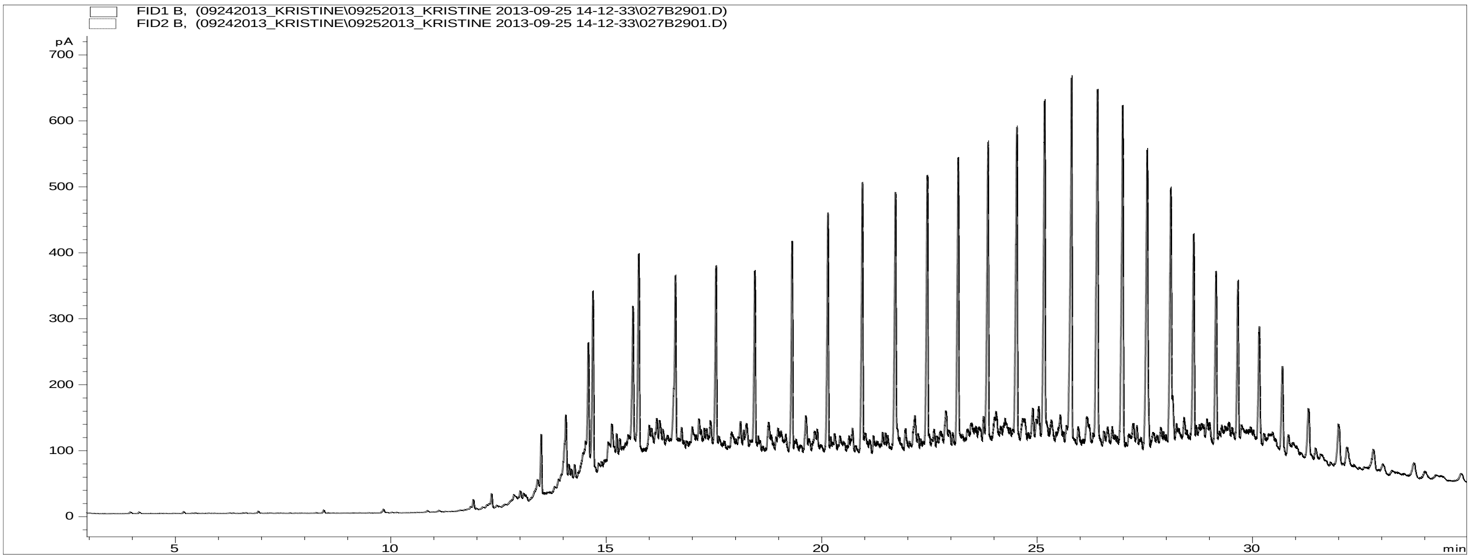

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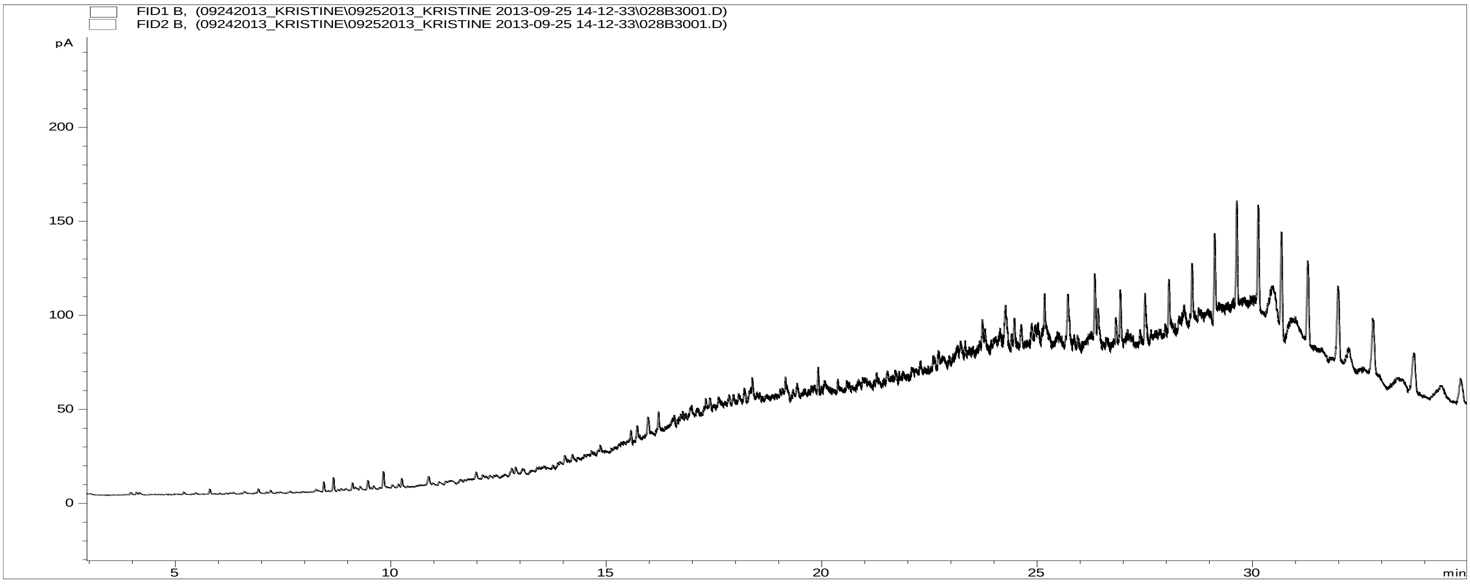

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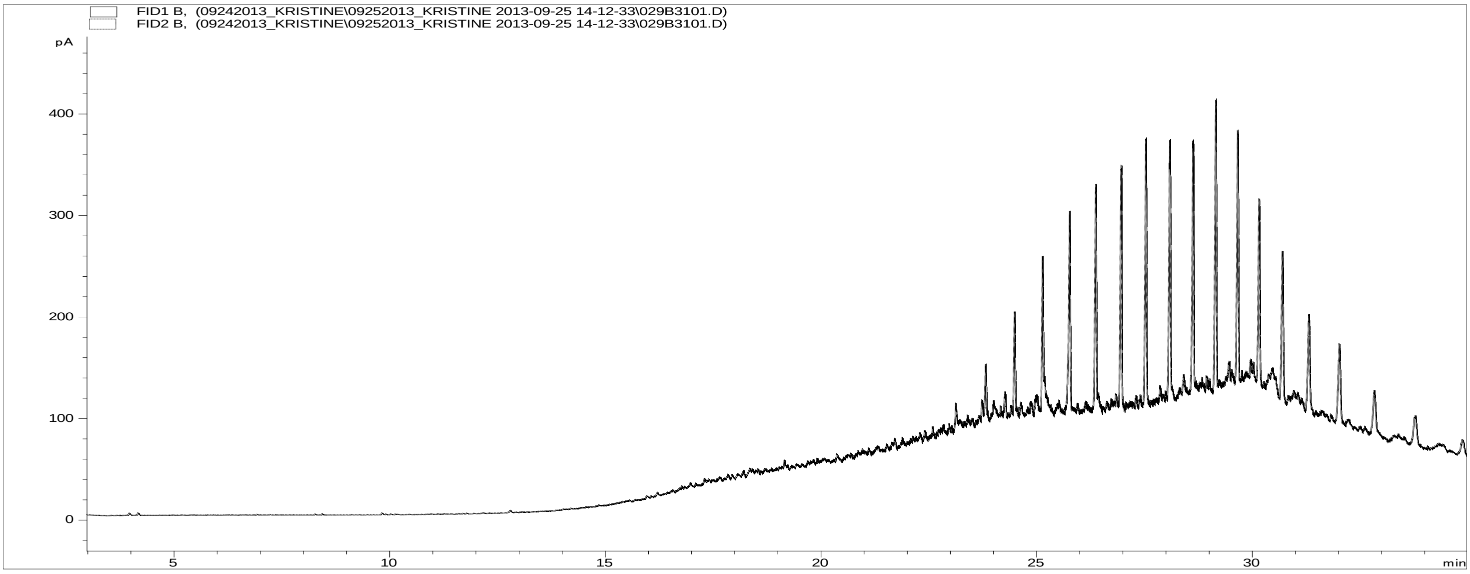

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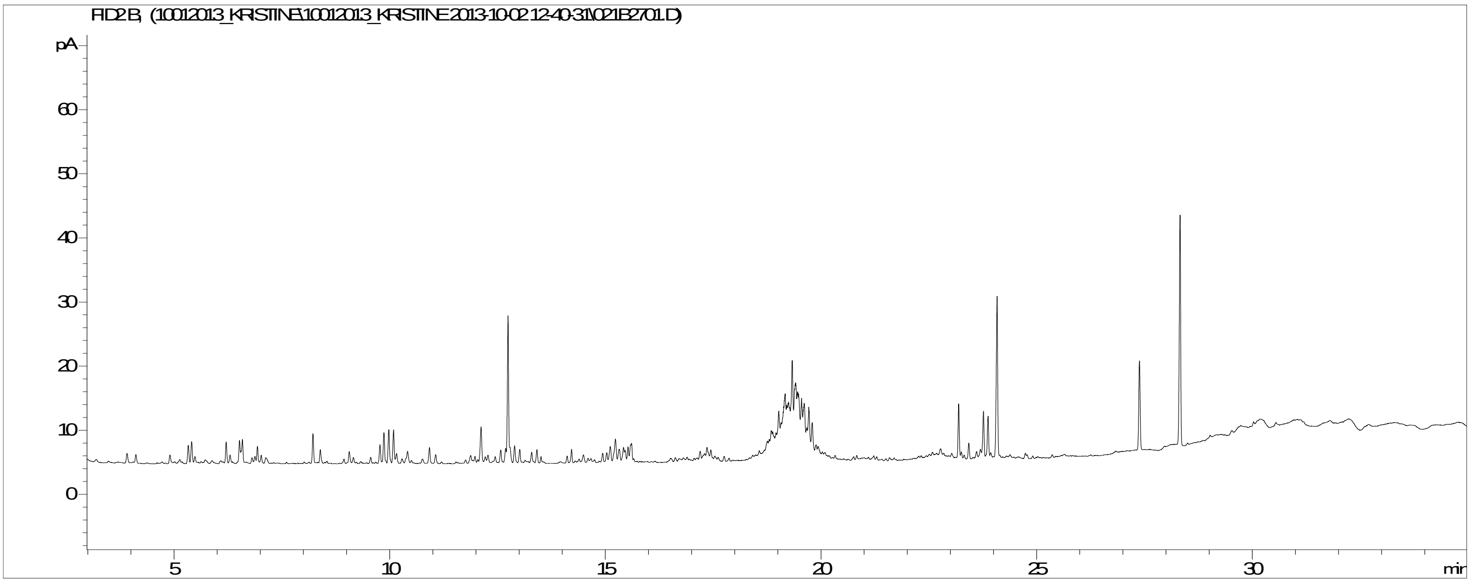

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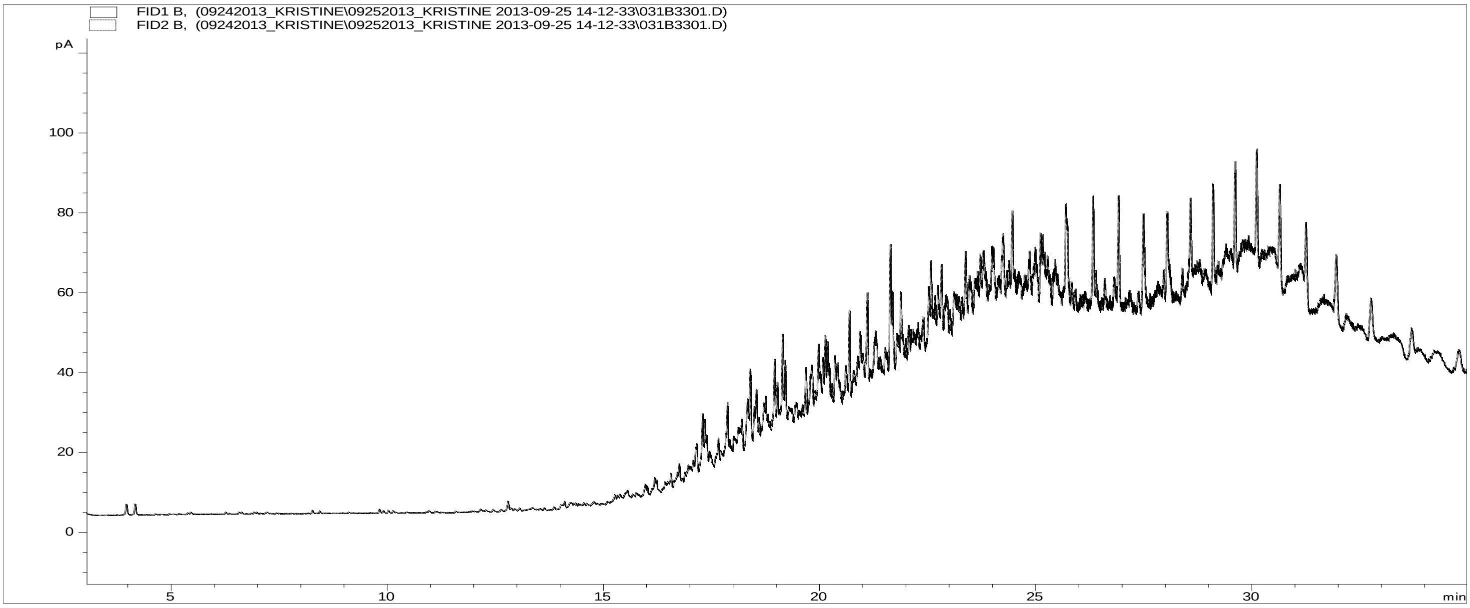

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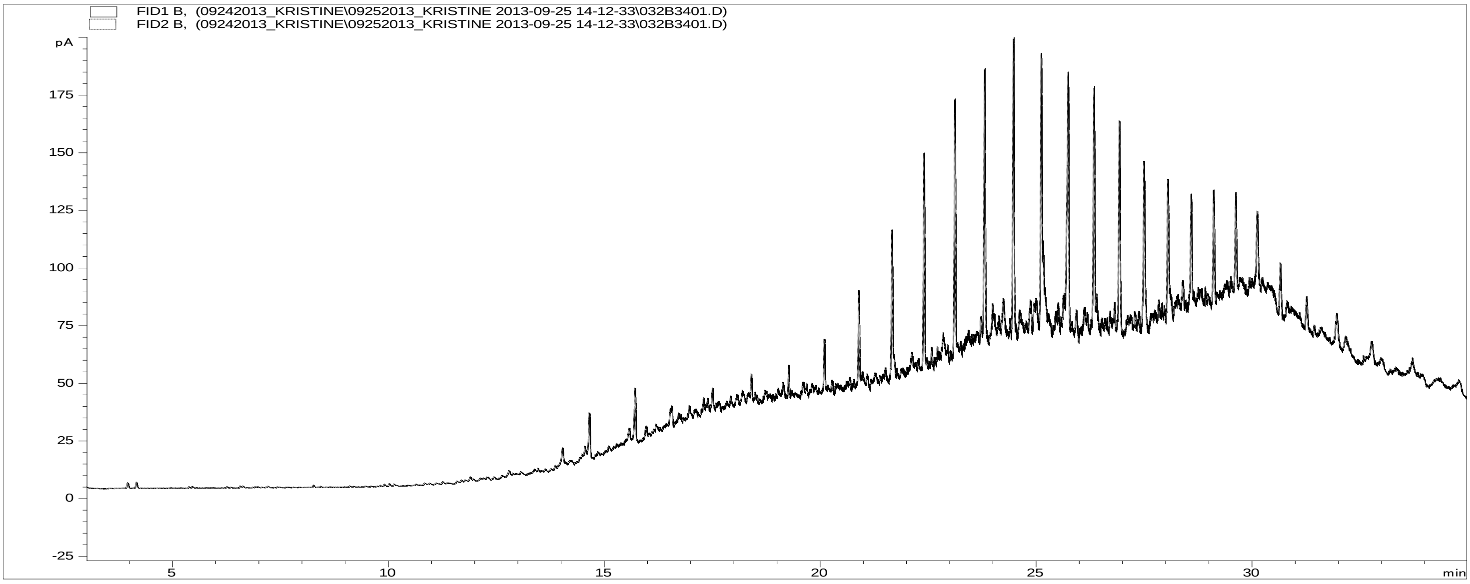

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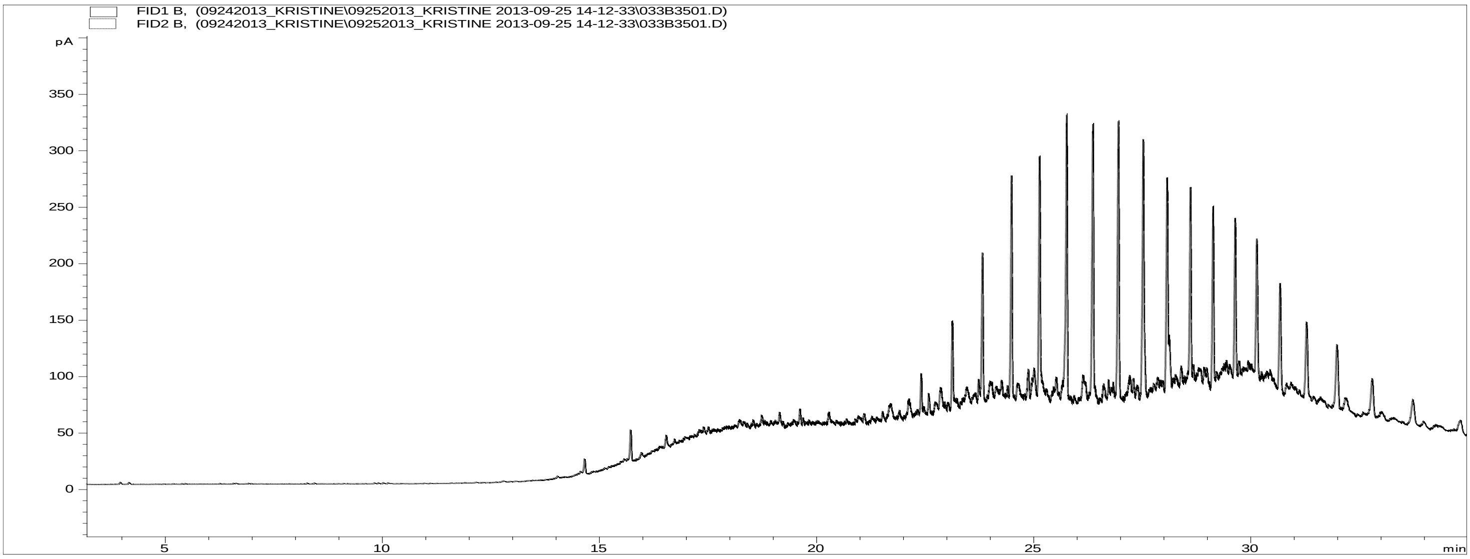

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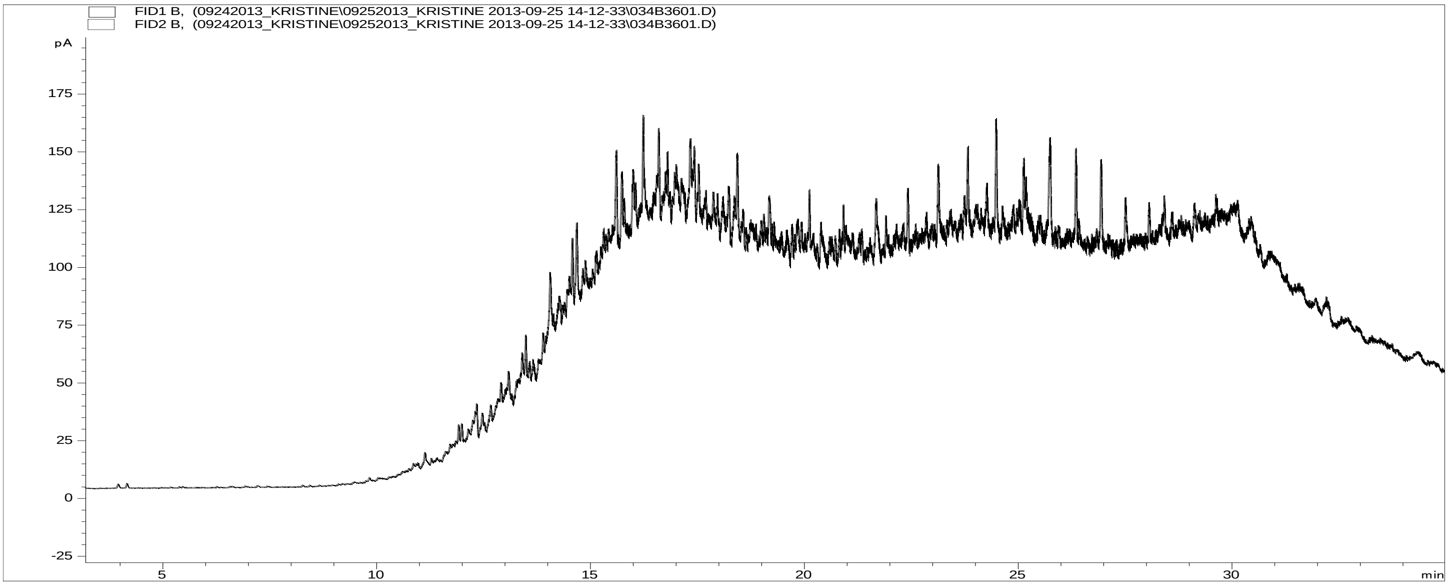

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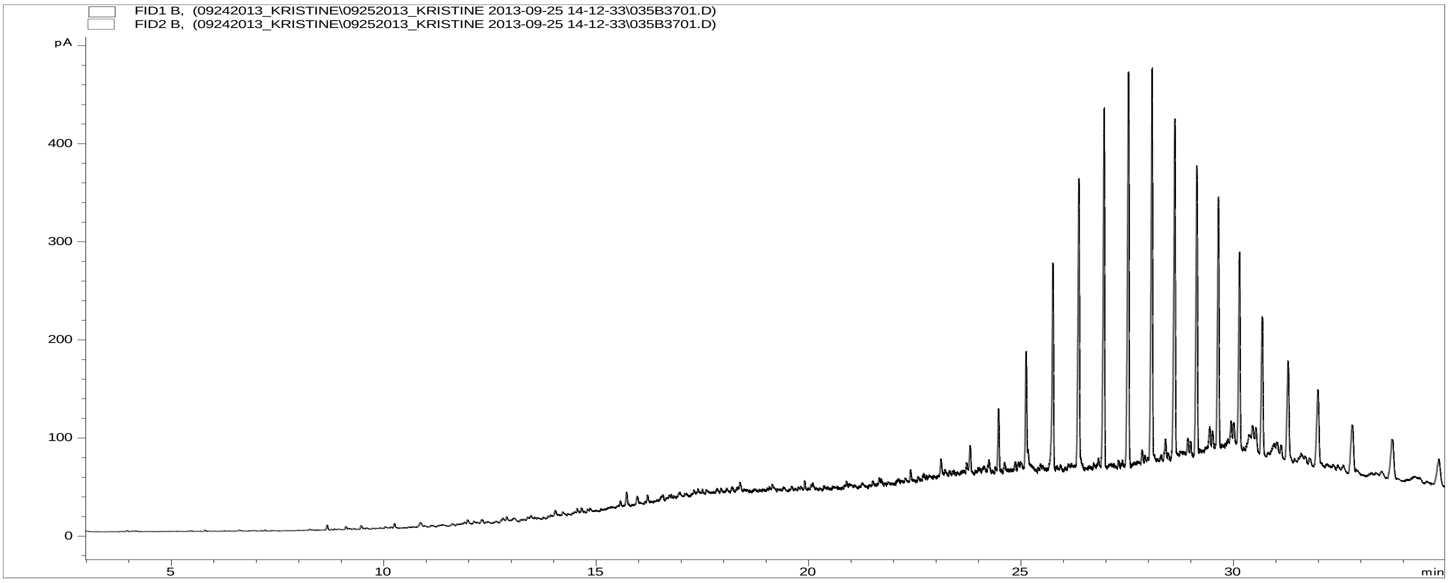

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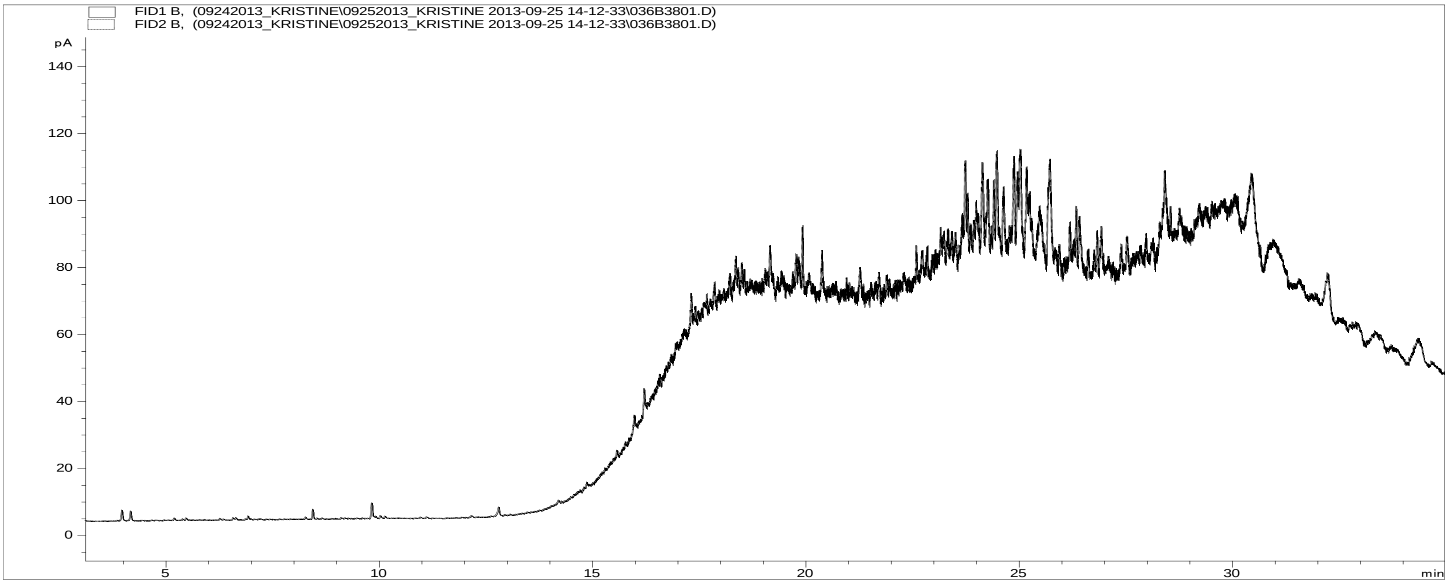

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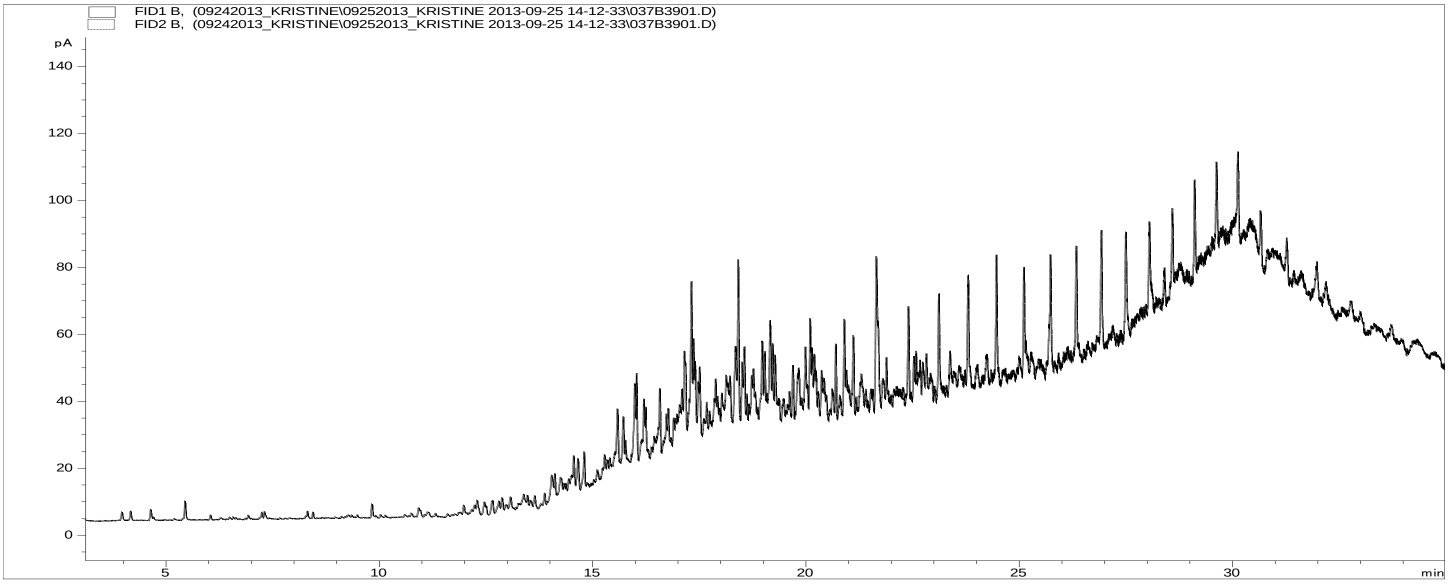

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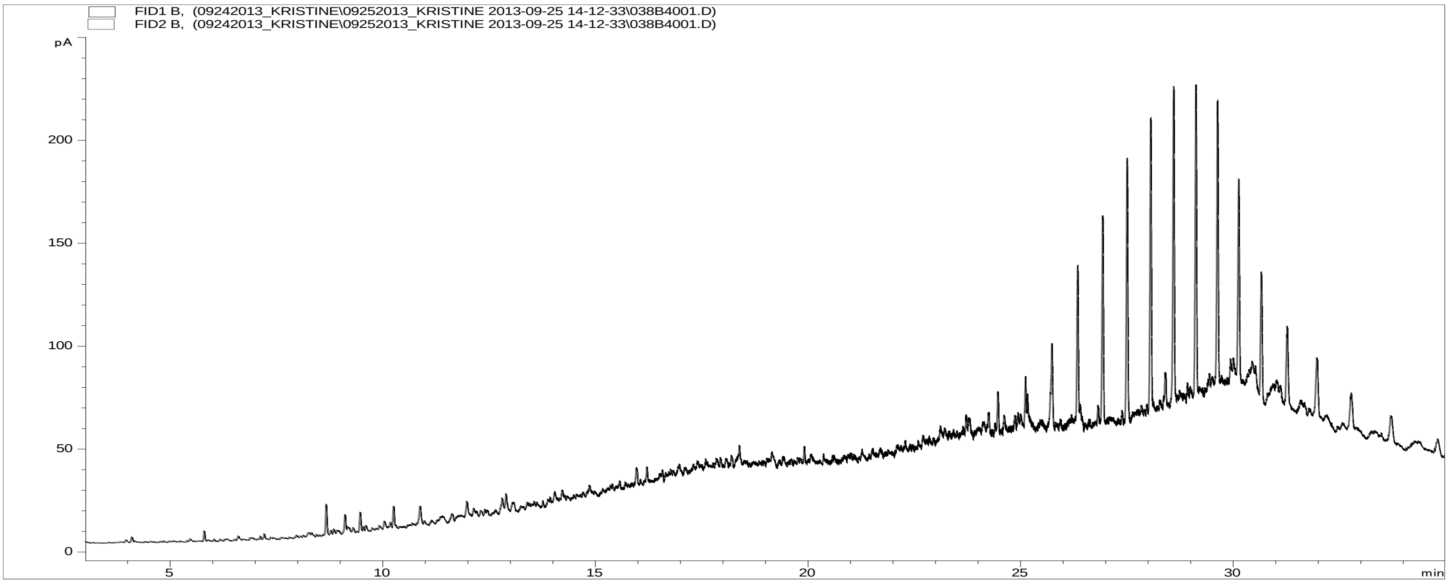

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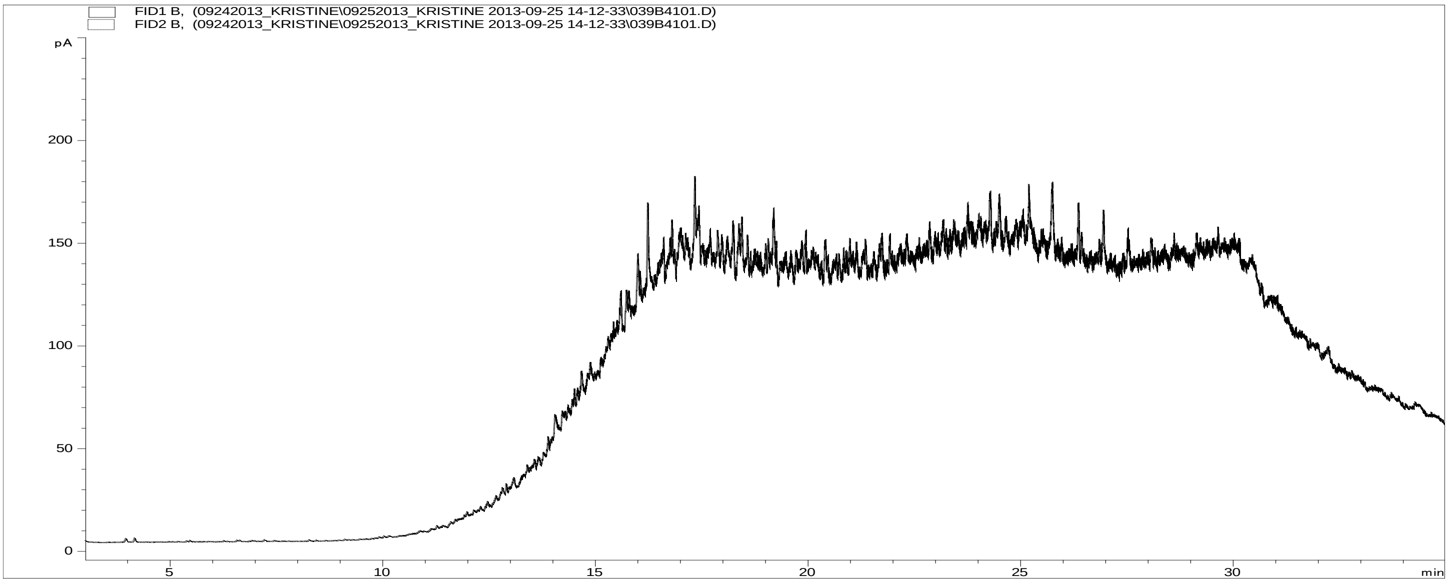

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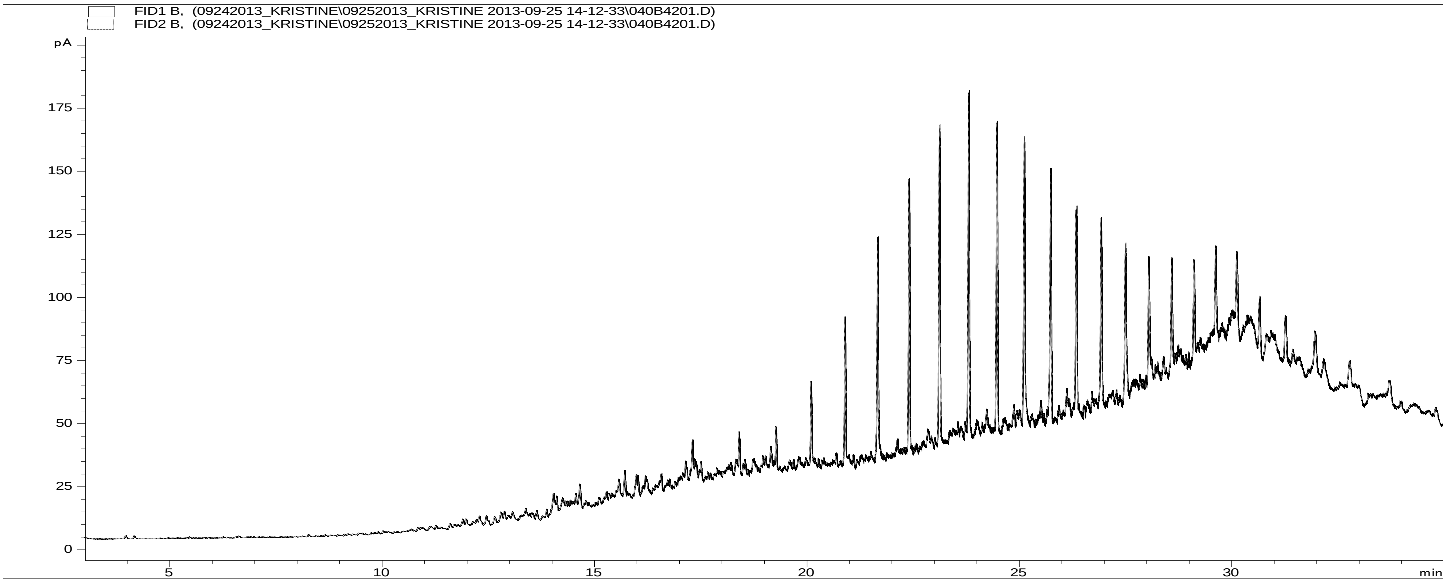

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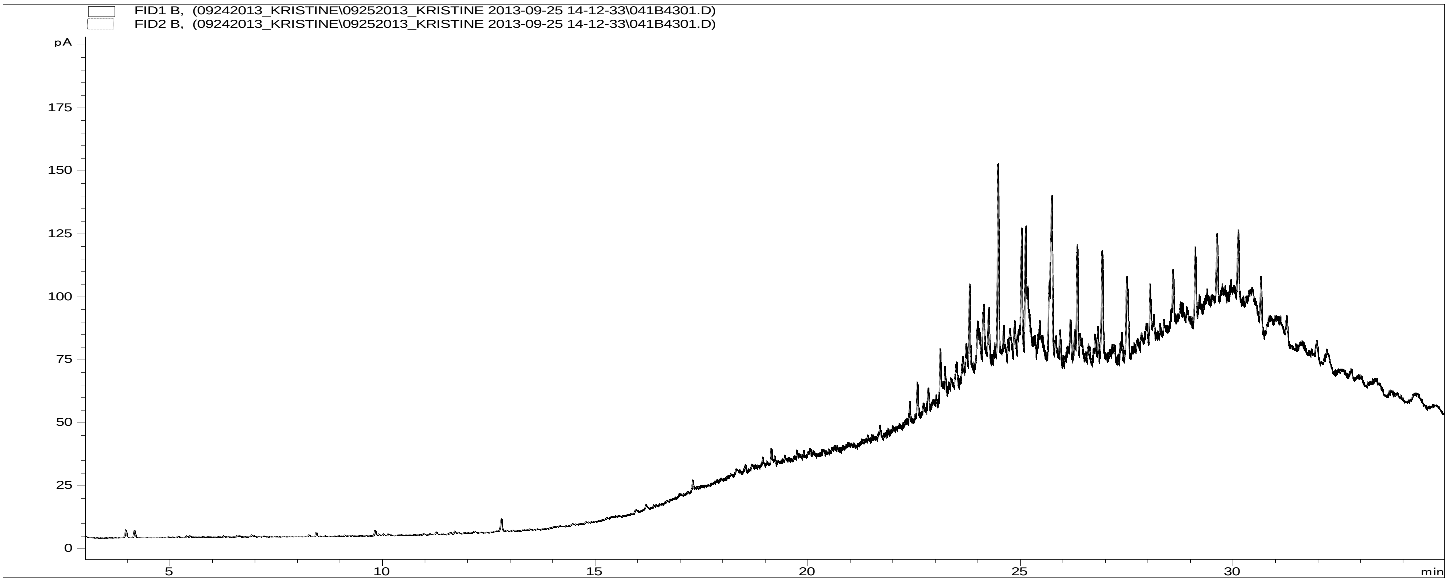

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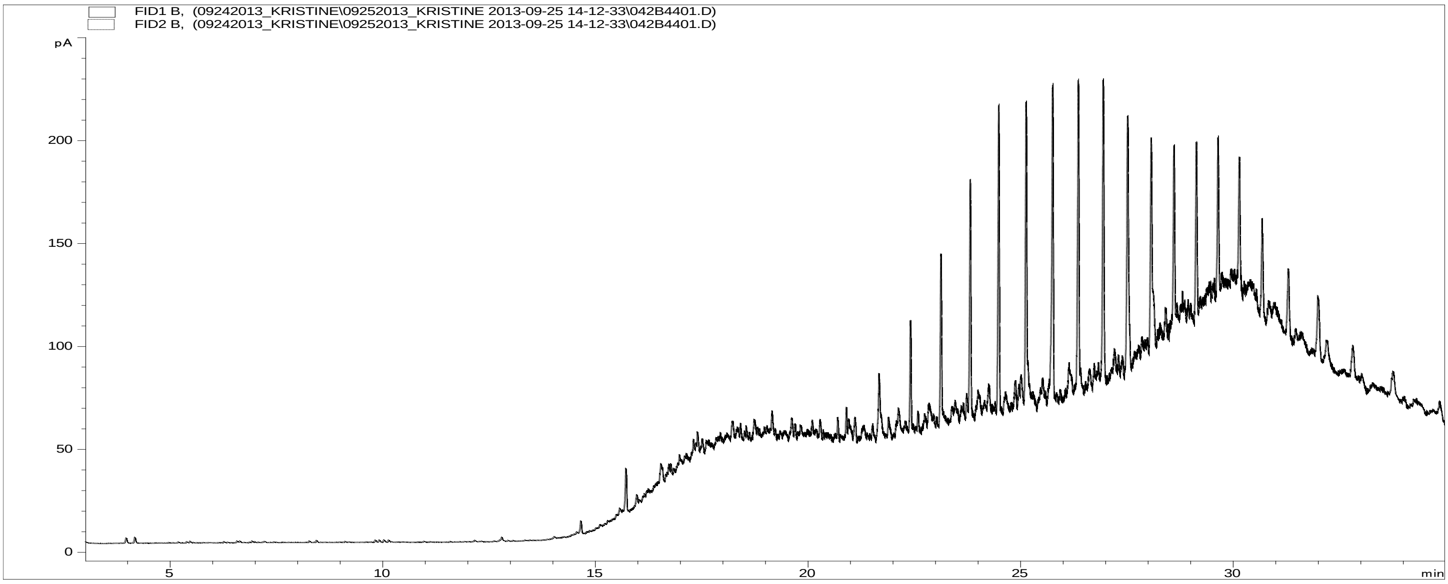

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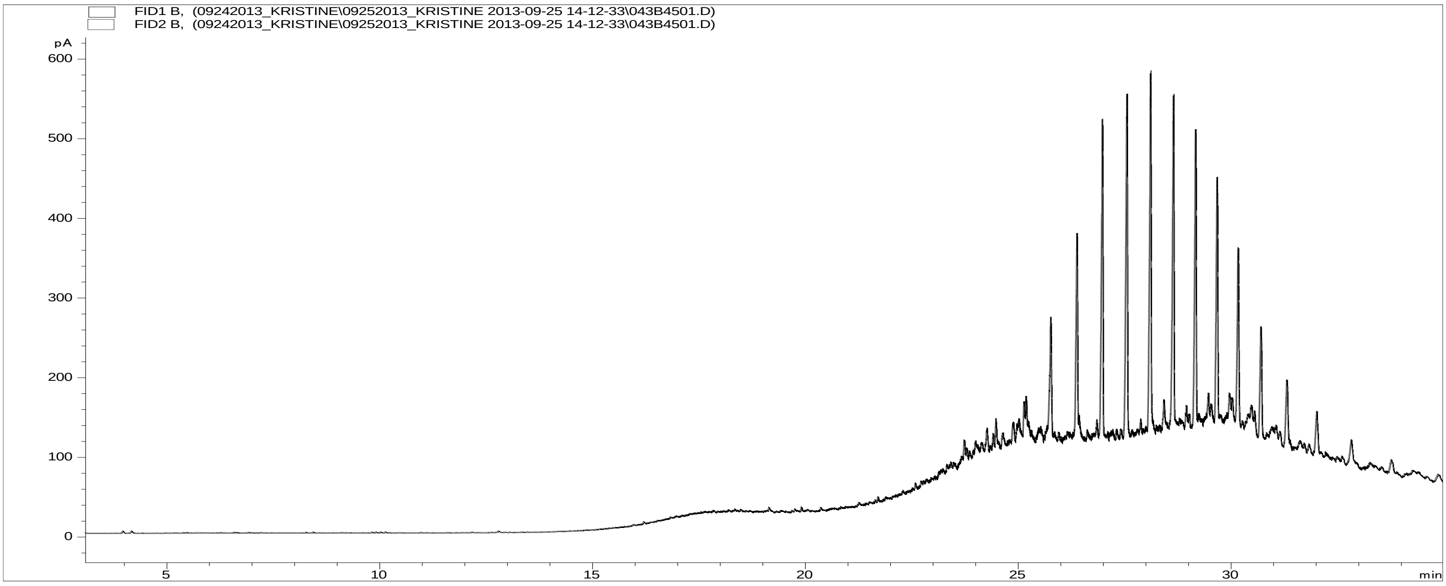

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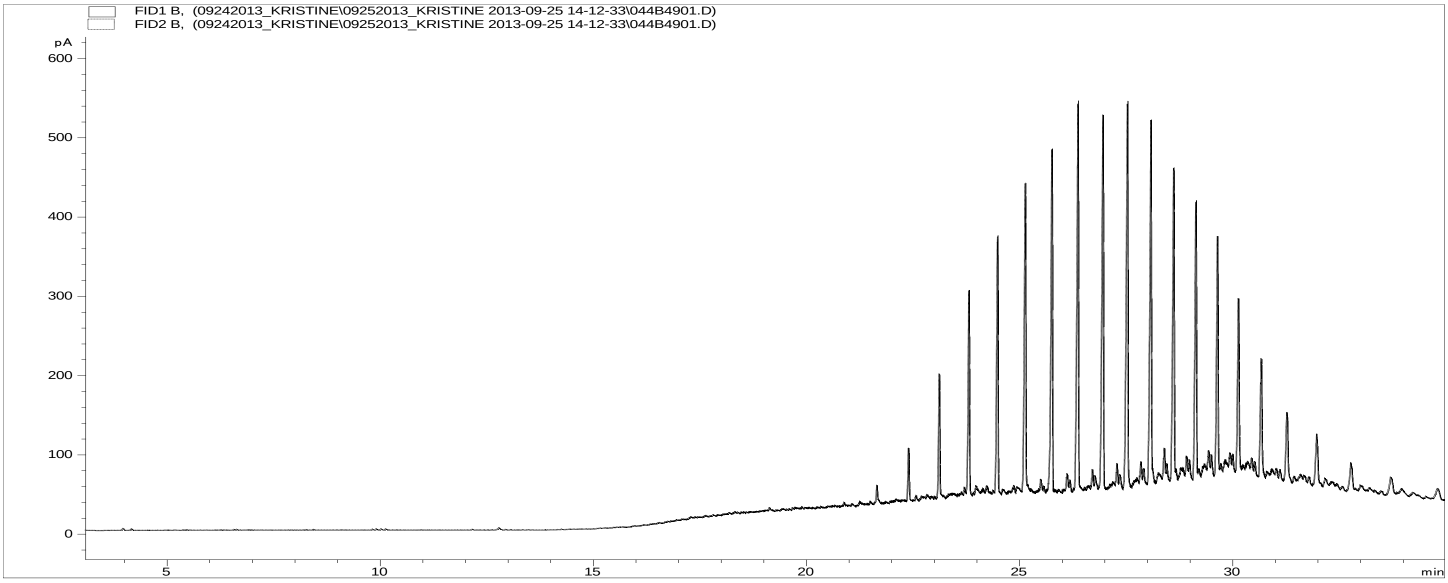

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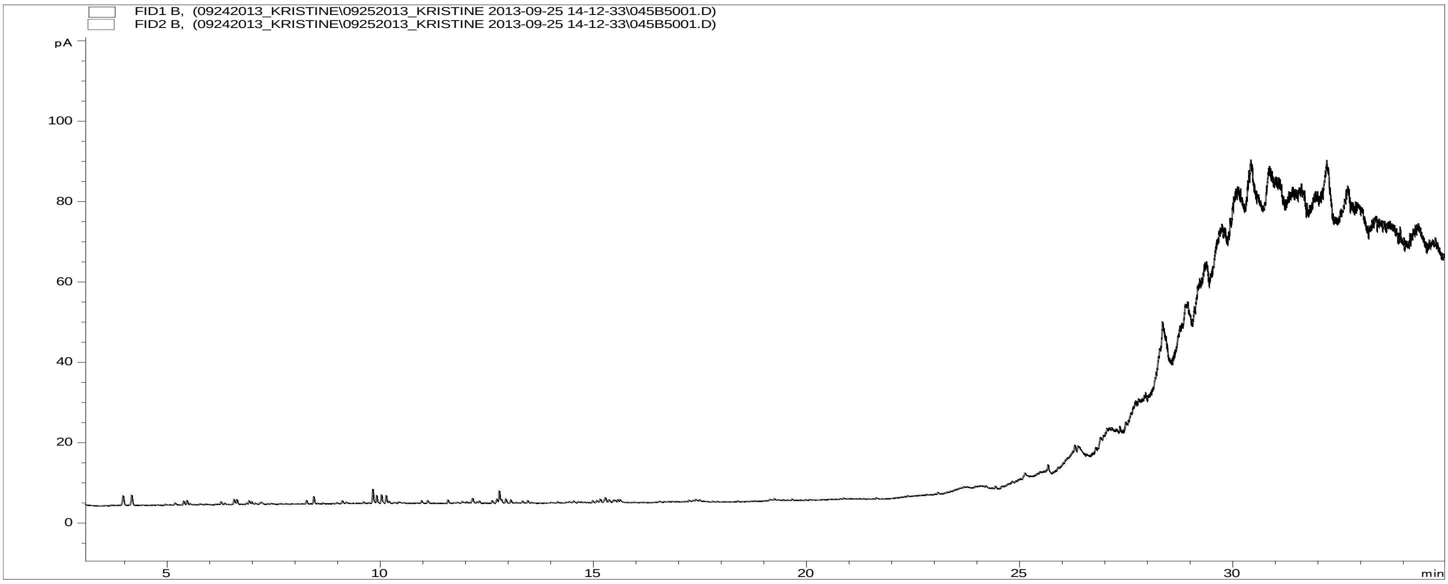

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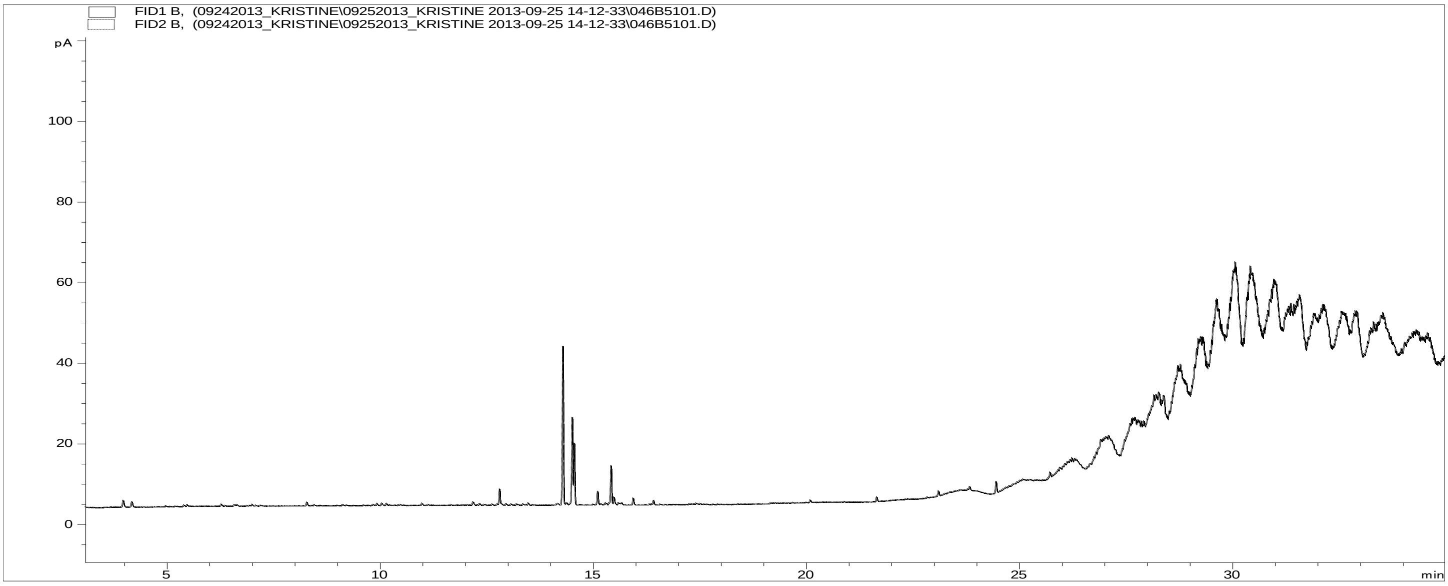

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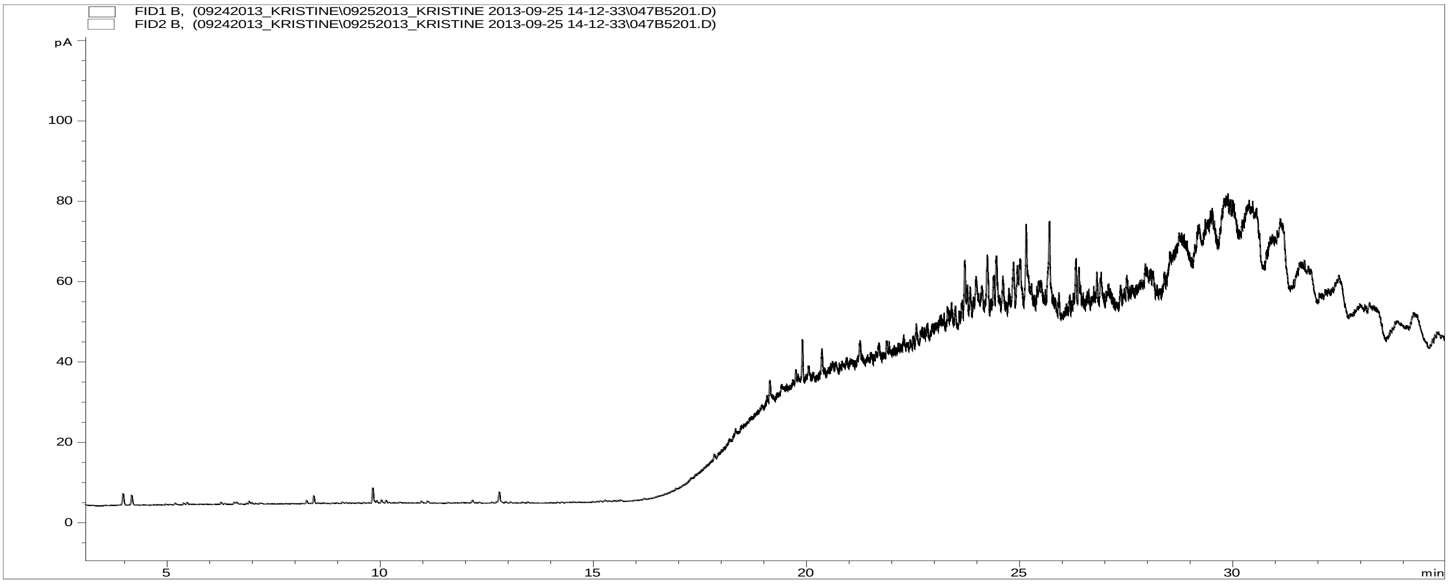

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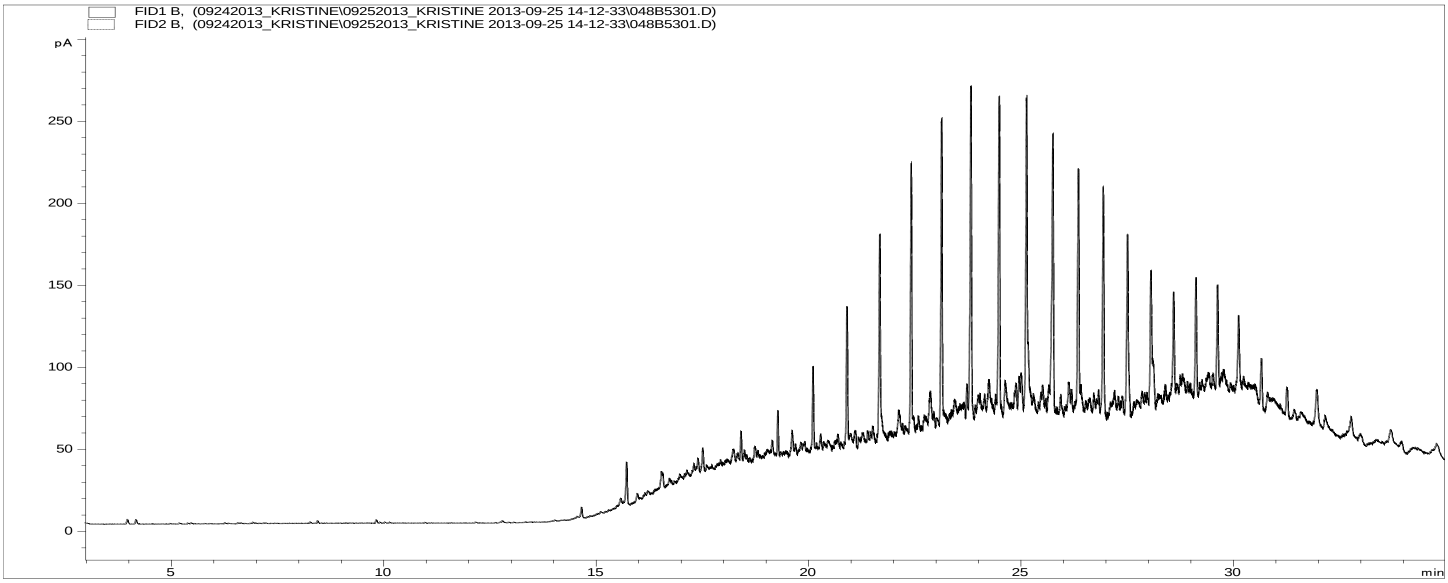

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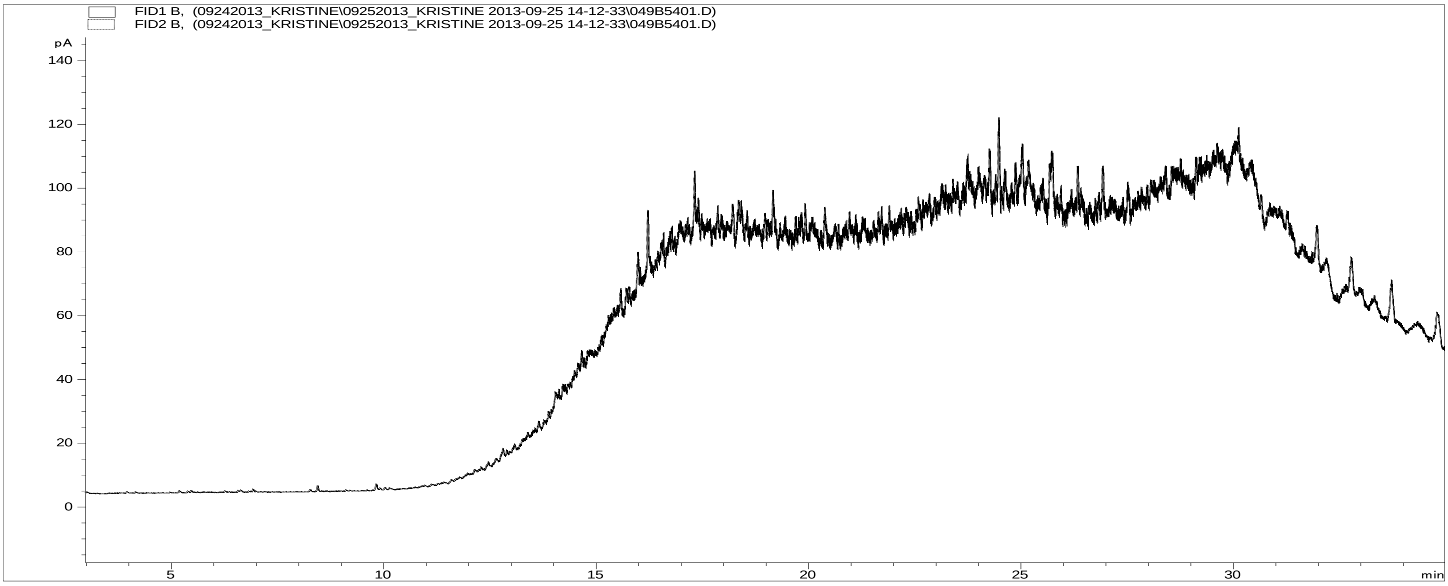

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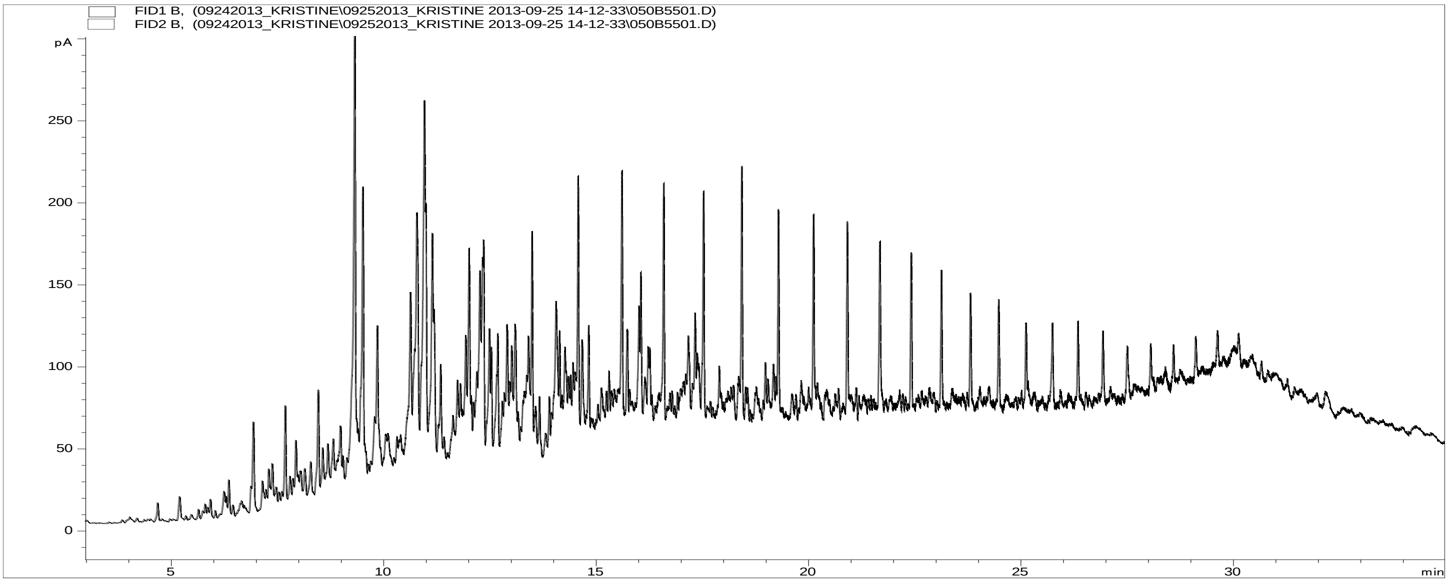

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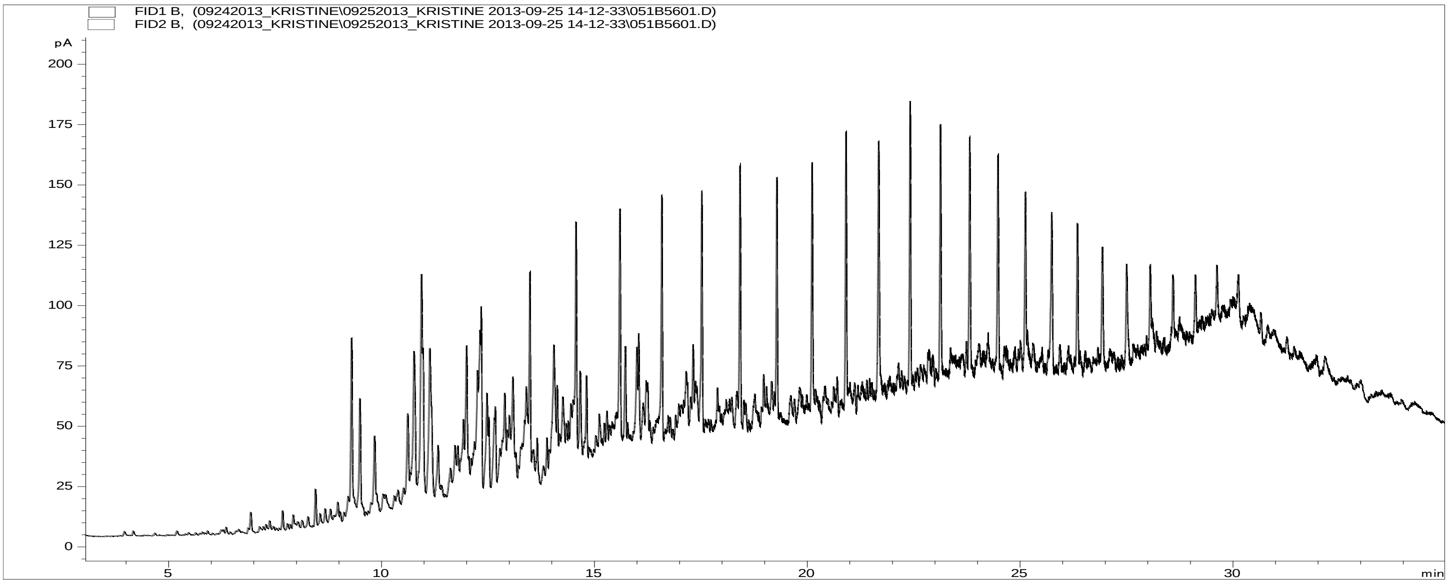

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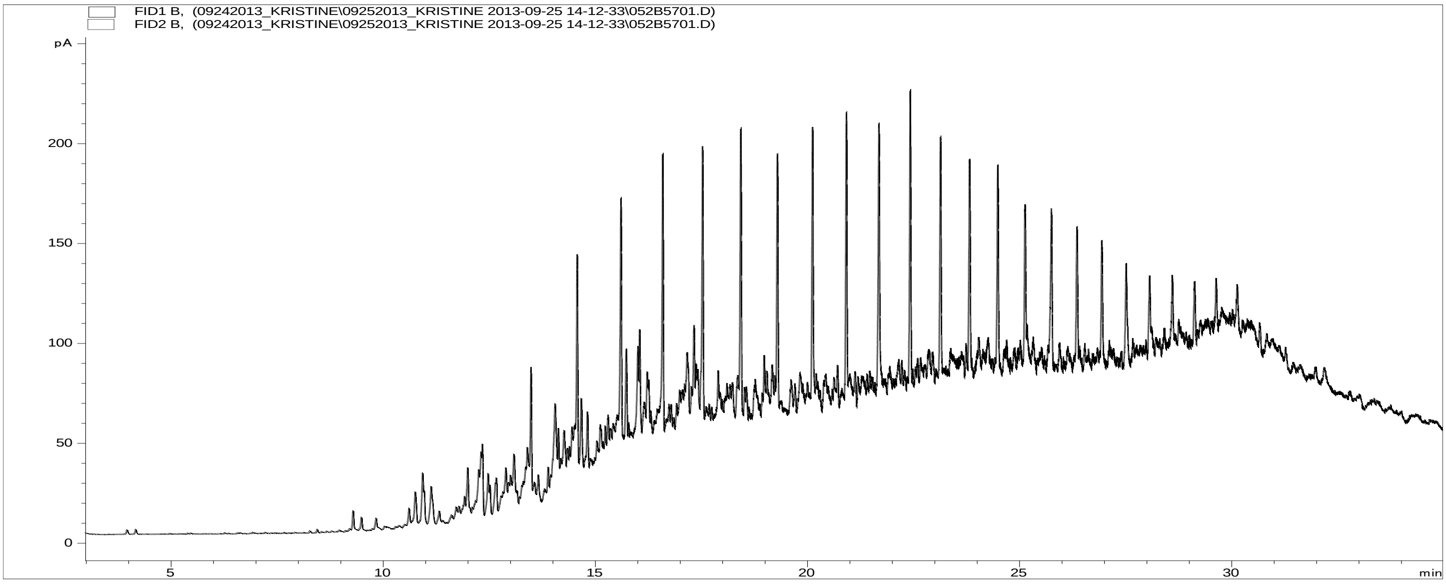

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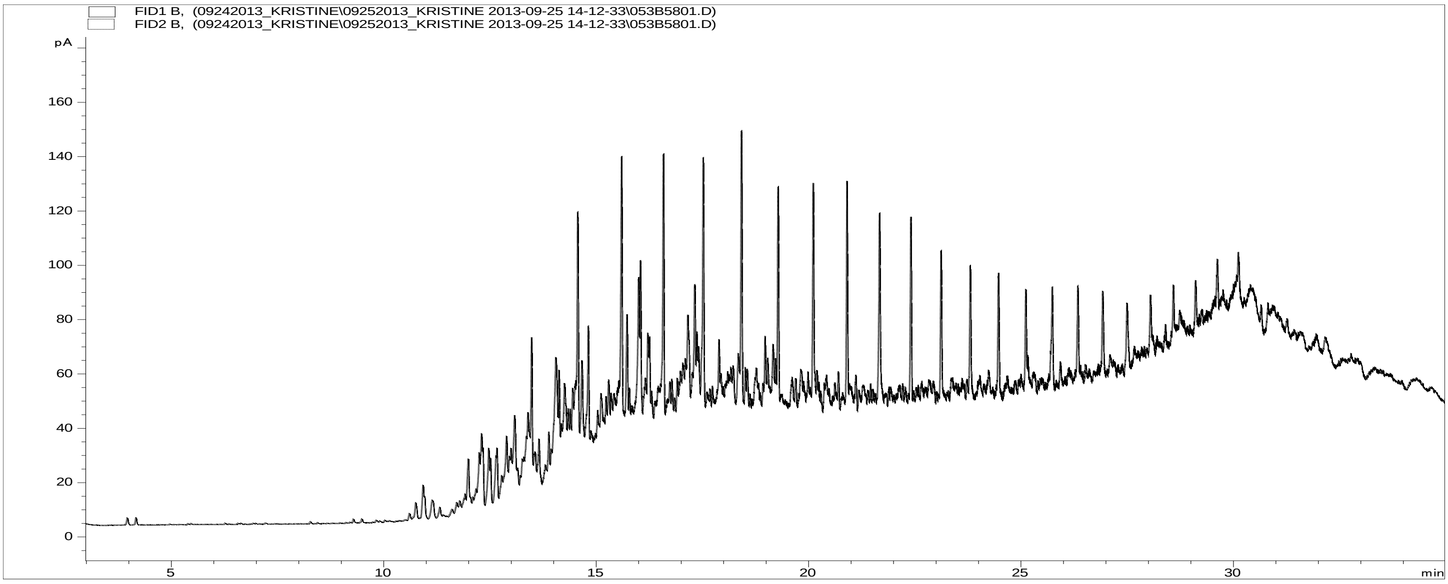

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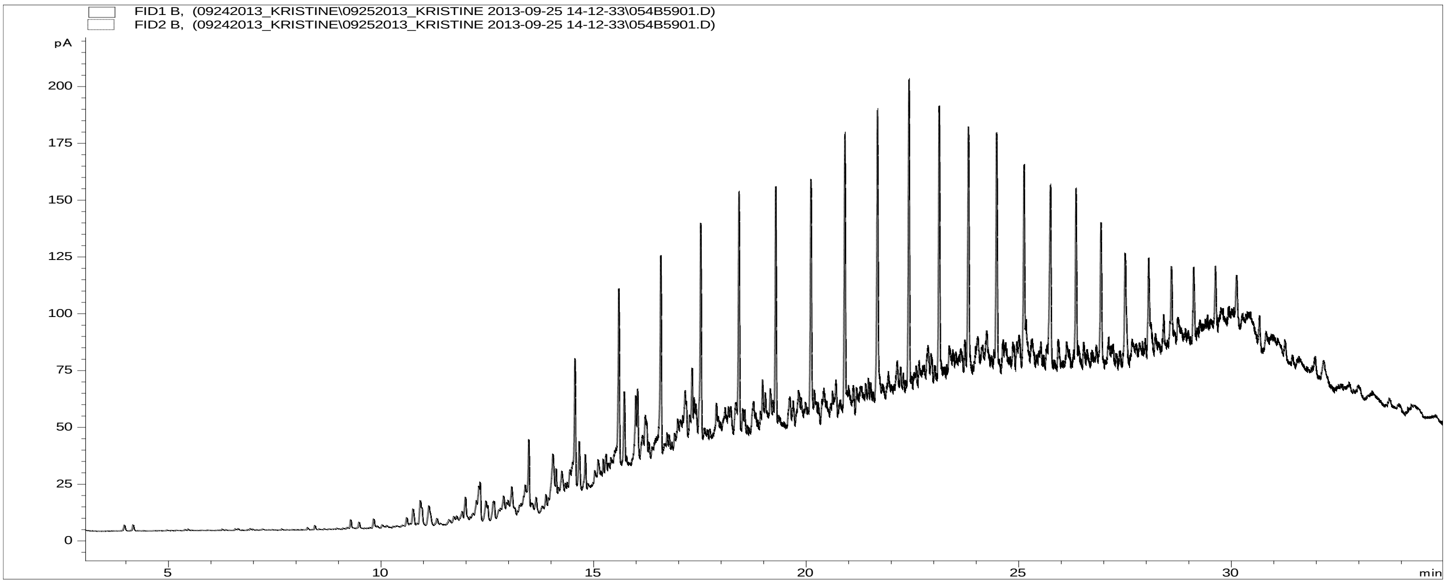

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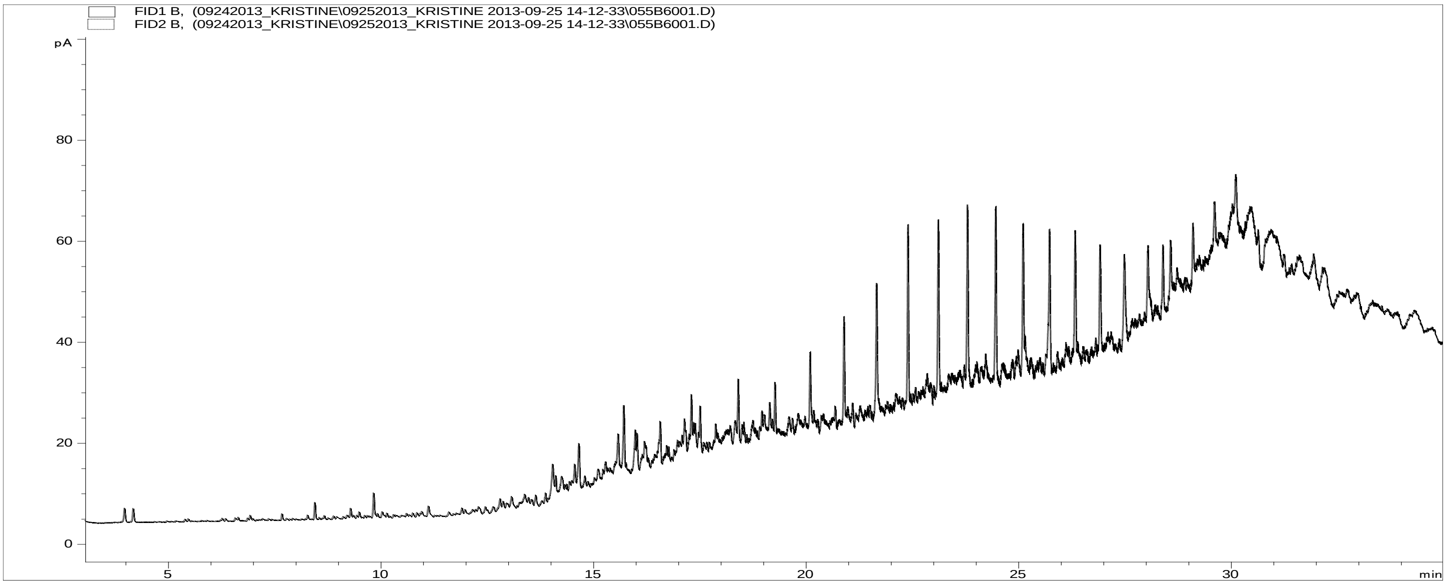

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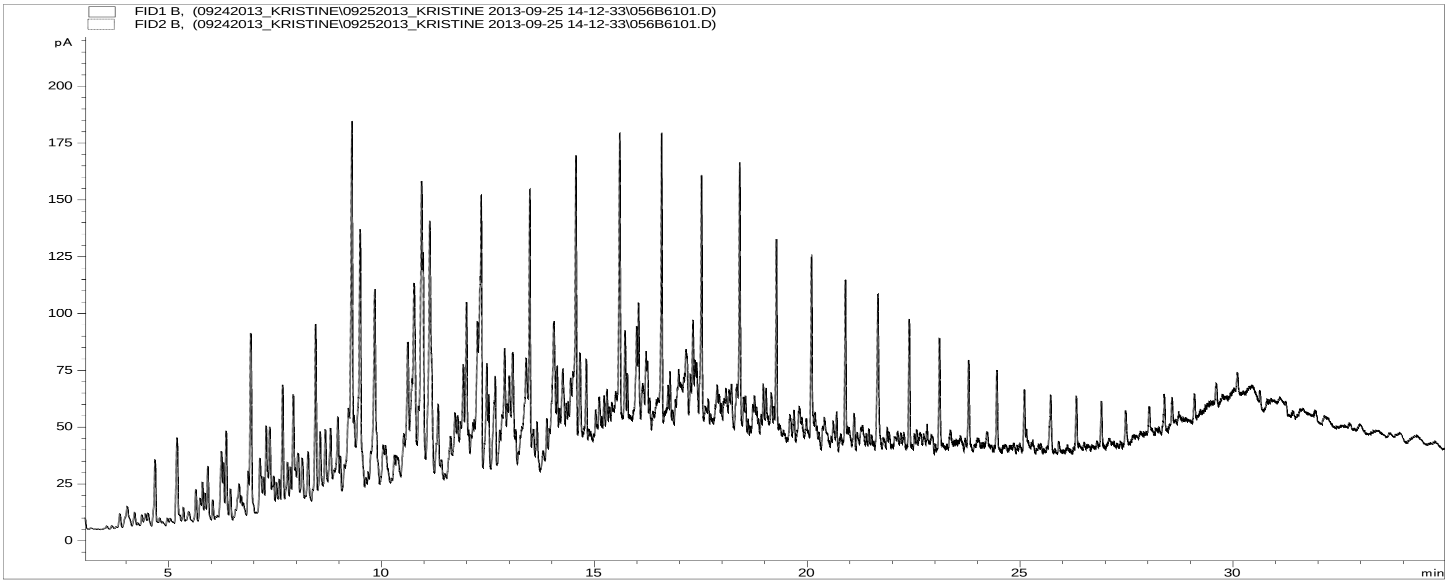

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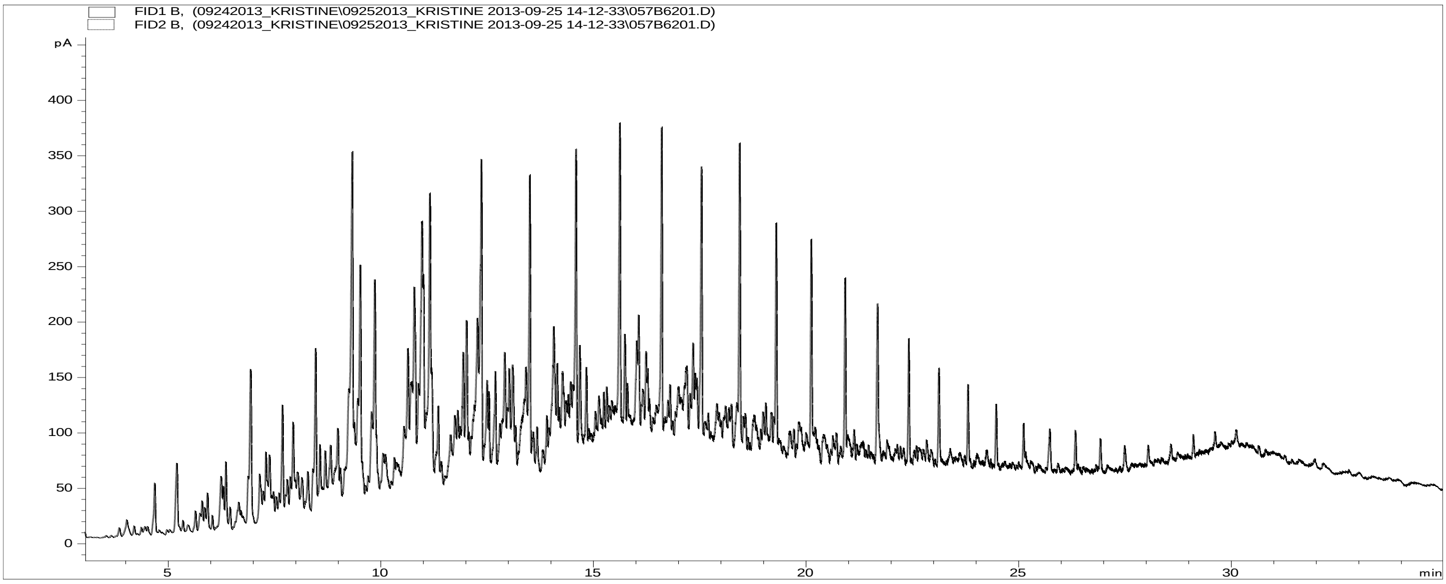

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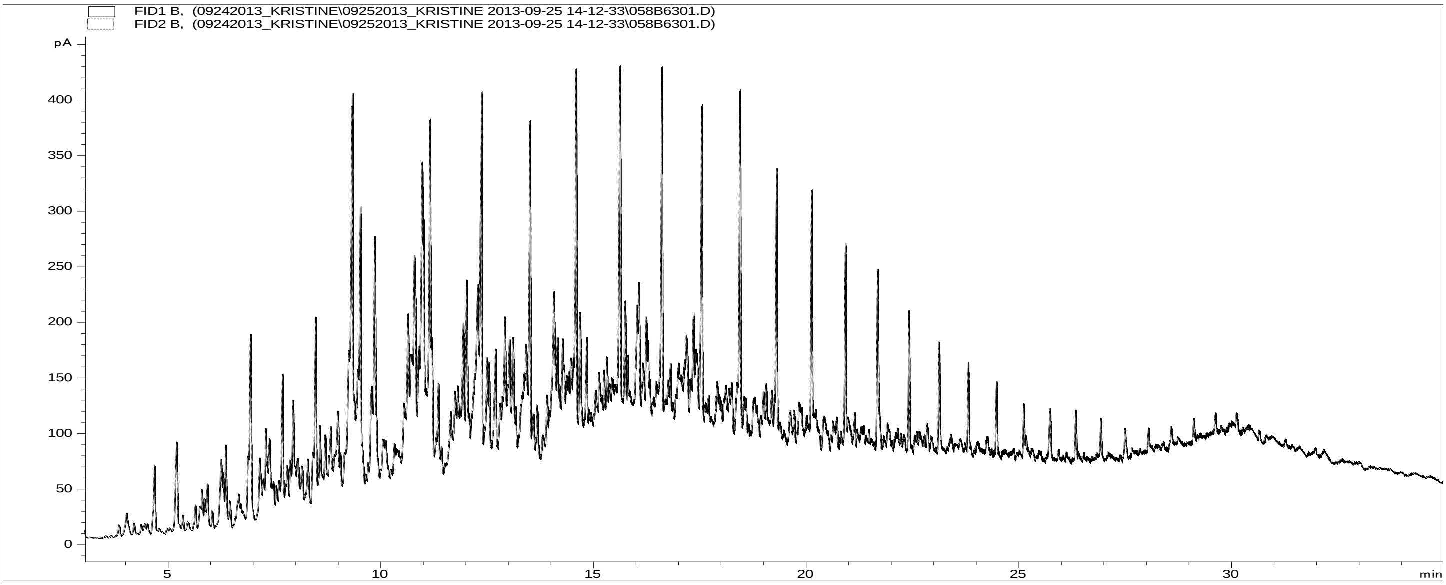

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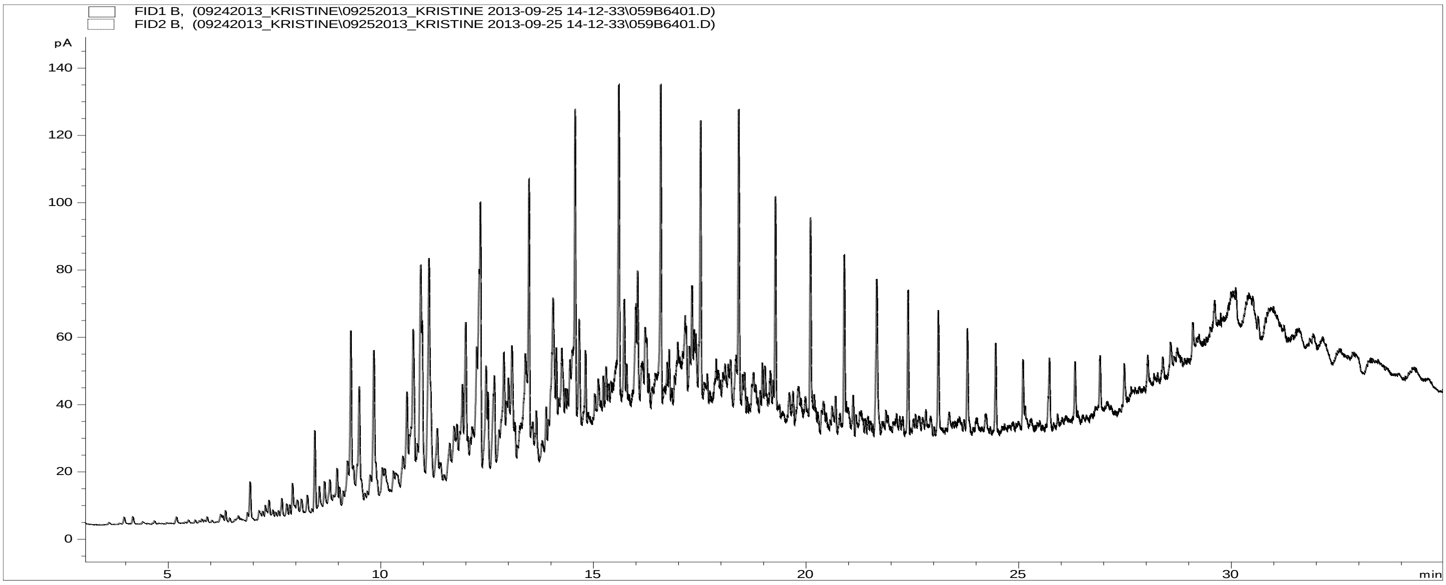

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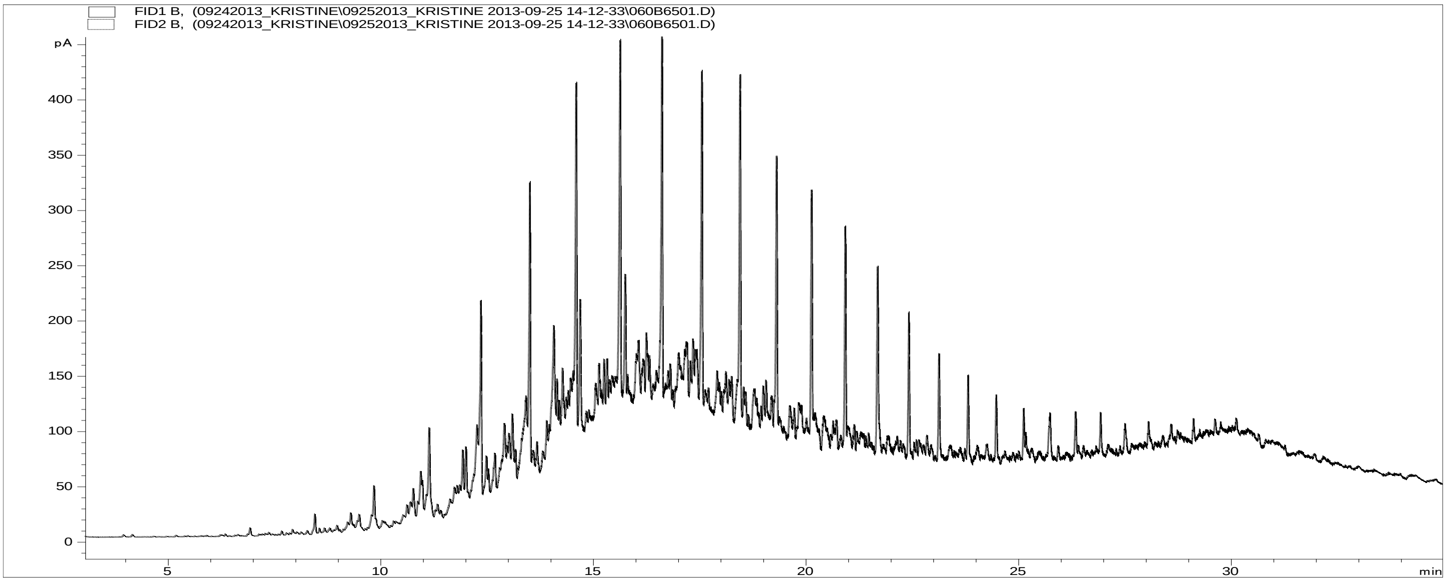

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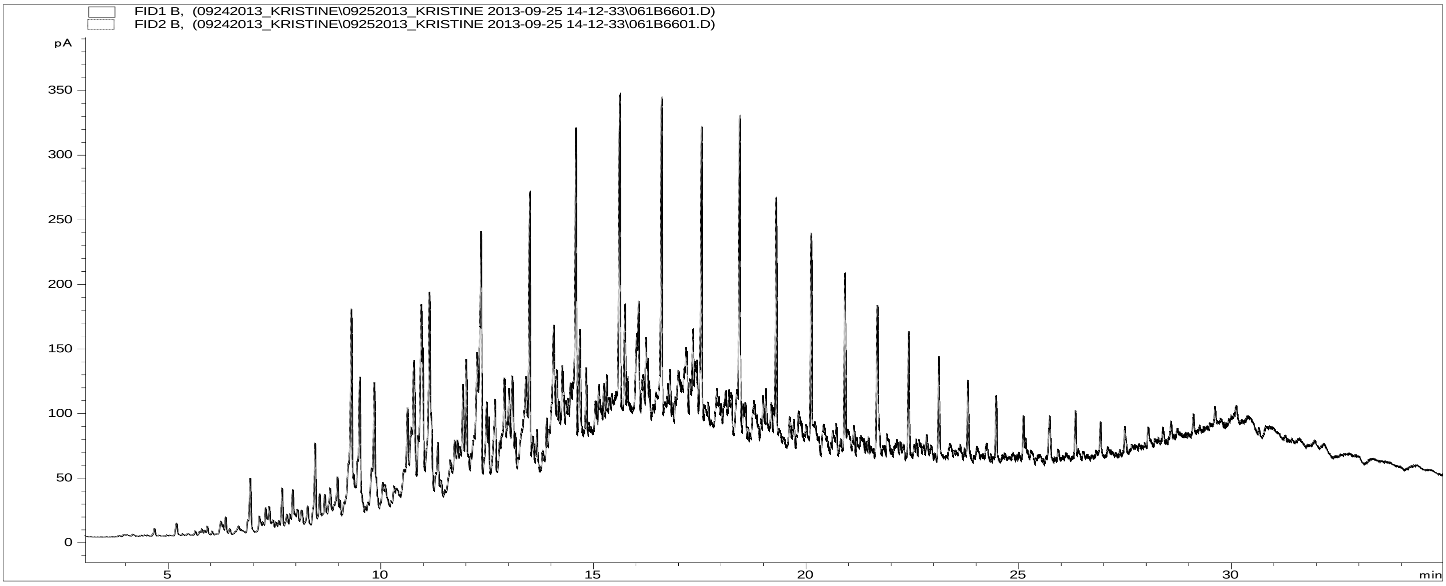

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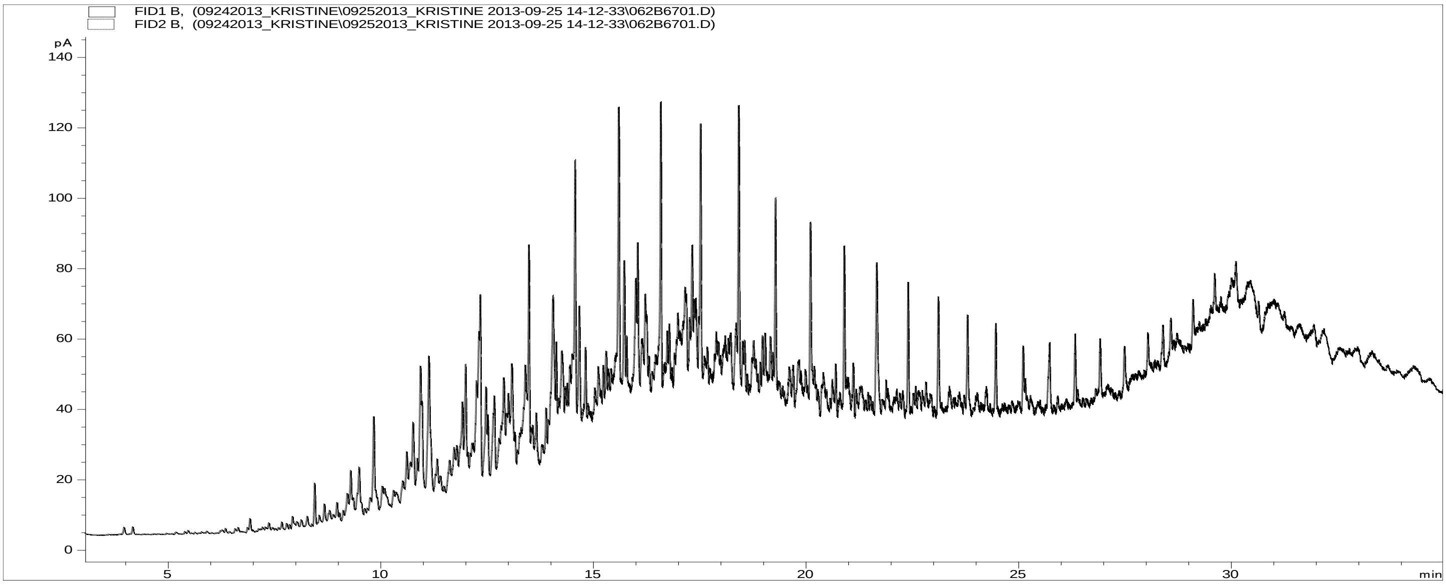

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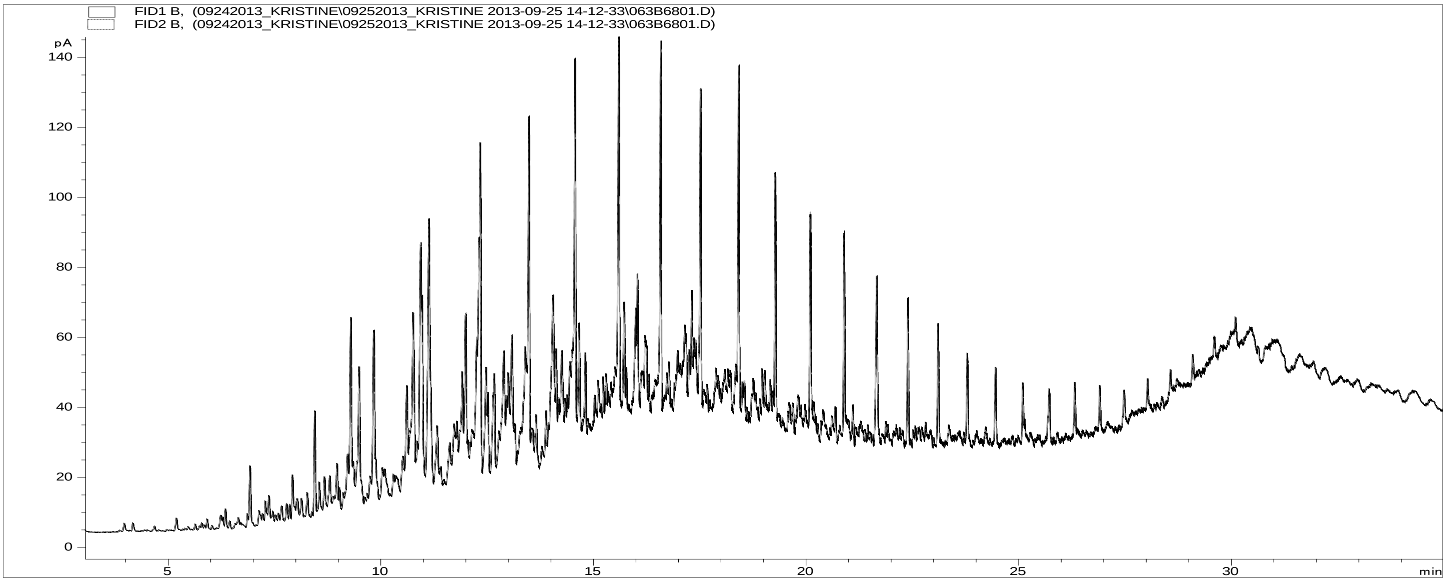

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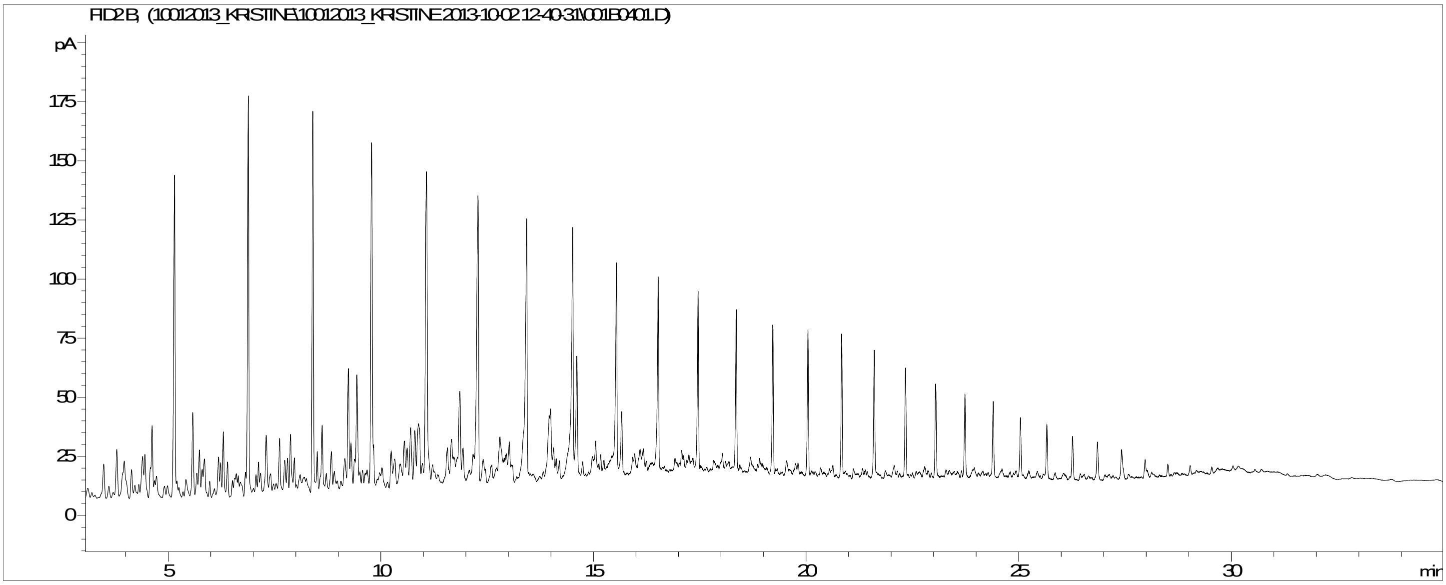

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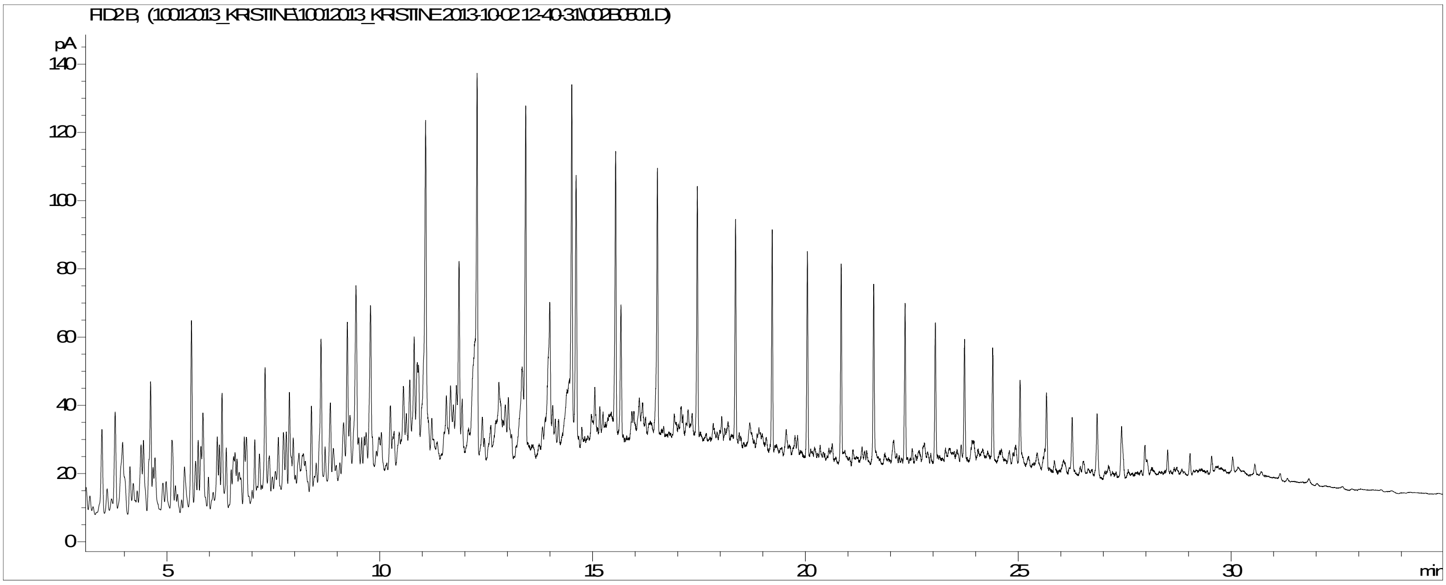

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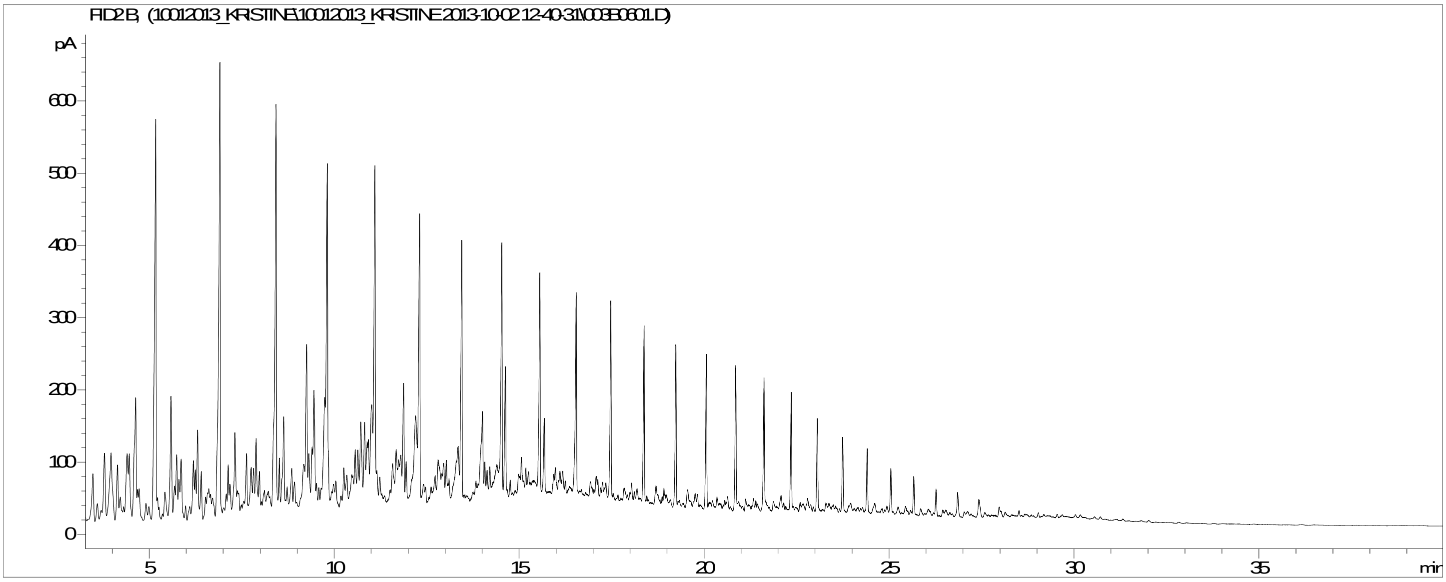

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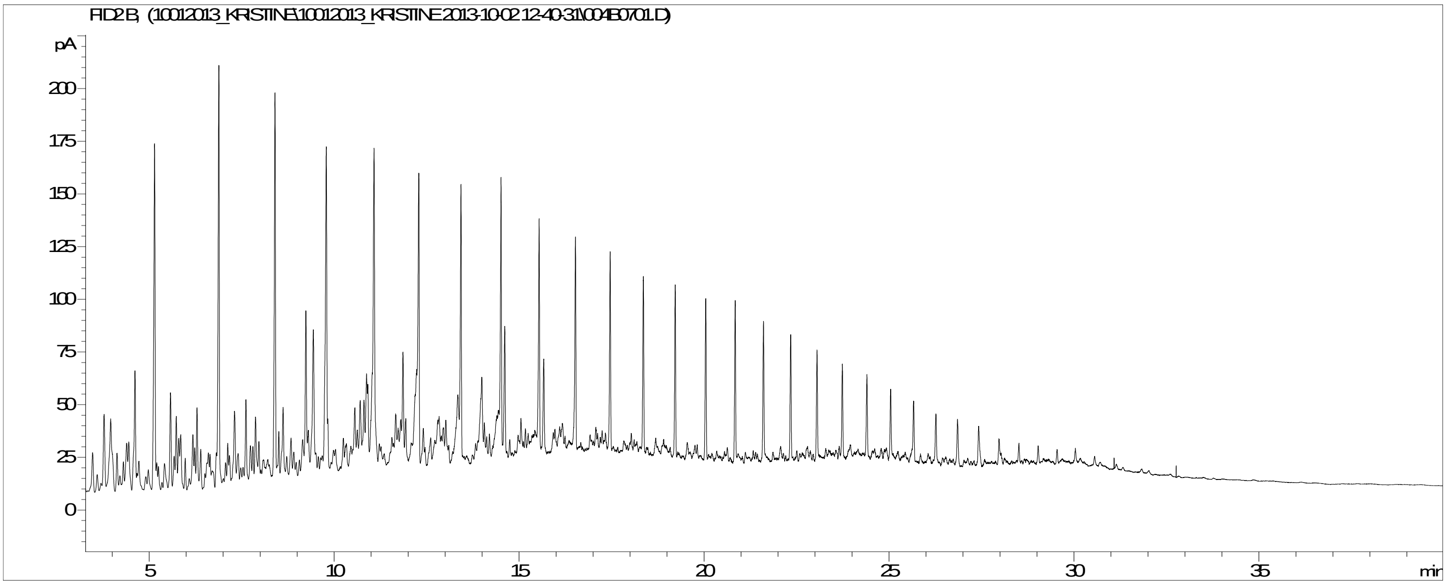

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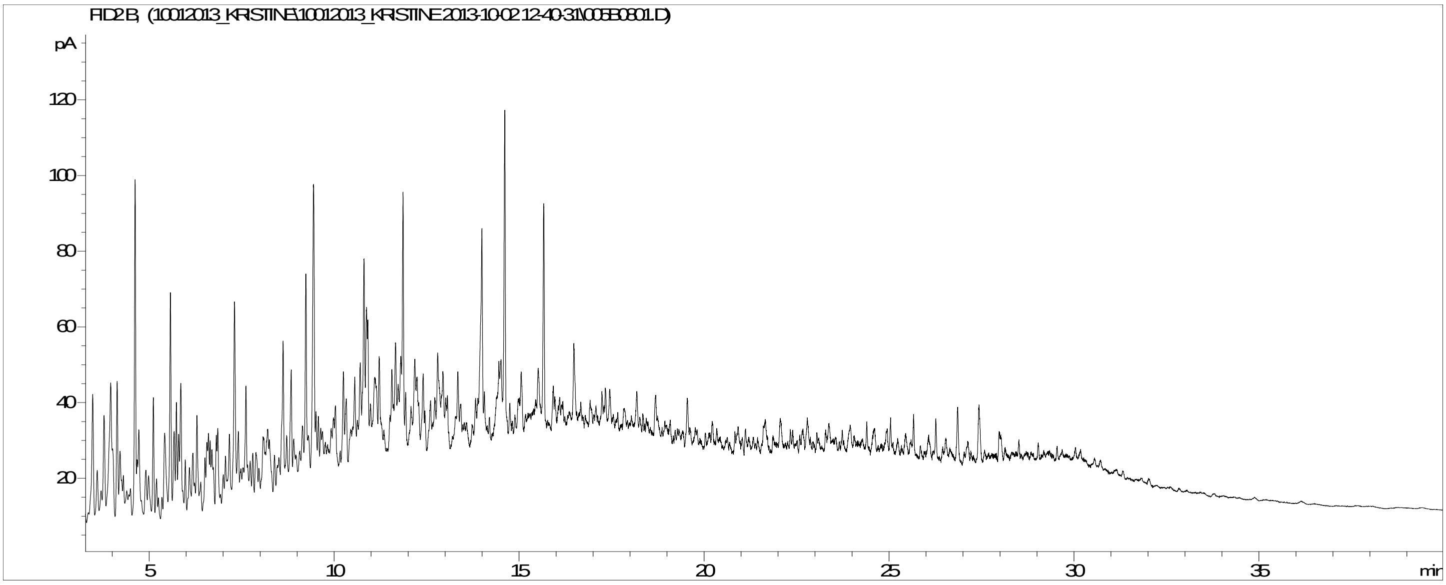

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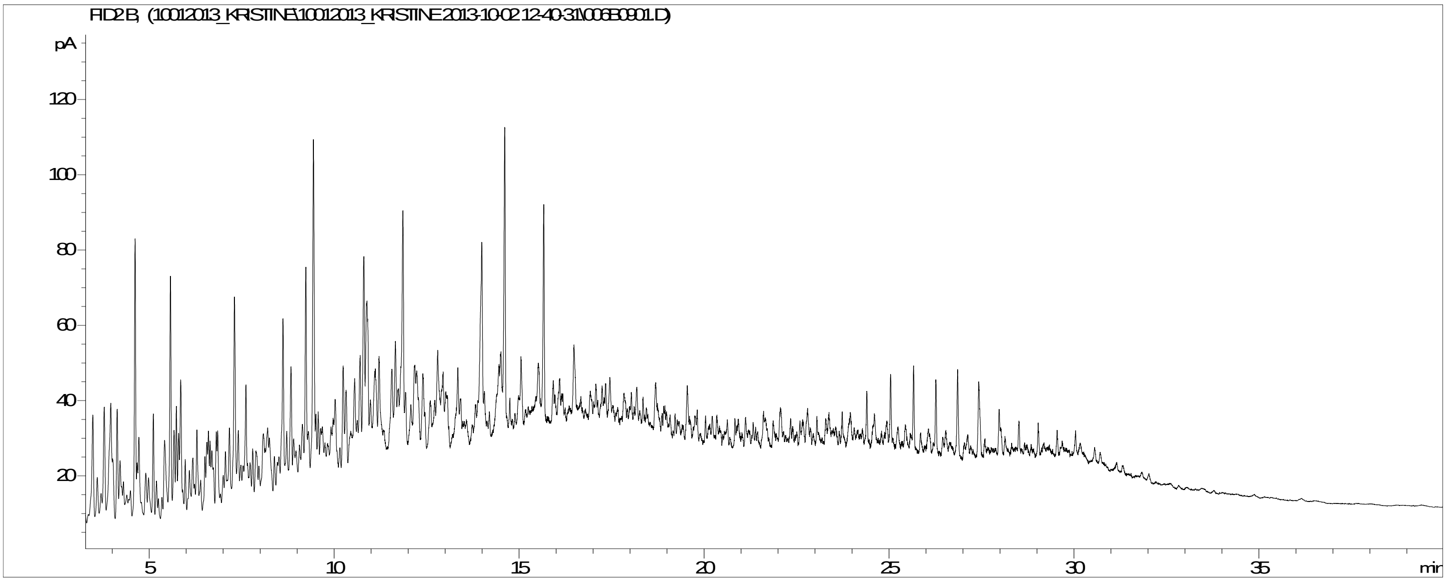

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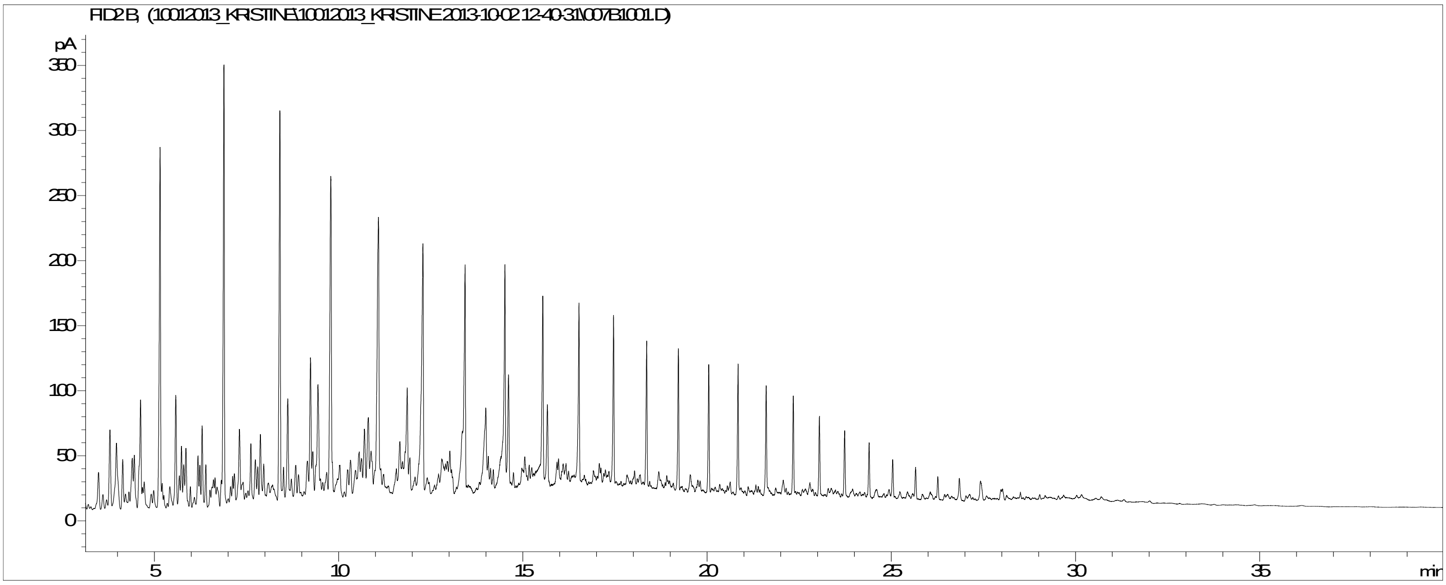

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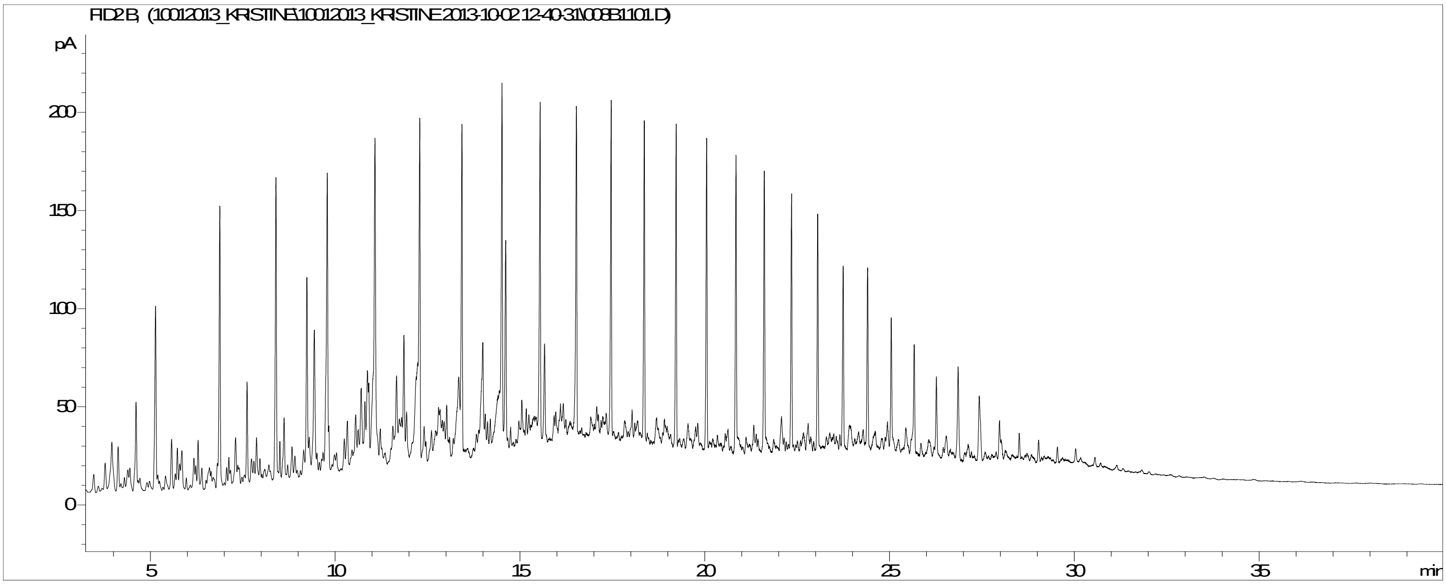

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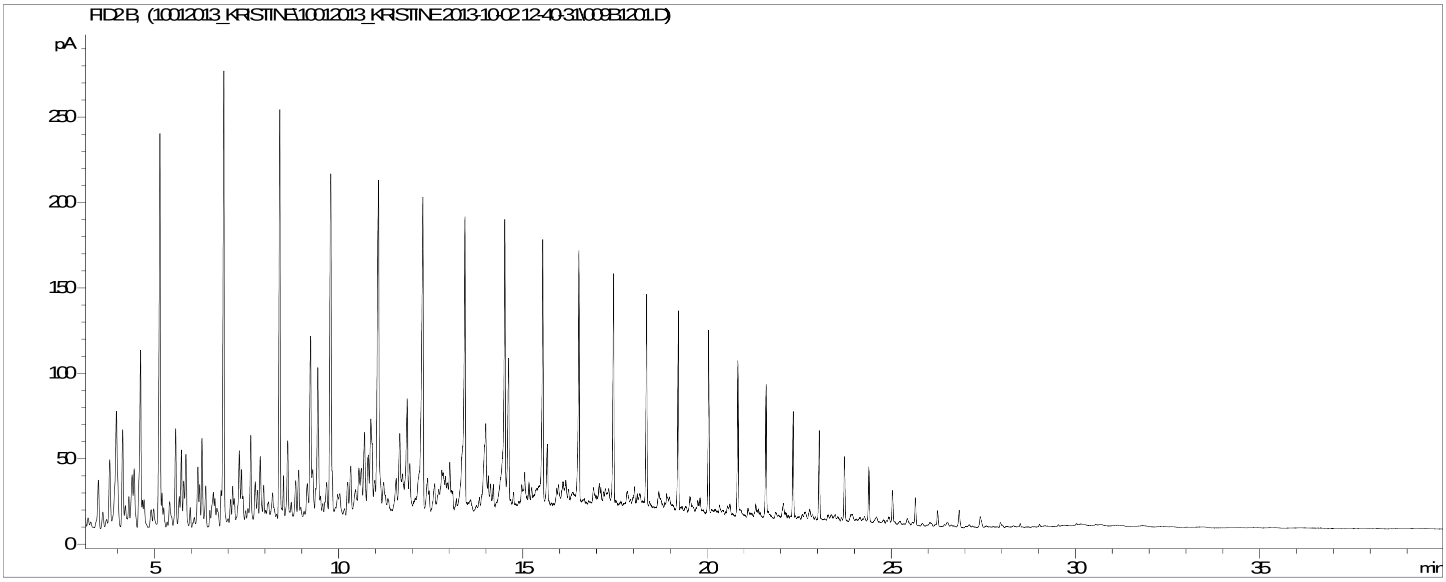

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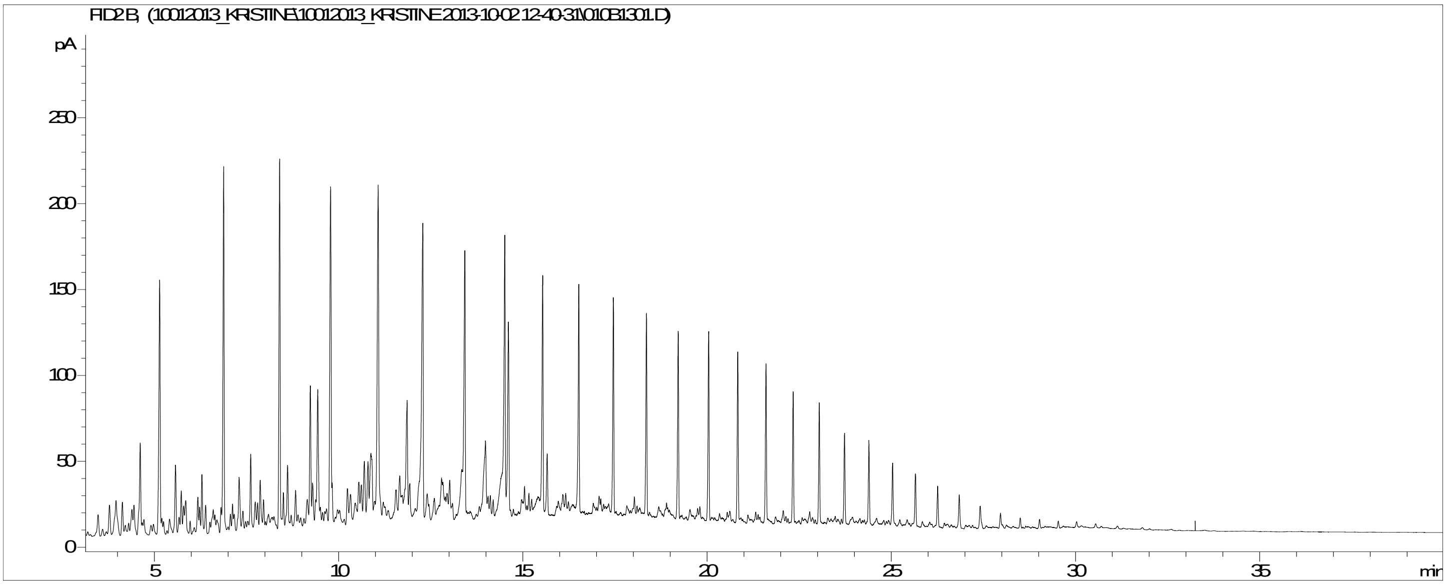

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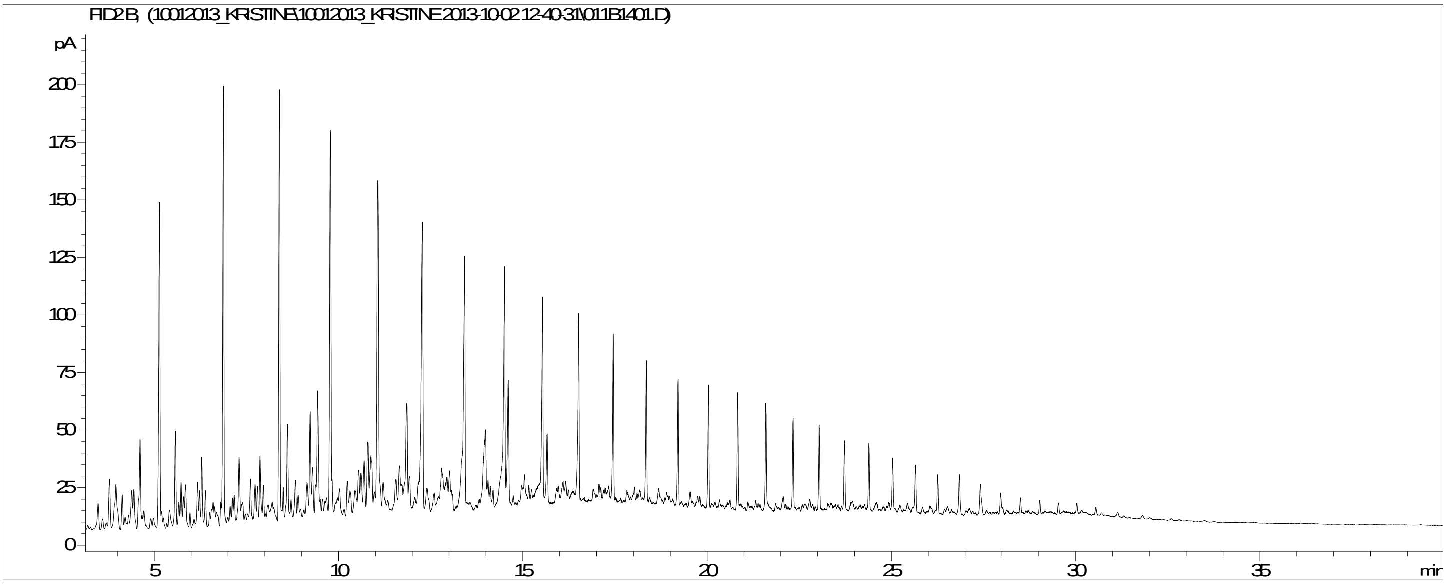

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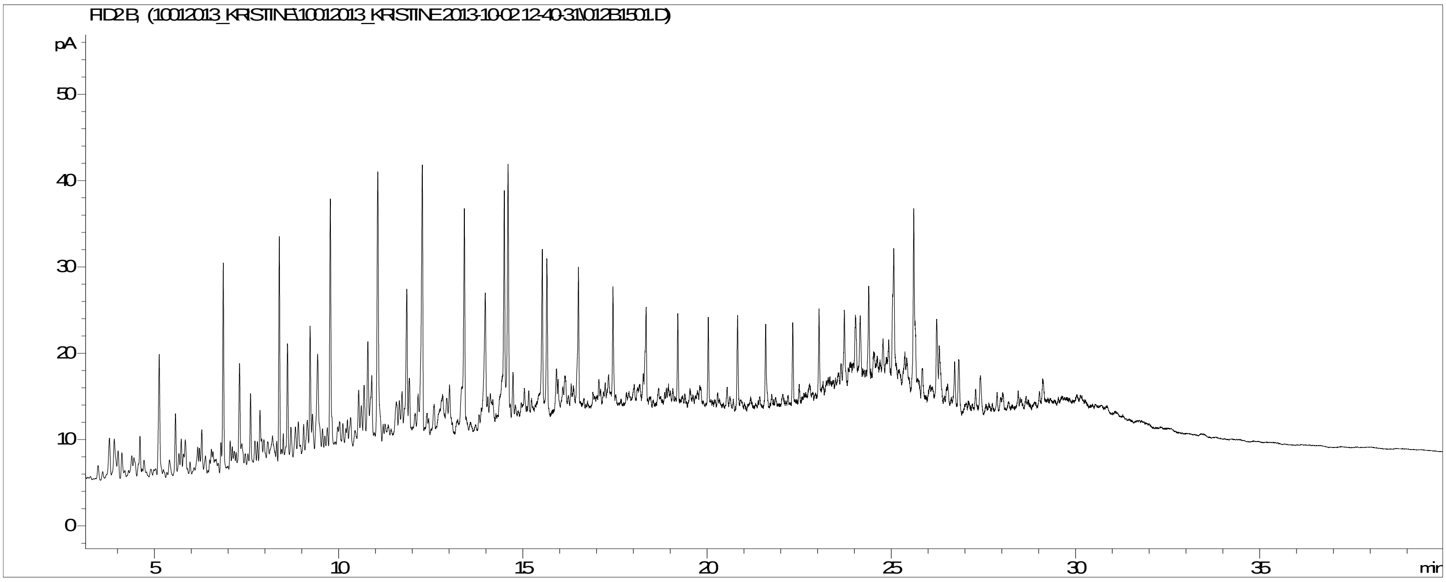

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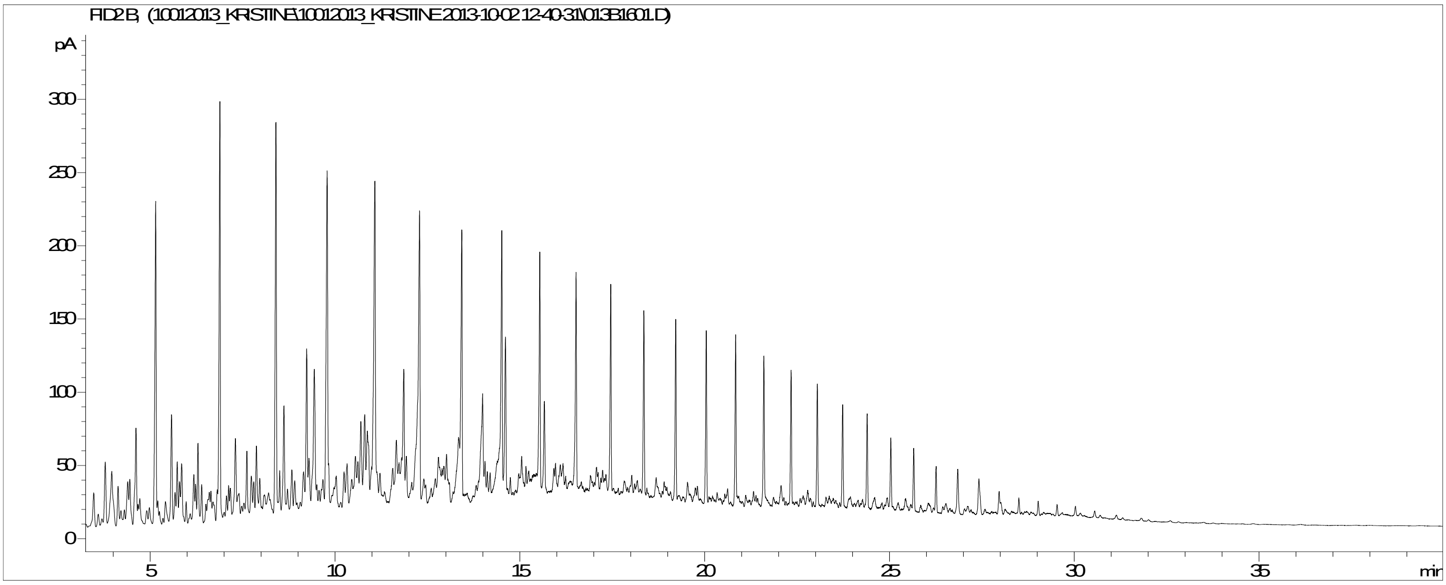

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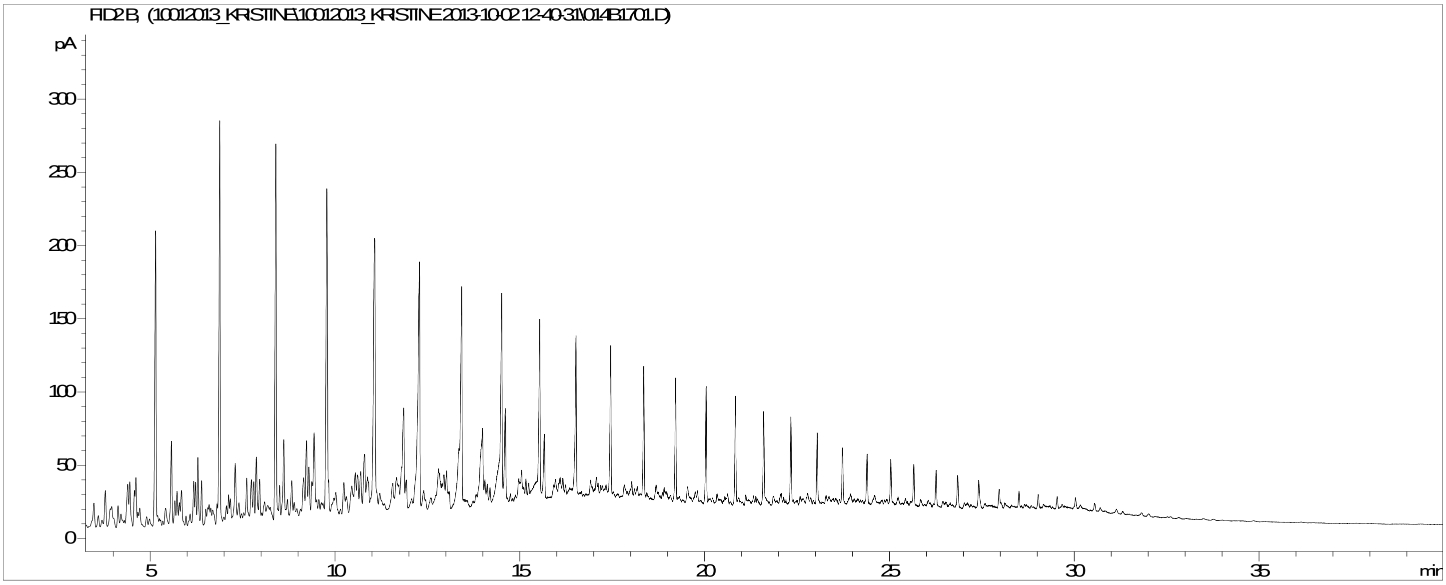

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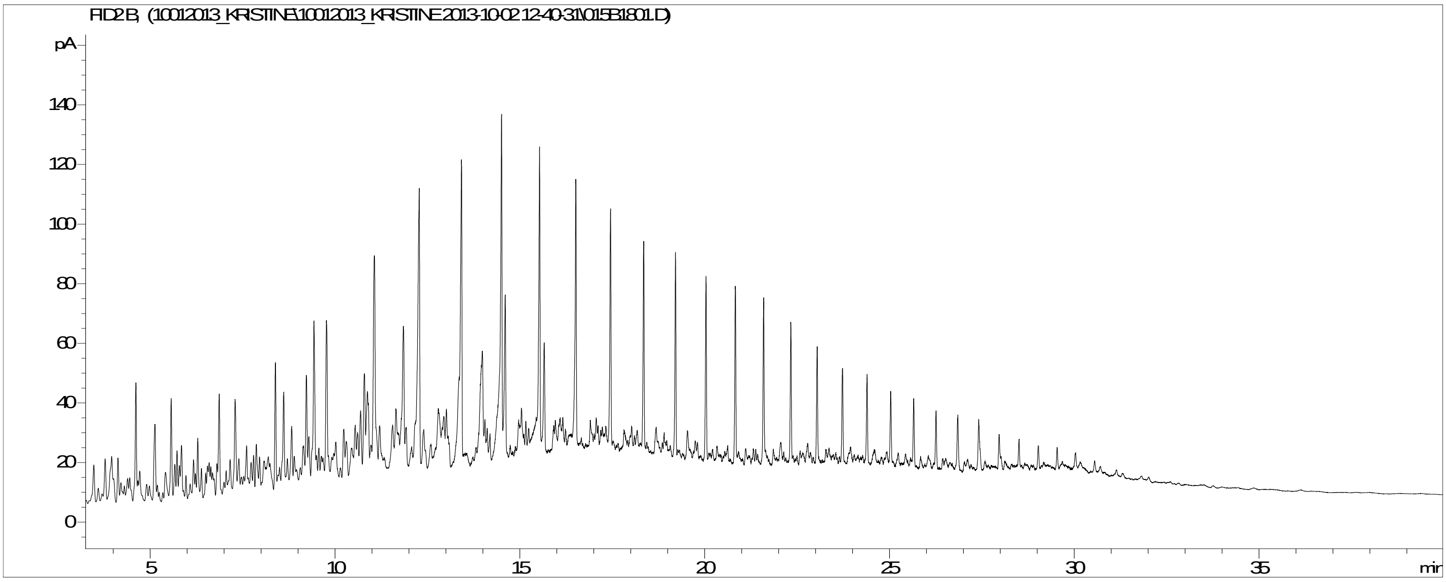

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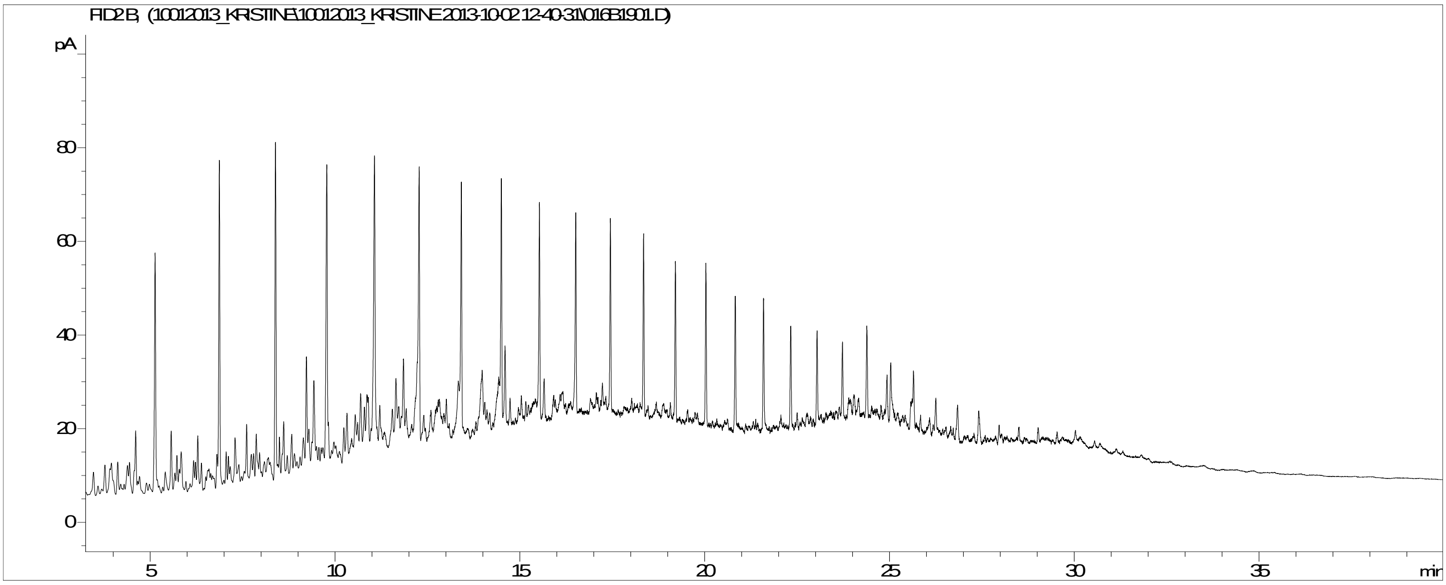

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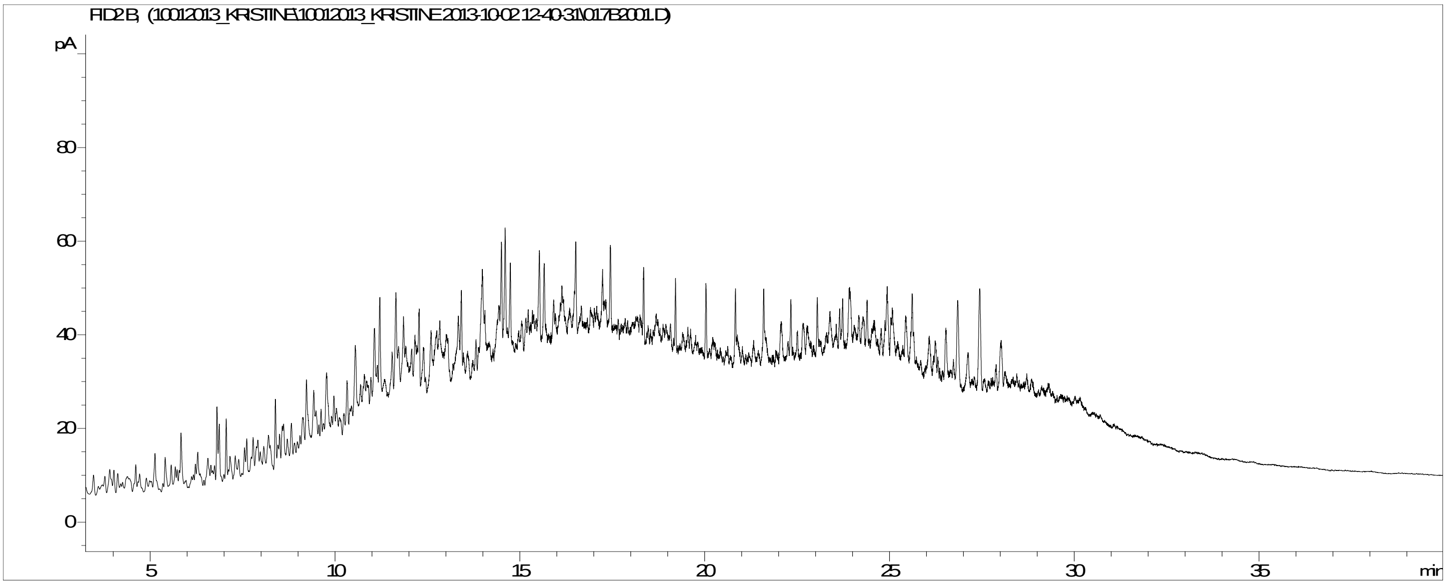

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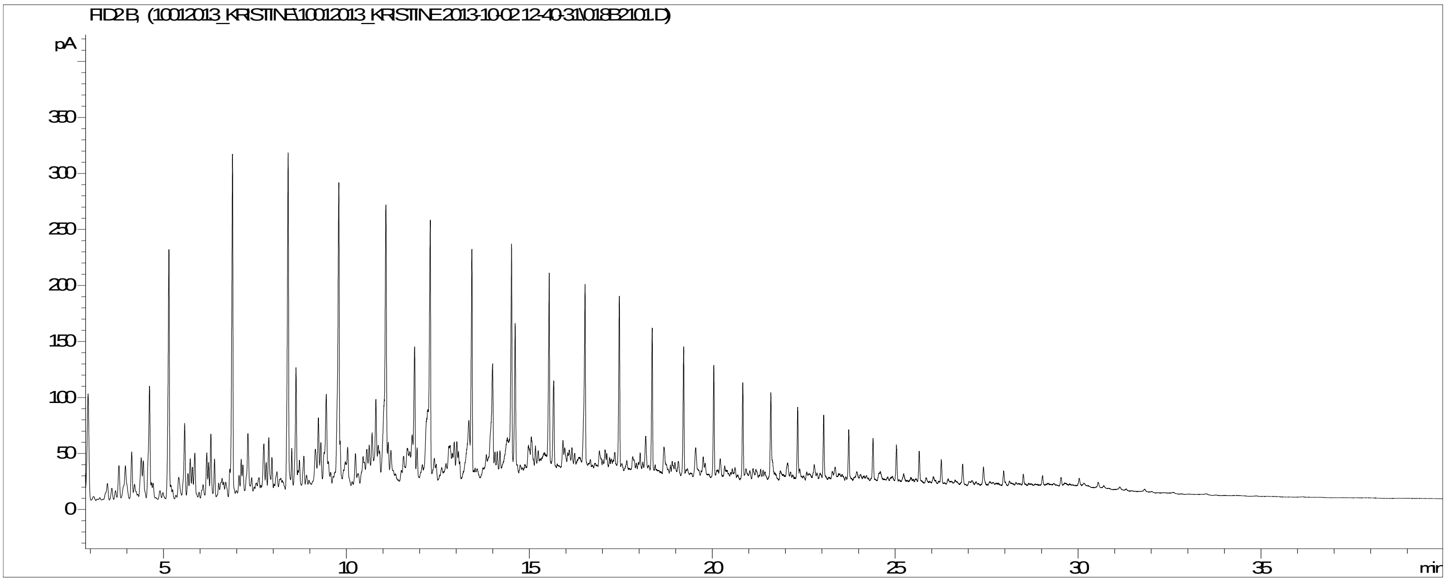

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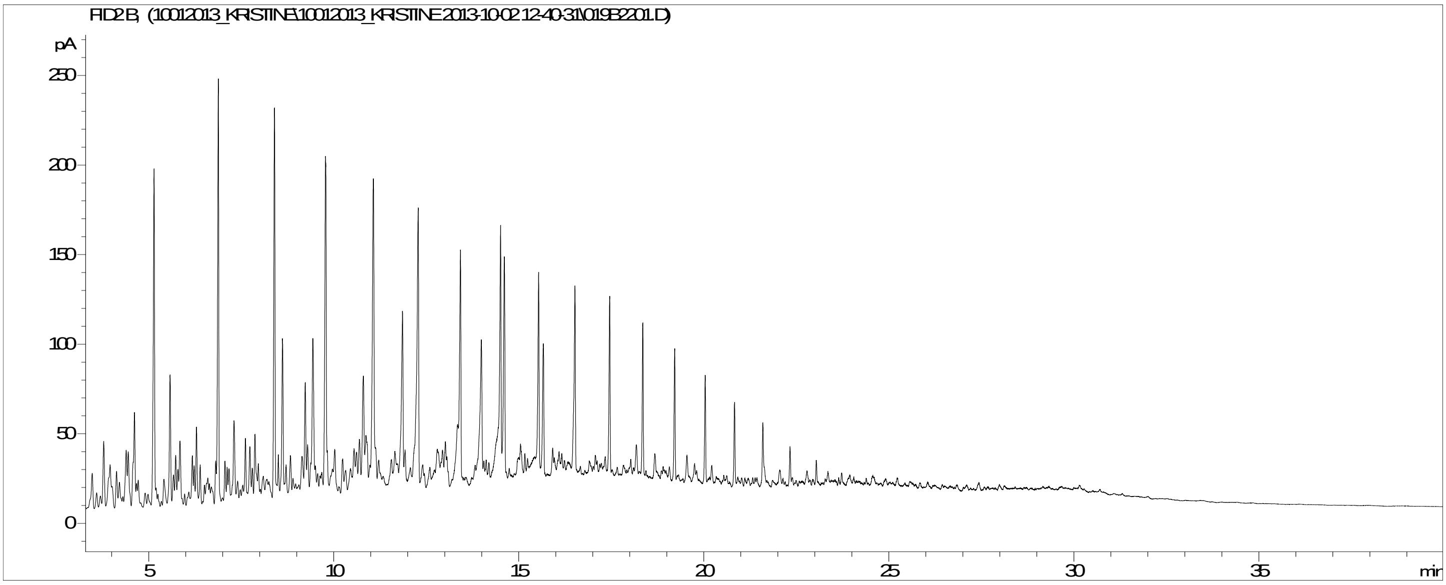

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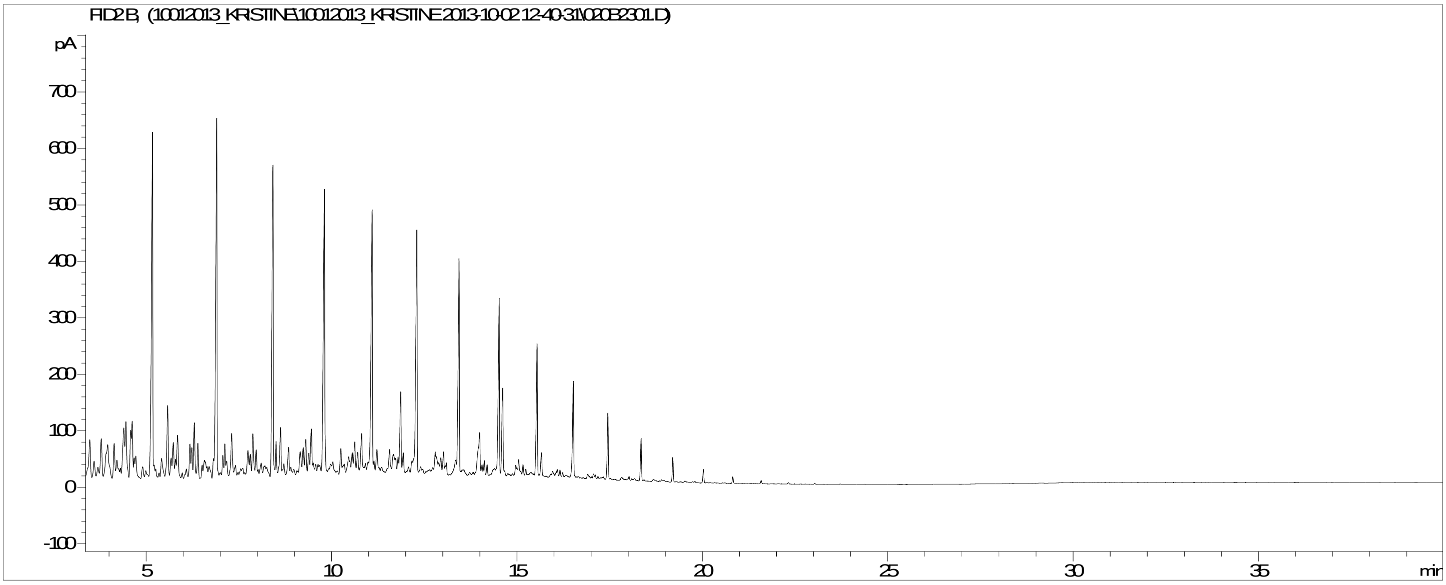
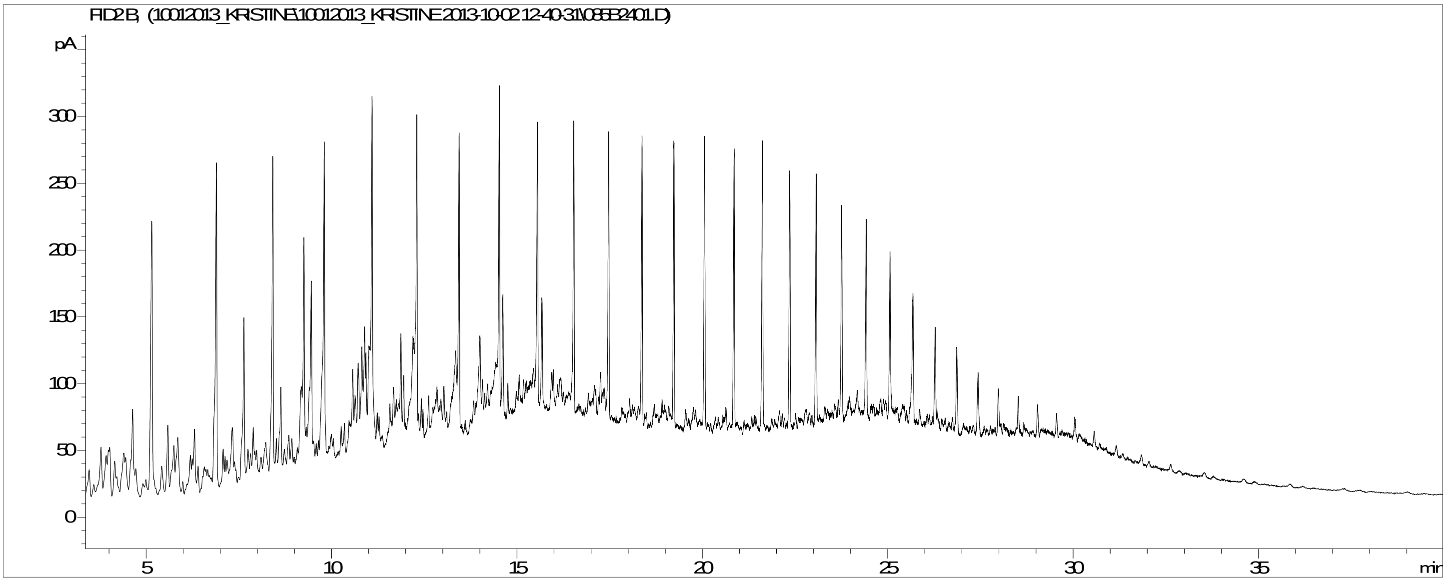
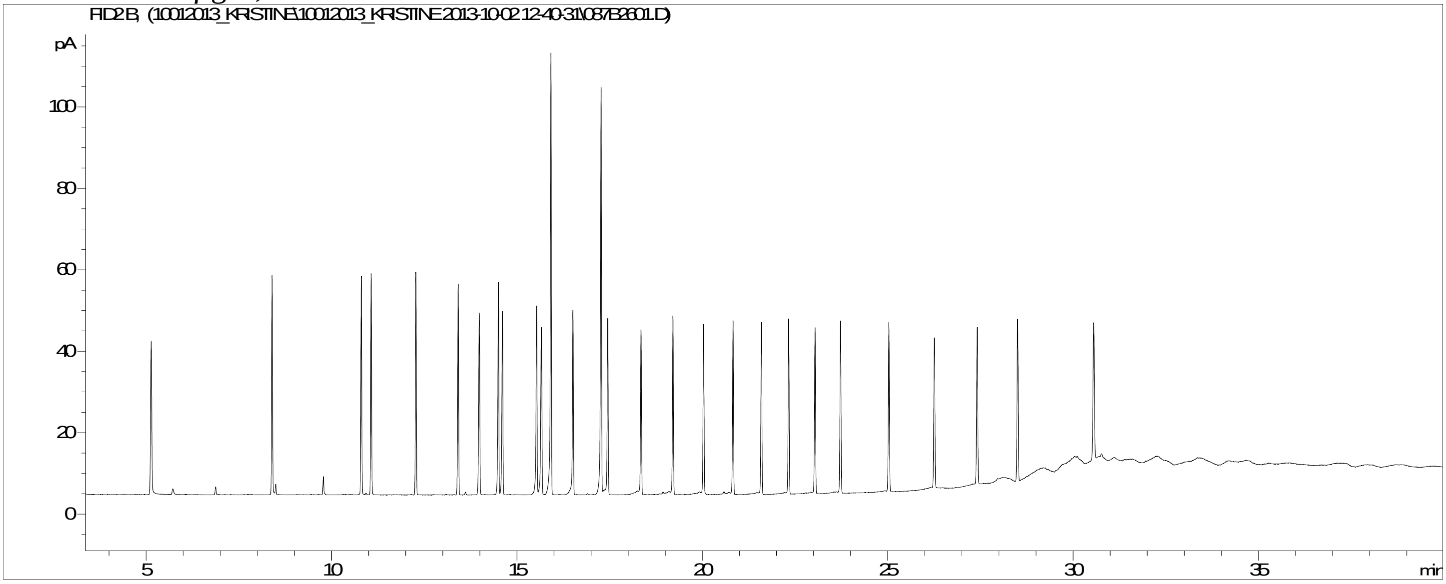


Sintef-mix:



n-alkan std 0.5µg/L, CCV A448:



Appendix F: Biomarker ratios provided by COSIWeb

Table 7: Biomarkers provided by COSIWeb, first 16 of 29.

Sample	C17/Pr	C18/Ph	Pr/Ph	Ts	Tm	28ab	29ab	30O	31abS	30G	27dbR	27bb	TASC26	TASC28	TARC27	TARC28
KV0001	1,540	0,470	0,220	0,140	0,280	0,090	0,870	0,080	0,480	0,200	0,660	1,100	0,240	0,590	0,590	0,630
KV0002	1,040	0,870	0,620	0,210	0,290	0,230	0,640	0,090	0,560	0,150	0,720	1,100	0,260	0,510	0,640	0,610
KV0003	1,120	1,050	0,740	0,130	0,150	0,510	0,440	0,000	0,560	0,070	0,860	0,330	0,090	0,850	0,690	0,880
KV0004	1,220	1,230	0,590	0,120	0,420	0,050	0,910	0,020	0,550	0,120	0,610	0,750	0,370	0,930	0,610	0,950
KV0005	0,970	1,180	0,550	0,250	0,310	0,210	0,630	0,071	0,540	0,160	0,640	1,120	0,200	0,500	0,600	0,550
KV0006	1,560	1,850	1,120	0,170	0,210	0,200	0,690	0,040	0,520	0,100	0,660	0,870	0,230	0,600	0,580	0,560
KV0007	0,930	0,880	0,520	0,190	0,280	0,040	0,970	0,210	0,520	0,190	0,680	0,770	0,250	0,740	0,670	0,760
KV0008	0,660	0,930	1,130	0,090	0,320	0,140	0,850	0,030	0,640	0,140	1,200	0,260	0,130	0,520	0,640	0,550
KV0009	0,340	0,300	0,310	0,140	0,140	0,320	0,380	0,000	0,560	0,060	0,630	1,020	0,190	0,670	0,600	0,730
KV0011	0,340	0,260	0,650	0,190	0,290	0,000	0,920	0,080	0,600	0,100	0,640	0,980	0,150	0,540	0,690	0,610
KV0012	0,770	0,640	0,840	0,180	0,280	0,000	0,940	0,100	0,550	0,100	0,650	0,860	0,190	0,560	0,700	0,620
KV0013	0,890	1,060	0,470	0,190	0,150	0,050	0,640	0,000	0,360	0,130	0,660	1,090	0,000	0,860	1,190	0,510
KV0015	1,170	1,020	0,360	0,120	0,130	0,440	0,440	0,000	0,610	0,000	0,610	1,020	0,560	0,740	0,840	0,530
KV0017	1,190	0,480	0,860	0,200	0,290	0,000	0,960	0,090	0,620	0,090	0,640	0,950	0,160	0,610	0,710	0,680
KV0019	0,350	0,280	0,390	0,210	0,280	0,000	0,930	0,090	0,600	0,090	0,590	0,910	0,170	0,600	0,710	0,690
KV0020	0,140	0,440	0,720	0,140	0,420	0,090	0,730	0,050	0,410	0,090	0,630	0,970	0,350	0,780	0,630	0,840
KV0021	0,690	0,670	0,760	0,160	0,130	0,270	0,460	0,000	0,570	0,070	0,580	0,970	0,260	0,740	0,640	0,810
KV0022	0,700	0,520	0,650	0,200	0,280	0,000	0,920	0,080	0,590	0,090	0,630	0,850	0,150	0,560	0,640	0,650
KV0023	0,290	0,230	0,460	0,140	0,160	0,360	0,440	0,000	0,560	0,070	0,710	1,000	0,200	0,730	0,630	0,760
KV0025	0,790	0,840	0,680	0,090	0,340	0,190	0,800	0,020	0,720	0,140	0,650	1,150	0,320	0,410	0,600	0,470
KV0026	1,050	0,910	0,690	0,170	0,280	0,000	0,840	0,050	0,490	0,140	0,660	0,730	0,190	0,650	0,640	0,730
KV0028	1,260	1,380	0,530	0,190	0,190	0,180	0,550	0,060	0,440	0,080	0,680	0,920	0,360	0,760	0,590	0,720
KV0029	0,420	0,400	0,860	0,140	0,210	0,000	0,780	0,350	0,380	0,120	0,650	0,910	0,250	0,680	0,670	0,750
KV0030	0,410	0,310	0,490	0,140	0,170	0,330	0,500	0,020	0,490	0,070	0,690	1,020	0,230	0,660	0,570	0,700
KV0031	0,900	1,180	1,270	0,160	0,320	0,130	0,720	0,120	0,380	0,110	0,000	1,250	0,280	0,490	0,600	0,540
KV0032	0,990	0,550	0,540	0,090	0,330	0,160	0,970	0,000	0,690	0,140	0,510	1,220	0,310	0,430	0,630	0,490
KV0033	0,000	0,000	0,490	0,150	0,370	0,420	0,750	0,000	0,540	0,270	0,670	1,110	0,250	0,530	0,630	0,580

Table 7: Cont

Sample	C17/Pr	C18/Ph	Pr/Ph	Ts	Tm	28ab	29ab	30O	31abS	30G	27dbR	27bb	TASC26	TASC28	TARC27	TARC28
KV0034	1,060	1,110	0,680	0,110	0,260	0,040	0,520	0,040	0,420	0,070	0,590	0,970	0,440	0,620	0,600	0,650
KV0035	0,970	0,960	0,910	0,080	0,350	0,190	0,930	0,000	0,670	0,150	0,570	1,140	0,310	0,410	0,650	0,460
KV0036	0,790	0,990	0,980	0,150	0,350	0,140	0,710	0,110	0,420	0,120	0,580	1,320	0,280	0,520	0,620	0,560
KV0037	0,730	0,740	0,940	0,140	0,370	0,110	0,660	0,040	0,380	0,080	0,640	0,960	0,450	0,750	0,600	0,790
KV0038	0,940	1,020	0,830	0,210	0,230	0,160	0,530	0,000	0,400	0,160	0,700	0,930	0,660	0,690	0,590	0,790
KV0039	0,430	0,360	0,310	0,150	0,230	0,160	0,680	0,030	0,490	0,090	0,650	0,930	0,270	0,790	0,620	0,750
KV0040	0,930	0,920	0,500	0,120	0,310	0,160	0,860	0,220	0,510	0,140	0,790	0,880	0,230	0,580	0,610	0,590
KV0041	0,810	0,950	0,350	0,310	0,220	0,000	0,890	0,030	0,490	0,110	0,610	0,940	0,280	0,700	0,620	0,740
KV0042	1,310	3,810	2,170	0,050	0,150	0,080	0,530	0,060	0,610	0,180	0,810	0,690	0,310	0,640	0,790	0,980
KV0044	1,410	4,970	7,850	0,170	0,390	0,190	0,820	0,130	0,510	0,150	0,690	1,020	0,200	0,500	0,520	0,450
KV0045	0,380	0,320	0,270	0,100	0,260	0,040	0,770	0,110	0,500	0,220	0,680	1,080	0,220	0,460	0,670	0,510
KV0046	0,830	0,990	1,060	0,260	0,380	0,240	0,820	0,090	0,550	0,210	0,630	1,070	0,220	0,470	0,620	0,540
KV0047	2,420	2,570	1,140	0,120	0,390	0,060	0,770	0,120	0,450	0,100	0,640	1,000	0,460	0,650	0,570	0,690
KV0048	2,360	2,260	1,000	0,150	0,320	0,060	0,750	0,050	0,490	0,110	0,610	0,910	0,360	0,700	0,610	0,780
KV0049	2,420	2,300	0,870	0,150	0,320	0,060	0,770	0,060	0,480	0,110	0,670	0,840	0,380	0,730	0,670	0,850
KV0050	2,260	2,230	0,920	0,120	0,360	0,050	0,850	0,120	0,470	0,100	0,590	0,880	0,460	0,670	0,620	0,710
KV0051	2,200	2,070	0,720	0,150	0,310	0,060	0,750	0,040	0,520	0,110	0,700	0,840	0,360	0,740	0,610	0,810
KV0052	0,660	0,650	0,730	0,160	0,320	0,060	0,760	0,040	0,520	0,110	0,650	0,950	0,350	0,760	0,610	0,780
KV0053	2,750	2,770	1,010	0,170	0,330	0,050	0,830	0,120	0,460	0,150	0,580	0,890	0,360	0,800	0,630	0,810
KV0054	2,560	2,960	1,160	0,150	0,310	0,050	0,790	0,100	0,400	0,150	0,600	1,000	0,400	0,800	0,640	0,870
KV0055	2,650	2,870	1,170	0,160	0,320	0,050	0,860	0,100	0,430	0,170	0,570	0,950	0,380	0,780	0,630	0,820
KV0056	2,530	2,710	1,090	0,150	0,310	0,050	0,800	0,090	0,430	0,160	0,580	0,990	0,390	0,800	0,630	0,860
KV0057	2,280	2,600	1,160	0,150	0,280	0,040	0,870	0,090	0,470	0,160	0,640	0,850	0,400	0,810	0,660	0,890
KV0059	1,950	1,950	0,950	0,160	0,320	0,050	0,900	0,100	0,460	0,170	0,570	0,950	0,360	0,800	0,620	0,830
KV0060	2,910	3,130	1,070	0,160	0,310	0,050	0,830	0,100	0,430	0,170	0,640	1,000	0,400	0,820	0,680	0,880

Table 8: Biomarkers provided by COSIWeb, last 13 of 29.

Sample	C17/Pr	C18/Ph	Pr/Ph	2MP	MA	4MD	2MF	B(a)F	B(b+c)F	2MPy	1MPy	Retene	BNT
KV0001	0,670	0,530	0,540	0,420	0,000	0,780	0,090	0,100	0,000	0,390	0,330	0,000	2,750
KV0002	0,960	0,240	0,280	0,000	0,000	0,560	0,000	0,000	0,000	0,310	0,440	0,000	0,080
KV0003	0,620	0,550	0,600	0,000	0,000	1,400	0,050	0,050	0,000	0,240	0,350	5,890	0,520
KV0004	5,500	6,530	0,330	1,010	0,110	1,190	0,100	0,180	0,090	0,760	0,720	0,000	1,580
KV0005	7,710	6,180	0,210	0,380	0,000	1,460	0,150	0,290	0,080	0,350	0,350	1,060	1,280
KV0006	6,100	9,510	0,530	1,010	0,190	1,430	0,070	0,060	0,000	1,030	0,440	0,000	1,520
KV0007	1,060	1,410	0,300	0,290	0,000	0,650	0,040	0,080	0,030	0,480	0,410	0,000	0,320
KV0008	3,240	10,990	0,600	0,000	0,000	1,340	0,050	0,000	0,030	0,330	0,370	0,000	1,760
KV0009	0,020	0,110	0,240	0,570	0,000	1,450	0,420	0,530	0,110	0,330	0,250	11,450	3,380
KV0011	0,040	0,050	0,430	0,320	0,000	1,350	0,050	0,190	0,080	0,300	0,440	0,000	1,580
KV0012	1,050	0,630	0,560	0,650	0,020	2,460	0,080	0,480	0,220	0,330	0,510	0,000	1,640
KV0013	0,760	0,210	0,350	1,200	0,050	2,450	0,160	0,120	0,000	0,800	0,460	0,000	1,180
KV0015	2,650	0,930	0,250	0,000	0,000	1,200	1,000	1,210	0,000	0,000	0,000	0,000	0,000
KV0017	3,050	1,180	0,210	0,510	0,020	1,940	0,090	0,300	0,130	0,300	0,380	0,000	3,170
KV0019	0,020	0,030	0,260	0,790	0,000	1,960	0,120	0,210	0,000	0,330	0,300	0,000	4,250
KV0020	0,310	0,110	0,130	1,200	0,000	0,990	0,270	0,160	0,000	0,960	0,300	0,000	1,550
KV0021	0,880	0,720	0,540	0,660	0,000	1,810	0,370	0,950	0,320	0,440	0,340	4,640	4,020
KV0022	0,100	0,060	0,280	0,360	0,000	1,040	0,060	0,140	0,060	0,290	0,410	0,000	2,180
KV0023	0,010	0,050	0,320	0,000	0,000	0,190	0,310	0,280	0,000	0,370	0,190	9,390	2,290
KV0025	1,930	4,460	0,680	0,680	0,030	1,120	0,140	0,380	0,230	0,460	0,560	0,000	2,040
KV0026	0,930	0,920	0,330	0,380	0,000	1,260	0,050	0,200	0,070	0,270	0,380	0,000	1,460
KV0028	0,760	0,950	0,500	0,840	0,140	2,130	0,110	0,130	0,070	0,840	0,660	0,000	1,050
KV0029	0,220	0,200	0,650	0,480	0,050	1,520	0,070	0,370	0,160	0,390	0,500	0,000	0,970
KV0030	0,050	0,020	0,370	0,620	0,000	0,840	0,120	0,160	0,050	0,630	0,460	2,050	1,020
KV0031	1,150	1,060	0,910	1,010	0,220	2,040	0,120	0,390	0,200	0,560	0,660	0,000	1,760
KV0032	1,140	0,130	0,270	0,670	0,070	1,210	0,220	0,770	0,570	0,540	0,600	0,000	2,020
KV0033	0,370	0,950	0,920	0,970	0,000	1,640	0,210	0,200	0,000	0,590	0,410	0,000	1,400
KV0034	1,460	1,160	0,530	1,710	0,140	3,710	0,120	0,210	0,140	1,000	0,820	0,000	0,690
KV0035	0,430	0,360	0,290	0,370	0,270	0,750	0,200	0,680	0,530	0,570	0,670	0,000	1,760

Table 8: Cont.

Sample	C17/Pr	C18/Ph	Pr/Ph	2MP	MA	4MD	2MF	B(a)F	B(b+c)F	2MPy	1MPy	Retene	BNT
KV0036	0,070	0,090	0,680	0,900	0,110	1,930	0,120	0,230	0,110	0,550	0,630	0,000	1,850
KV0037	0,510	0,400	0,670	1,290	0,220	2,930	0,190	0,360	0,230	0,880	0,730	0,000	0,700
KV0038	4,100	4,080	0,350	0,460	0,030	1,720	0,150	0,280	0,000	0,390	0,430	6,330	2,420
KV0039	0,060	0,050	0,220	0,640	0,050	1,030	0,150	0,270	0,130	0,800	0,470	0,880	3,320
KV0040	4,340	2,220	0,260	0,000	0,000	0,500	0,060	0,030	0,020	0,200	0,280	0,000	0,770
KV0041	4,100	1,260	0,160	0,960	0,000	1,470	0,110	0,070	0,000	0,550	0,240	0,000	1,070
KV0042	3,300	4,660	0,810	0,890	0,320	1,870	0,090	0,080	0,050	0,410	0,660	0,000	2,000
KV0044	1,950	4,890	1,210	0,000	0,000	0,950	0,160	0,100	0,000	0,300	0,180	0,000	4,190
KV0045	0,040	0,130	0,190	0,790	0,000	0,990	0,180	0,140	0,000	0,800	0,340	0,000	1,550
KV0046	0,100	0,100	0,550	0,820	0,050	1,900	0,130	0,330	0,180	0,570	0,640	0,000	1,150
KV0047	4,390	3,070	0,720	2,290	0,440	3,250	0,090	0,180	0,160	1,110	0,920	0,000	0,770
KV0048	3,950	2,770	0,670	2,080	0,350	3,000	0,100	0,240	0,190	1,070	0,950	0,000	0,950
KV0049	4,540	3,080	0,560	2,120	0,290	2,860	0,100	0,200	0,160	1,110	0,930	0,000	0,880
KV0050	4,000	2,890	0,620	2,250	0,120	3,320	0,100	0,170	0,130	1,120	0,910	0,000	0,830
KV0051	4,140	2,680	0,490	1,970	0,210	2,730	0,110	0,240	0,160	1,020	0,920	0,000	0,860
KV0052	0,570	0,500	0,500	1,480	0,150	2,340	0,100	0,220	0,160	1,050	0,840	0,000	1,030
KV0053	4,820	3,390	0,700	1,950	0,430	2,960	0,100	0,220	0,140	0,920	0,910	0,000	1,320
KV0054	5,470	3,680	0,690	1,890	0,430	2,940	0,100	0,270	0,240	1,000	0,910	0,000	1,240
KV0055	5,060	3,570	0,700	1,930	0,430	2,990	0,100	0,310	0,250	0,990	1,010	0,000	1,120
KV0056	4,660	3,360	0,680	1,880	0,400	2,730	0,100	0,290	0,230	1,020	0,920	0,000	1,280
KV0057	4,620	3,600	0,740	1,270	0,670	2,320	0,100	0,250	0,190	0,970	0,950	0,000	0,920
KV0059	3,240	2,330	0,650	1,900	0,430	2,790	0,100	0,290	0,230	0,920	0,910	0,000	1,200
KV0060	5,250	3,770	0,690	1,900	0,380	3,040	0,100	0,280	0,240	1,000	0,900	0,000	1,280

Appendix G: Metals analysed by ICP-MS

Table 9: Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Li7(LR)		Be9(LR)		B11(LR)		Se82(LR)		Se78(HR)		Y89(LR)		Zr90(LR)		Cd111(LR)		Cd114(LR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0001	0,351	1,6	0,0344	6,4	3,1	3,1	0,19	2,0	0,17	11,1	0,4574	3,7	0,485	5,4	0,112	7,2	0,1195	4,6
KV0002	0,106	9,1	0,0103	12,5	11,9	0,8	0,24	4,7	0,23	13,0	0,1383	1,2	0,289	2,8	0,137	6,4	0,1423	5,1
KV0003	0,262	3,0	0,0188	1,9	5,8	1,4	0,27	4,0	0,23	2,7	0,1786	0,3	0,308	3,7	0,264	4,1	0,2764	1,7
KV0004	0,130	3,0	0,0055	9,2	11,9	2,8	0,33	5,2	0,34	6,4	0,1142	3,1	0,244	0,8	0,085	3,7	0,0882	1,9
KV0005	0,166	2,8	0,0132	5,8	7,0	4,2	0,27	1,3	0,27	4,2	0,2564	4,7	0,236	2,2	0,047	7,1	0,0480	1,0
KV0006	1,072	4,6	0,0172	9,6	6,1	3,8	0,34	10,7	0,32	11,5	0,3302	3,4	0,508	1,9	0,050	7,8	0,0523	7,7
KV0007	0,953	1,4	0,0526	4,0	10,5	3,9	0,37	4,6	0,32	6,3	0,6906	3,8	0,718	1,6	0,273	1,9	0,2872	3,6
KV0008	0,179	1,0	0,0206	4,0	5,3	6,4	0,48	3,1	0,47	1,7	0,5095	1,4	0,524	4,7	0,041	4,2	0,0463	12,4
KV0009	0,327	5,1	0,0093	20,7	17,5	3,7	0,33	5,8	0,26	1,3	0,1360	2,0	0,159	1,5	0,190	6,0	0,1852	4,7
KV0010	1,512	5,3	0,0592	2,8	3,7	4,2	0,48	4,7	0,29	19,9	1,0086	3,8	1,214	5,2	9,336	2,5	9,6718	2,4
KV0011	0,024	3,7	0,0018	11,9	1,8	3,5	0,09	5,1	0,07	4,6	0,0231	0,1	0,194	4,3	0,025	9,3	0,0254	11,5
KV0012	0,061	2,6	0,0227	3,6	1,5	3,8	0,07	4,4	0,06	20,6	0,0205	0,7	0,205	3,8	0,018	5,8	0,0186	3,0
KV0013	0,116	0,3	0,0071	8,3	8,6	5,6	0,14	7,1	0,14	15,3	0,1040	3,7	0,153	3,7	0,013	15,2	0,0120	15,0
KV0014	0,001	8,1	0,0010	10,1	0,4	5,1	0,21	4,1	0,21	7,4	0,0013	1,9	0,010	4,3	0,001	5,5	0,0013	16,7
KV0015	0,405	5,4	0,0147	12,2	14,2	1,3	0,20	7,7	0,19	19,3	0,1654	3,1	0,247	2,0	0,067	3,9	0,0692	4,4
KV0016	0,025	4,4	0,0064	2,4	2,0	3,7	0,04	11,6	0,03	9,5	0,2004	3,8	0,056	4,3	0,006	26,9	0,0070	28,5
KV0017	0,031	3,1	0,0003	6,6	1,5	2,7	0,08	14,8	0,10	11,1	0,0177	4,9	0,038	9,4	0,089	7,1	0,0958	1,8
KV0018	1,086	4,6	0,1036	7,7	1,8	4,3	0,13	1,2	0,08	4,7	6,3037	4,4	2,230	4,5	0,023	9,8	0,0229	5,4
KV0019	0,054	5,2	0,0011	22,8	1,2	0,2	0,07	11,1	0,07	13,0	0,0563	4,5	0,073	3,0	0,029	10,8	0,0321	5,7
KV0020	0,485	7,1	0,0192	7,4	8,8	7,3	0,17	3,9	0,18	5,5	0,1781	2,3	0,359	3,3	0,022	20,2	0,0249	5,2
KV0021	0,410	6,6	0,0119	4,7	3,5	3,0	0,06	8,9	0,06	5,8	0,0694	1,2	0,106	3,8	0,542	2,1	0,5380	2,4
KV0022	0,090	3,3	0,0030	2,0	1,9	1,6	0,10	6,3	0,09	13,2	0,0274	2,6	0,074	3,0	0,025	14,2	0,0255	5,5
KV0023	0,400	1,8	0,0138	6,0	5,5	3,3	0,22	3,7	0,22	12,2	0,1576	2,4	0,173	1,9	0,140	7,1	0,1434	2,2
KV0024	0,176	1,6	0,0090	5,5	1,6	2,9	0,05	14,7	0,04	21,2	0,0456	4,1	0,082	2,6	0,030	10,4	0,0318	5,7
KV0025	0,182	4,0	0,0259	2,7	7,6	4,7	0,45	5,5	0,44	8,4	0,2328	5,8	0,241	4,2	0,117	4,1	0,1247	1,9
KV0026	0,157	3,1	0,0085	3,3	3,1	6,3	0,18	7,0	0,17	19,5	0,2222	4,4	0,169	3,7	0,125	7,6	0,1245	1,7
KV0027	0,017	2,2	0,0003	20,1	2,0	5,4	0,01	98,3	0,00	102,0	0,0004	24,5	0,003	5,5	0,002	14,3	0,0019	16,7
KV0028	1,979	1,5	0,0492	5,1	48,3	2,1	0,27	3,9	0,39	77,6	0,9861	1,1	2,143	4,0	0,386	2,4	0,3898	3,6

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Li7(LR)		Be9(LR)		B11(LR)		Se82(LR)		Se78(HR)		Y89(LR)		Zr90(LR)		Cd111(LR)		Cd114(LR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0029	0,715	4,3	0,0262	7,3	30,4	3,3	0,25	1,6	0,23	10,2	0,5271	5,8	1,042	4,4	0,073	4,8	0,0692	4,9
KV0030	2,299	2,5	0,0390	2,9	14,0	2,8	0,26	5,8	0,27	11,6	0,1966	4,2	0,579	1,2	2,770	1,3	2,7750	3,5
KV0031	0,134	5,8	0,0039	8,0	13,6	9,3	0,36	6,4	0,37	3,6	0,0496	0,6	0,097	1,3	0,165	3,0	0,1718	6,1
KV0032	0,175	6,2	0,0161	9,1	22,3	4,6	0,42	1,5	0,39	9,0	0,1250	2,2	0,368	0,4	0,111	2,7	0,1121	6,3
KV0033	0,119	2,7	0,0081	1,9	7,1	2,8	0,41	1,6	0,40	6,1	0,1556	1,2	0,399	2,4	0,011	13,1	0,0107	14,0
KV0034	2,105	5,8	0,0576	3,4	10,2	2,8	0,71	4,2	0,71	7,6	0,7527	4,5	1,643	9,0	0,921	3,2	0,9188	2,5
KV0035	0,115	2,8	0,0130	4,4	2,5	2,7	0,42	2,4	0,40	6,2	0,1493	2,8	0,152	1,4	0,092	2,7	0,1152	13,7
KV0036	0,094	6,3	0,0020	18,8	9,3	1,9	0,38	2,7	0,38	3,9	0,0325	6,4	0,117	8,0	0,012	6,3	0,0116	5,3
KV0037	0,308	4,8	0,0081	7,3	8,6	4,3	0,14	10,9	0,12	5,6	0,0864	0,2	0,134	2,8	0,023	9,0	0,0252	7,0
KV0038	0,264	3,4	0,0218	7,3	4,3	3,3	0,16	1,9	0,16	6,8	0,2689	1,6	0,421	3,0	0,097	2,7	0,0967	2,4
KV0039	1,903	1,5	0,0253	6,9	12,8	3,9	0,30	1,4	0,29	9,5	0,2928	1,1	0,578	2,9	0,118	6,9	0,1255	2,1
KV0040	0,300	4,8	0,0666	2,0	3,5	3,3	0,22	6,0	0,20	16,9	0,3786	1,3	0,260	9,5	0,022	13,9	0,0268	22,1
KV0041	0,216	3,3	0,0228	3,8	1,4	4,9	0,08	9,8	0,07	9,7	0,1240	1,1	0,618	0,8	0,051	1,9	0,0470	7,6
KV0042	0,065	5,9	0,0056	9,7	0,6	1,5	0,18	2,6	0,19	3,4	0,0179	4,9	0,024	4,6	0,012	1,9	0,0147	3,1
KV0043	0,410	6,3	0,0153	6,7	7,2	2,9	1,43	0,9	1,45	2,8	0,1986	3,5	0,460	5,9	0,152	6,4	0,1496	0,8
KV0044	0,704	2,5	0,0352	1,3	17,4	5,4	0,40	2,9	0,41	7,8	0,4754	2,2	0,594	3,8	0,089	0,9	0,0939	3,8
KV0045	0,443	1,7	0,0558	5,6	2,5	1,8	0,32	6,0	0,33	1,0	0,2408	6,8	0,367	3,7	0,181	1,4	0,1733	1,5
KV0046	0,169	1,2	0,0196	2,7	29,1	2,6	0,35	2,8	0,28	3,8	0,2814	6,0	0,192	3,4	0,165	2,2	0,1613	4,0
KV0047	0,084	6,3	0,0029	11,6	2,3	1,8	0,08	7,6	0,07	4,7	0,0842	4,7	0,511	1,4	0,004	21,7	0,0045	25,5
KV0048	0,067	2,6	0,0011	13,2	3,1	0,7	0,08	9,6	0,08	2,6	0,0306	2,4	0,039	5,3	0,005	9,4	0,0062	10,6
KV0049	0,710	5,0	0,0408	3,4	5,3	1,9	0,16	2,7	0,15	15,2	0,4458	3,7	0,923	6,1	0,008	16,0	0,0094	25,8
KV0050	0,151	1,0	0,0075	8,8	3,7	3,0	0,18	13,2	0,14	5,6	0,1947	3,0	1,042	0,3	0,013	14,9	0,0162	10,5
KV0051	0,328	5,9	0,0079	8,9	5,2	1,6	0,13	4,5	0,13	9,7	0,1611	4,9	0,099	4,3	0,007	4,9	0,0075	21,7
KV0052	0,268	7,6	0,0084	3,6	32,0	4,1	0,18	2,3	0,16	4,8	0,1743	5,7	0,194	2,3	0,092	1,6	0,0977	3,1
KV0053	0,115	4,4	0,0008	40,2	2,7	1,3	0,01	340,3	0,03	23,0	0,0043	2,4	0,030	5,2	0,003	8,5	0,0023	18,2
KV0054	0,120	1,7	0,0009	7,5	2,5	4,5	0,03	3,1	0,04	13,8	0,0050	1,9	0,017	1,6	0,002	21,0	0,0018	8,1
KV0055	0,131	7,5	0,0000	17,6	2,8	4,1	0,03	10,3	0,03	12,3	0,0059	5,5	0,020	7,5	0,002	22,7	0,0021	25,8
KV0056	0,288	4,4	0,0031	6,5	4,0	5,9	0,06	21,1	0,04	13,9	0,2202	2,7	0,068	2,5	0,004	8,0	0,0042	13,5
KV0057	0,203	3,1	0,0020	24,3	3,7	4,5	0,08	3,4	0,07	12,8	0,0332	1,2	0,055	2,7	0,005	9,1	0,0039	18,1

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Li7(LR)		Be9(LR)		B11(LR)		Se82(LR)		Se78(HR)		Y89(LR)		Zr90(LR)		Cd111(LR)		Cd114(LR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0059	1,740	8,3	0,0029	16,5	7,7	1,8	0,06	4,6	0,04	3,1	0,0701	6,2	0,113	3,0	0,004	7,4	0,0057	12,3
KV0060	0,203	5,5	0,0050	15,8	4,0	6,1	0,05	16,4	0,03	18,3	0,1122	4,0	0,104	3,2	0,004	16,5	0,0044	24,3
KV0061	0,000	8,1	0,0005	6,6	0,5	5,0	0,01	19,2	0,01	59,7	0,0011	6,2	0,004	3,9	0,000	42,5	0,0010	65,4
KV0062	0,000	14,0	-0,0001	9,7	0,3	4,2	0,04	11,7	0,04	24,0	0,0007	13,1	0,003	2,2	0,000	14,3	0,0003	1,0
KV0063	0,000	4,9	0,0004	42,1	0,2	2,8	0,00	82,2	0,00	168,7	0,0002	4,4	0,000	2,4	0,000	68,0	0,0001	195,2
KV0064	-0,001	6,2	0,0003	46,5	0,1	4,3	0,03	8,2	0,03	12,4	0,0003	8,2	0,000	10,6	0,000	11,1	0,0005	45,0
KV0065	-0,002	7,0	-0,0001	31,3	0,1	1,9	0,01	40,9	0,01	19,6	0,0003	10,4	-0,001	6,4	0,000	87,7	0,0001	104,2
KV0066	-0,001	7,3	0,0008	38,2	0,2	2,6	0,01	22,0	0,01	70,3	0,0013	4,9	0,010	1,5	0,000	87,0	0,0000	191,3
KV0067	-0,003	6,6	-0,0002	31,6	0,2	4,4	0,00	21,2	0,00	240,5	0,0002	19,2	-0,002	14,0	0,000	63,0	0,0005	63,0
KV0068	0,003	2,4	0,0004	21,0	0,1	1,7	0,02	10,8	0,02	29,0	0,0003	16,2	-0,001	5,0	0,000	116,7	0,0004	36,7
KV0069	-0,002	9,6	0,0003	18,9	0,1	1,8	0,00	34,4	0,00	152,9	0,0003	7,0	-0,001	3,1	0,000	37,8	0,0000	186,9
KV0070	0,007	4,7	0,0003	7,6	0,1	2,1	0,00	65,9	0,00	126,9	0,0012	9,0	0,006	3,9	0,001	10,5	0,0007	11,2
KV0071	0,017	2,2	0,0004	10,8	0,1	5,6	0,01	17,8	0,01	109,3	0,0011	5,8	0,006	1,3	0,001	46,5	0,0012	52,6
KV0072	0,004	2,8	0,0001	41,4	0,1	6,2	0,05	14,7	0,04	8,3	0,0012	8,1	0,007	8,1	0,001	19,9	0,0015	9,3
KV0073	-0,001	3,0	0,0005	43,4	0,0	6,2	0,01	38,7	0,00	62,1	0,0006	11,3	-0,001	7,7	0,000	40,4	0,0003	38,0
KV0074	0,003	8,7	0,0007	15,8	0,1	8,7	0,03	29,9	0,02	7,8	0,0014	9,6	0,001	4,7	0,001	37,3	0,0006	69,2
KV0075	0,002	2,1	0,0002	30,7	0,1	1,7	0,01	9,9	0,02	23,4	0,0019	6,0	0,003	10,0	0,001	20,5	0,0002	23,6
KV0076	-0,003	8,1	0,0007	33,8	0,0	3,0	0,04	6,7	0,06	20,8	0,0056	10,1	-0,001	11,5	0,001	5,6	0,0003	268,3
KV0077	0,003	2,0	0,0000	1,7	0,3	3,7	0,04	18,2	0,05	12,2	0,0006	12,3	0,000	5,7	0,001	16,7	0,0000	772,6
KV0078	0,000	6,8	-0,0003	30,3	0,0	2,9	0,01	31,5	0,01	28,0	0,0007	8,5	0,000	6,7	0,001	33,5	0,0003	172,0
KV0079	-0,002	5,4	0,0000	19,9	0,0	1,5	0,01	22,4	0,01	103,3	0,0006	10,8	-0,002	14,2	0,001	47,3	0,0006	21,2
KV0080	0,000	8,8	0,0000	31,0	0,0	3,6	0,01	31,4	0,00	139,3	0,0007	14,9	0,002	5,2	0,001	40,5	0,0001	137,7

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	**Mo98(MR)**		**In115(LR)**		**Sn118(LR)**		**Cs133(LR)**		**Ce140(LR)**		**Pr141(LR)**		**Nd146(LR)**		**Sm147(LR)**		**Tb159(LR)**	
	µg/g	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**
KV0001	0,750	1,9	0,0085	1,0	0,837	1,7	0,0636	1,6	2,8581	0,6	0,3784	4,1	1,5426	2,5	0,2734	0,9	0,0217	1,0
KV0002	8,454	3,0	0,0041	2,6	0,202	2,2	0,0145	4,2	0,4746	5,9	0,0592	5,1	0,2295	5,0	0,0378	2,9	0,0038	5,0
KV0003	0,808	0,6	0,0056	3,8	0,324	5,6	0,0557	3,8	1,8562	3,1	0,1698	2,2	0,5594	0,8	0,0689	3,0	0,0064	3,4
KV0004	0,968	1,0	0,0009	20,2	0,058	4,0	0,0118	8,3	0,9350	3,1	0,1419	2,7	0,3596	2,0	0,0415	5,3	0,0040	4,0
KV0005	0,831	1,7	0,0024	6,8	0,530	2,2	0,0235	4,1	0,7374	2,2	0,0884	2,0	0,3186	4,3	0,0525	3,9	0,0069	2,9
KV0006	1,394	3,2	0,0043	1,0	0,851	2,6	0,0380	5,2	3,8596	6,9	1,1341	4,6	3,4831	0,6	0,2472	1,4	0,0186	2,3
KV0007	45,867	2,2	0,0113	5,2	3,221	0,5	0,1248	0,3	5,4964	1,7	0,5839	4,1	2,1186	2,9	0,3280	6,7	0,0289	3,2
KV0008	3,512	2,9	0,0065	7,4	1,816	2,1	0,0311	4,3	4,4504	2,2	0,5054	1,6	1,8714	0,7	0,2960	3,4	0,0230	1,5
KV0009	0,673	3,3	0,0009	4,2	0,060	0,2	0,0418	2,7	0,3140	4,9	0,0412	3,5	0,1564	2,6	0,0324	5,3	0,0037	9,5
KV0010	0,621	2,0	0,0622	4,6	2,476	1,2	0,2480	1,2	3,6624	3,2	0,3988	1,2	1,4829	0,6	0,2576	1,5	0,0298	2,3
KV0011	0,330	6,1	0,0018	5,1	0,590	5,0	0,0044	7,2	0,1537	4,4	0,0169	3,8	0,0624	4,3	0,0095	12,6	0,0009	5,8
KV0012	3,232	0,3	0,0020	5,6	0,374	3,0	0,0063	1,7	0,2597	2,4	0,1256	2,0	0,1997	1,0	0,0097	5,6	0,0009	5,0
KV0013	0,422	3,8	0,0025	1,4	0,605	1,9	0,0158	2,8	0,3633	3,8	0,0446	3,0	0,1621	3,5	0,0268	4,3	0,0032	6,5
KV0014	0,263	6,3	0,0001	16,4	-0,003	5,5	0,0002	3,4	0,0049	4,8	0,0005	7,6	0,0018	10,0	0,0003	51,2	0,0001	53,5
KV0015	0,545	3,6	0,0076	5,5	0,881	6,3	0,0480	2,9	0,6212	2,2	0,0713	2,0	0,2644	1,3	0,0478	4,5	0,0053	3,0
KV0016	0,076	8,8	0,0007	8,5	0,238	3,8	0,0008	1,9	0,1226	3,3	0,0224	0,6	0,0911	2,9	0,0157	3,6	0,0030	2,3
KV0017	0,291	5,9	0,0026	7,7	0,728	2,9	0,0051	4,9	0,0679	3,4	0,0075	3,5	0,0270	8,4	0,0055	8,8	0,0006	28,4
KV0018	0,234	2,4	0,0068	1,0	0,213	1,8	0,1322	2,8	44,5732	2,6	5,8538	2,6	23,3359	3,1	4,2309	1,0	0,3210	0,1
KV0019	0,310	4,2	0,0022	6,2	0,646	0,4	0,0048	0,3	0,4185	5,8	0,0502	3,4	0,1821	6,1	0,0291	3,9	0,0023	9,2
KV0020	0,720	5,9	0,0147	5,6	0,376	0,7	0,0427	1,7	3,1694	3,4	0,5585	3,0	1,7458	0,9	0,0987	0,9	0,0094	6,3
KV0021	1,763	6,0	0,0026	2,6	0,152	3,5	0,0482	0,6	0,2640	0,7	0,0294	3,4	0,1172	2,0	0,0269	2,7	0,0024	2,1
KV0022	0,381	1,0	0,0025	3,7	0,628	1,3	0,0084	3,7	0,1526	3,8	0,0156	3,5	0,0610	4,6	0,0102	3,6	0,0011	5,5
KV0023	0,422	1,8	0,0012	2,7	0,130	0,9	0,0537	4,4	0,8379	2,3	0,0903	4,1	0,3071	5,9	0,0578	6,0	0,0055	4,7
KV0024	0,598	1,0	0,0024	1,6	0,213	2,5	0,0407	2,1	0,1642	2,1	0,0171	3,2	0,0625	6,2	0,0126	5,5	0,0014	2,3
KV0025	4,336	1,0	0,0030	3,4	0,558	2,3	0,0262	1,4	0,5088	3,6	0,0620	4,1	0,2568	1,4	0,0501	4,6	0,0068	1,9
KV0026	1,199	2,1	0,0028	2,3	0,527	2,3	0,0203	4,9	1,5709	3,2	0,1913	2,9	0,6507	4,1	0,0933	1,6	0,0085	3,1
KV0027	0,014	17,2	0,0000	38,9	-0,014	5,4	0,0012	4,6	0,0009	18,2	0,0001	18,2	0,0003	43,4	0,0000	106,4	0,0000	60,9
KV0028	1,972	5,2	0,0043	7,8	0,975	3,6	0,1366	1,7	13,7268	2,2	3,8262	1,2	7,9189	0,6	0,5448	3,2	0,0434	2,0
KV0029	0,276	0,3	0,0013	5,3	0,086	4,5	0,0188	0,3	0,7855	2,7	0,0963	3,4	0,3957	4,3	0,0778	5,3	0,0076	1,7
KV0030	5,706	2,3	0,0552	2,2	0,885	3,8	0,0401	5,6	1,6142	1,8	0,2620	3,7	0,8706	2,4	0,0877	3,2	0,0078	4,6
KV0031	0,425	4,0	0,0008	7,0	0,118	1,9	0,0064	4,8	0,1612	2,7	0,0162	2,5	0,0589	3,2	0,0121	0,8	0,0023	6,2
KV0032	3,344	4,3	0,0033	6,4	0,919	2,0	0,0222	4,2	0,6156	3,9	0,0662	4,5	0,2267	4,2	0,0360	4,3	0,0039	5,3
KV0033	2,118	2,2	0,0021	4,2	0,294	1,0	0,0090	2,8	0,8566	3,2	0,1790	1,6	0,5013	2,1	0,0441	5,7	0,0045	8,1
KV0034	0,359	3,6	0,0035	2,0	0,222	1,5	0,2406	3,7	7,3700	3,7	0,7464	2,3	2,4447	1,3	0,3463	3,7	0,0315	2,1
KV0035	2,768	2,8	0,0244	2,0	10,237	6,0	0,0248	4,1	0,3052	2,7	0,0417	1,8	0,1610	2,7	0,0286	5,5	0,0040	3,7

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Mo98(MR)		In115(LR)		Sn118(LR)		Cs133(LR)		Ce140(LR)		Pr141(LR)		Nd146(LR)		Sm147(LR)		Tb159(LR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0036	0,342	1,9	0,0007	3,0	0,119	2,0	0,0023	1,8	0,0599	2,0	0,0074	2,7	0,0306	0,7	0,0067	5,5	0,0011	3,7
KV0037	0,736	4,3	0,0018	3,1	0,335	0,8	0,0215	2,9	2,0303	2,8	0,3794	3,3	1,0503	2,9	0,0437	4,2	0,0052	1,3
KV0038	0,162	4,3	0,0014	11,6	0,279	3,8	0,0181	2,0	0,6726	1,9	0,0764	0,9	0,2725	3,3	0,0509	1,7	0,0079	2,7
KV0039	2,216	3,9	0,0044	3,8	0,622	3,8	0,0501	1,1	2,8085	2,6	1,5601	3,3	2,4081	5,8	0,1436	2,4	0,0150	4,1
KV0040	1,089	4,4	0,0058	7,0	1,562	7,2	0,0379	1,3	0,4796	0,3	0,0569	0,6	0,2350	2,5	0,0542	1,3	0,0098	4,2
KV0041	0,448	1,6	0,0037	3,7	0,941	2,2	0,0232	2,2	6,6180	2,1	0,7091	1,2	2,1106	1,5	0,1688	4,7	0,0097	2,5
KV0042	0,239	0,5	0,0003	18,2	0,039	2,8	0,0010	4,1	0,1059	2,2	0,0111	1,1	0,0369	7,1	0,0059	3,7	0,0006	21,5
KV0043	0,617	2,7	0,0016	14,1	0,114	2,4	0,0545	1,0	2,4431	1,4	0,2373	2,4	0,8088	0,6	0,1047	1,2	0,0088	5,8
KV0044	0,294	5,4	0,0045	3,3	0,713	3,3	0,0718	4,4	1,3025	6,3	0,1443	1,6	0,5706	1,1	0,1077	0,5	0,0142	2,0
KV0045	1,500	2,7	0,0019	7,7	0,144	2,3	0,0464	4,1	5,2911	5,5	1,2290	5,1	1,9425	1,5	0,2647	2,6	0,0163	3,6
KV0046	1,572	0,1	0,0012	5,9	0,080	2,7	0,0184	5,9	0,6716	2,8	0,0948	2,9	0,2969	1,3	0,0637	4,3	0,0070	7,6
KV0047	0,479	4,1	0,0004	10,8	0,047	4,6	0,0055	3,3	0,2286	2,1	0,0261	3,0	0,0952	1,4	0,0175	2,6	0,0026	0,6
KV0048	0,446	17,5	0,0001	22,3	-0,008	3,9	0,0026	9,1	0,0626	6,3	0,0095	2,1	0,0335	1,8	0,0068	9,9	0,0011	6,6
KV0049	0,638	3,0	0,0028	5,8	0,568	2,0	0,1104	0,7	1,5772	1,5	0,1830	2,5	0,6675	1,9	0,1244	3,9	0,0167	3,0
KV0050	1,404	1,1	0,0021	12,1	0,506	4,6	0,0138	5,5	0,3919	2,5	0,0480	3,6	0,1829	2,7	0,0398	7,6	0,0062	6,2
KV0051	0,498	1,3	0,0007	12,0	0,058	4,9	0,0082	7,3	0,2876	3,1	0,0384	2,5	0,1554	2,2	0,0345	1,8	0,0052	3,0
KV0052	0,590	8,0	0,0010	7,9	0,079	4,5	0,0131	5,7	0,3105	0,4	0,0422	2,6	0,1563	5,3	0,0321	2,5	0,0049	7,9
KV0053	0,161	3,0	0,0005	11,1	0,040	5,2	0,0008	4,1	0,0455	3,5	0,0065	4,1	0,0113	1,8	0,0016	15,8	0,0002	4,8
KV0054	0,144	3,9	0,0003	14,7	0,028	2,9	0,0008	10,7	0,0462	2,6	0,0060	6,3	0,0117	6,6	0,0021	5,7	0,0002	22,2
KV0055	0,142	10,0	0,0004	9,1	0,110	2,5	0,0010	2,9	0,0645	4,0	0,0079	4,1	0,0198	6,9	0,0027	14,6	0,0002	20,2
KV0056	0,202	3,0	0,0005	2,4	0,073	1,0	0,0065	6,0	0,1694	3,4	0,0242	4,2	0,0921	5,7	0,0264	1,1	0,0060	7,9
KV0057	0,227	3,7	0,0005	13,7	0,055	4,8	0,0062	5,5	0,1683	2,3	0,0210	3,1	0,0624	4,1	0,0108	6,3	0,0012	9,3
KV0059	0,685	4,4	0,0005	2,0	0,077	0,6	0,0062	6,7	0,2736	6,5	0,0411	2,6	0,1356	0,9	0,0239	4,5	0,0025	6,7
KV0060	0,158	4,1	0,0005	7,3	0,026	6,2	0,0102	4,4	0,2789	1,7	0,0420	2,0	0,1559	4,1	0,0307	4,0	0,0038	9,7
KV0061	0,004	10,8	0,0001	24,0	0,038	1,7	0,0001	27,0	0,0010	4,4	0,0002	18,5	0,0007	46,7	0,0001	31,2	0,0000	38,2
KV0062	0,005	7,8	0,0000	14,6	-0,005	6,4	0,0000	30,4	0,0002	9,8	0,0001	46,1	0,0004	17,2	0,0000	64,6	0,0000	103,6
KV0063	0,001	51,5	0,0001	38,2	-0,008	6,9	0,0001	19,8	-0,0003	19,2	0,0000	9,1	0,0002	36,7	0,0000	91,7	0,0000	84,8
KV0064	0,010	14,3	0,0001	7,1	-0,004	1,9	0,0002	4,8	-0,0002	11,7	0,0000	26,5	0,0002	24,0	0,0000	45,8	0,0000	34,7
KV0065	0,003	40,0	0,0000	26,8	-0,015	6,0	0,0010	2,7	0,0002	9,8	0,0000	13,2	0,0002	16,2	0,0000	37,8	0,0000	64,4
KV0066	0,002	36,3	0,0000	16,9	-0,018	5,9	0,4435	3,2	0,0020	6,5	0,0002	23,0	0,0012	36,7	0,0002	21,3	0,0000	47,8
KV0067	0,002	42,2	0,0003	14,5	0,110	2,0	0,0031	2,3	-0,0004	17,5	0,0000	30,0	0,0002	40,2	0,0002	64,0	0,0000	87,4
KV0068	0,003	43,1	0,0001	15,1	-0,013	4,9	0,0002	12,7	-0,0003	12,2	0,0000	28,0	0,0002	31,2	0,0001	96,8	0,0000	48,1
KV0069	0,001	53,2	0,0000	18,7	-0,021	1,2	0,0000	10,0	-0,0002	12,1	0,0000	33,0	0,0001	106,4	0,0000	135,8	0,0000	34,7
KV0070	0,012	6,3	0,0001	21,1	0,001	8,3	0,2162	1,0	0,0010	7,2	0,0002	16,5	0,0007	19,2	0,0001	37,7	0,0000	34,2
KV0071	0,012	18,7	0,0001	18,5	0,002	8,9	0,0003	2,9	0,0010	2,6	0,0002	11,8	0,0006	14,9	0,0002	44,2	0,0000	23,1

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Mo98(MR)		In115(LR)		Sn118(LR)		Cs133(LR)		Ce140(LR)		Pr141(LR)		Nd146(LR)		Sm147(LR)		Tb159(LR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0072	0,584	2,8	0,0004	8,4	0,003	1,5	0,0001	4,9	0,0006	3,3	0,0001	29,3	0,0005	14,5	0,0002	37,9	0,0000	51,9
KV0073	0,004	16,1	0,0000	27,4	-0,018	3,4	0,3122	1,3	0,0001	18,5	0,0001	22,7	0,0003	33,9	0,0002	47,7	0,0000	86,8
KV0074	0,010	28,3	0,0001	24,7	-0,012	11,7	0,0008	4,1	0,0004	14,1	0,0001	6,4	0,0005	31,3	0,0002	55,0	0,0001	51,3
KV0075	0,016	20,1	0,0001	29,5	0,002	5,4	0,0228	1,1	0,0031	4,0	0,0005	2,0	0,0020	42,3	0,0005	32,0	0,0001	27,2
KV0076	0,015	23,7	0,0001	12,1	0,012	0,8	0,0001	16,5	0,0168	2,1	0,0024	1,8	0,0128	15,9	0,0033	3,5	0,0004	16,8
KV0077	0,018	8,2	0,0003	16,6	0,085	6,9	0,0001	25,3	-0,0002	21,2	0,0000	13,6	0,0002	9,8	0,0002	58,8	0,0000	31,1
KV0078	0,020	6,1	0,0003	27,7	0,101	2,6	0,0001	35,2	-0,0001	24,5	0,0001	22,8	0,0003	13,1	0,0002	16,2	0,0000	33,2
KV0079	0,008	8,4	0,0003	20,9	0,141	2,0	0,0000	55,0	-0,0003	18,3	0,0000	46,9	0,0002	39,7	0,0001	65,3	0,0000	60,9
KV0080	0,031	10,2	0,0002	21,7	0,061	2,2	0,0001	20,1	-0,0001	16,7	0,0000	25,6	0,0003	37,1	0,0001	27,0	0,0000	18,8

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Dy163(LR)		Ho165(LR)		Er166(LR)		Tm169(LR)		Yb172(LR)		Lu175(LR)		Ta181(LR)		Hf178(LR)		Ir193(LR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0001	0,0999	1,6	0,0179	1,9	0,0465	5,2	0,0062	0,4	0,0373	2,4	0,0053	4,5	0,0023	6,0	0,0169	0,9	0,0000	62,4
KV0002	0,0199	4,1	0,0041	6,0	0,0131	2,2	0,0017	6,2	0,0104	12,4	0,0018	12,9	0,0011	10,4	0,0116	8,7	0,0001	104,9
KV0003	0,0320	1,8	0,0061	5,3	0,0176	8,8	0,0024	10,1	0,0156	10,3	0,0022	2,9	0,0004	9,1	0,0089	11,4	0,0000	81,8
KV0004	0,0184	6,2	0,0039	8,5	0,0113	9,2	0,0017	11,0	0,0105	4,3	0,0016	14,9	-0,0001	19,4	0,0065	13,6	0,0000	99,0
KV0005	0,0408	4,6	0,0081	2,1	0,0238	4,8	0,0033	4,1	0,0185	5,9	0,0029	2,3	-0,0004	14,0	0,0071	11,0	0,0000	91,7
KV0006	0,0750	1,0	0,0126	0,7	0,0351	6,9	0,0043	3,7	0,0278	1,7	0,0038	7,7	0,0023	16,7	0,0163	3,6	0,0000	66,8
KV0007	0,1371	2,7	0,0257	3,5	0,0705	2,2	0,0097	3,2	0,0605	3,4	0,0089	5,3	0,0011	25,5	0,0273	3,5	0,0000	28,2
KV0008	0,1055	1,6	0,0179	4,6	0,0519	5,6	0,0073	5,5	0,0478	3,9	0,0068	4,5	0,0014	3,0	0,0212	3,9	0,0000	55,1
KV0009	0,0232	3,9	0,0045	13,1	0,0125	3,7	0,0017	4,6	0,0112	6,6	0,0017	12,0	-0,0007	11,1	0,0076	2,8	0,0000	46,4
KV0010	0,1584	6,4	0,0306	3,9	0,0889	2,3	0,0128	3,7	0,0768	2,7	0,0111	6,9	0,0007	2,6	0,0415	3,6	0,0000	45,9
KV0011	0,0048	6,6	0,0010	7,3	0,0021	15,7	0,0003	9,7	0,0020	5,9	0,0003	26,1	-0,0005	34,2	0,0048	12,9	0,0000	91,7
KV0012	0,0043	7,9	0,0008	6,3	0,0024	9,6	0,0003	20,3	0,0019	20,6	0,0003	18,7	0,0103	7,2	0,0052	3,1	0,0000	40,1
KV0013	0,0169	2,9	0,0035	9,3	0,0101	1,7	0,0014	3,3	0,0084	9,2	0,0013	10,5	-0,0001	11,2	0,0044	10,3	0,0001	46,8
KV0014	0,0003	26,7	0,0001	10,9	0,0002	52,1	0,0000	90,4	0,0001	57,4	0,0000	35,9	-0,0006	14,5	0,0004	10,8	0,0000	173,2
KV0015	0,0294	4,4	0,0056	4,4	0,0154	0,7	0,0021	6,8	0,0124	5,7	0,0019	11,0	0,0010	25,6	0,0086	4,5	0,0000	25,0
KV0016	0,0192	4,8	0,0045	7,2	0,0139	8,3	0,0021	4,2	0,0127	8,0	0,0019	3,2	-0,0004	5,1	0,0015	10,4	0,0000	96,6
KV0017	0,0037	6,1	0,0007	16,6	0,0022	3,5	0,0003	9,4	0,0018	6,9	0,0002	11,2	-0,0005	18,5	0,0011	7,9	0,0000	173,2
KV0018	1,4464	2,3	0,2415	2,2	0,6373	3,0	0,0851	2,1	0,5434	3,4	0,0718	2,2	0,0024	8,9	0,1225	0,6	0,0001	48,8
KV0019	0,0125	1,7	0,0022	1,3	0,0052	14,1	0,0008	9,4	0,0045	10,2	0,0011	57,7	0,0000	22,0	0,0035	16,2	0,0000	87,0
KV0020	0,0393	3,9	0,0069	2,9	0,0210	3,7	0,0026	11,5	0,0153	4,1	0,0022	4,7	0,0002	12,4	0,0132	4,0	0,0000	60,6

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Dy163(LR)		Ho165(LR)		Er166(LR)		Tm169(LR)		Yb172(LR)		Lu175(LR)		Ta181(LR)		Hf178(LR)		Ir193(LR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0021	0,0129	5,9	0,0025	6,9	0,0060	7,7	0,0008	16,0	0,0052	5,8	0,0008	12,5	-0,0001	9,6	0,0064	5,8	0,0000	43,3
KV0022	0,0054	1,0	0,0011	5,6	0,0026	8,8	0,0004	17,1	0,0025	10,8	0,0004	28,3	-0,0002	6,2	0,0022	7,5	0,0000	91,7
KV0023	0,0278	3,3	0,0050	4,1	0,0134	5,6	0,0020	2,8	0,0118	4,6	0,0019	6,1	0,0006	13,2	0,0103	4,8	0,0000	24,9
KV0024	0,0081	2,3	0,0014	3,9	0,0038	2,6	0,0005	8,2	0,0030	2,0	0,0005	5,8	0,0004	14,4	0,0048	8,3	0,0000	87,7
KV0025	0,0417	3,4	0,0082	3,3	0,0234	3,3	0,0034	12,9	0,0214	1,7	0,0035	3,4	0,0001	9,4	0,0084	6,3	0,0000	50,0
KV0026	0,0420	3,7	0,0084	2,0	0,0242	3,4	0,0032	3,8	0,0200	2,8	0,0030	4,2	0,0005	6,6	0,0056	3,0	0,0000	100,0
KV0027	0,0001	28,2	0,0000	4,5	0,0001	31,1	0,0000	70,4	0,0000	132,3	0,0000	107,9	-0,0006	49,7	0,0000	39,0	0,0000	173,2
KV0028	0,1789	4,1	0,0332	4,8	0,1027	0,1	0,0132	2,8	0,0807	3,1	0,0123	0,6	-0,0001	8,4	0,0486	6,3	0,0000	9,6
KV0029	0,0392	3,3	0,0077	4,8	0,0214	5,2	0,0028	5,9	0,0157	7,2	0,0020	1,9	0,0007	1,8	0,0103	7,5	0,0000	25,8
KV0030	0,0373	3,0	0,0071	4,4	0,0220	3,6	0,0027	4,1	0,0174	5,3	0,0028	4,6	0,0050	7,0	0,0190	6,2	0,0000	48,5
KV0031	0,0098	8,1	0,0023	1,9	0,0053	2,9	0,0014	6,2	0,0048	18,1	0,0015	4,4	-0,0001	12,6	0,0023	23,5	0,0000	173,2
KV0032	0,0214	11,5	0,0043	9,8	0,0126	1,4	0,0017	7,7	0,0108	5,3	0,0017	6,7	0,0000	17,3	0,0092	3,9	0,0000	71,0
KV0033	0,0214	3,2	0,0044	0,2	0,0135	4,3	0,0016	3,9	0,0102	9,2	0,0016	2,8	0,0002	4,5	0,0063	4,2	0,0000	35,3
KV0034	0,1551	2,4	0,0292	2,5	0,0831	3,7	0,0102	2,5	0,0629	3,8	0,0092	1,3	-0,0003	22,8	0,0423	3,2	0,0000	22,9
KV0035	0,0222	4,4	0,0046	4,3	0,0124	7,9	0,0018	2,7	0,0102	1,5	0,0015	9,0	-0,0002	13,6	0,0041	10,9	0,0000	33,3
KV0036	0,0067	5,9	0,0013	3,0	0,0033	7,6	0,0005	0,5	0,0030	13,3	0,0005	10,9	-0,0003	28,2	0,0031	11,8	0,0000	173,2
KV0037	0,0191	2,0	0,0031	2,7	0,0093	5,5	0,0010	14,5	0,0056	5,7	0,0009	6,3	0,0002	9,2	0,0034	17,8	0,0000	107,9
KV0038	0,0467	3,6	0,0092	0,5	0,0265	3,1	0,0036	7,1	0,0220	8,6	0,0033	3,8	0,0027	5,1	0,0171	2,0	0,0001	71,1
KV0039	0,0641	0,7	0,0116	0,4	0,0338	3,0	0,0040	4,7	0,0236	3,2	0,0034	6,5	0,0009	38,8	0,0187	0,3	0,0000	41,9
KV0040	0,0598	3,2	0,0125	5,0	0,0356	3,2	0,0045	2,9	0,0273	4,5	0,0038	2,1	0,0013	35,9	0,0069	5,6	0,0000	89,2
KV0041	0,0283	6,0	0,0048	7,9	0,0153	3,7	0,0015	9,6	0,0088	8,7	0,0015	4,2	-0,0004	36,7	0,0171	4,7	0,0001	90,0
KV0042	0,0026	7,2	0,0006	10,2	0,0017	20,1	0,0002	13,5	0,0013	17,3	0,0002	18,4	0,0051	5,2	0,0006	17,7	0,0000	110,2
KV0043	0,0389	1,4	0,0069	2,0	0,0199	2,7	0,0028	6,6	0,0161	4,5	0,0025	0,5	0,0009	4,2	0,0128	6,3	0,0000	91,7
KV0044	0,0795	3,3	0,0166	5,2	0,0485	1,9	0,0061	3,6	0,0375	3,1	0,0058	7,2	0,0009	9,6	0,0175	4,3	0,0000	46,6
KV0045	0,0549	3,0	0,0092	3,9	0,0247	3,0	0,0030	7,4	0,0211	8,1	0,0028	8,2	0,0008	8,2	0,0124	9,6	0,0000	88,2
KV0046	0,0403	8,2	0,0087	2,1	0,0253	5,9	0,0033	6,2	0,0198	8,0	0,0034	9,2	0,0012	2,9	0,0054	6,8	0,0000	89,2
KV0047	0,0152	2,9	0,0032	9,5	0,0098	6,5	0,0015	6,9	0,0087	7,4	0,0014	11,7	-0,0001	15,8	0,0128	2,5	0,0000	50,9
KV0048	0,0055	2,7	0,0011	14,5	0,0030	19,6	0,0005	18,6	0,0029	15,1	0,0005	8,0	-0,0006	20,3	0,0008	18,4	0,0000	89,2
KV0049	0,0887	1,2	0,0171	3,0	0,0494	3,5	0,0068	4,9	0,0423	1,1	0,0062	8,6	0,0024	5,0	0,0306	5,1	0,0000	66,6
KV0050	0,0358	3,3	0,0073	4,4	0,0229	4,5	0,0033	3,1	0,0212	3,5	0,0034	6,2	0,0074	7,9	0,0380	6,6	0,0000	56,8
KV0051	0,0298	6,5	0,0062	4,1	0,0189	5,7	0,0024	1,2	0,0157	1,2	0,0023	2,5	0,0000	21,5	0,0038	8,5	0,0000	56,8
KV0052	0,0270	3,1	0,0060	3,0	0,0179	5,4	0,0025	5,6	0,0144	1,5	0,0023	4,0	0,0003	31,2	0,0044	10,9	0,0000	104,1
KV0053	0,0008	2,7	0,0001	20,0	0,0005	7,1	0,0001	55,4	0,0004	25,2	0,0001	15,2	-0,0004	11,7	0,0011	5,0	0,0000	56,8
KV0054	0,0010	10,8	0,0002	12,5	0,0005	11,1	0,0001	18,3	0,0005	24,1	0,0001	23,8	-0,0003	39,7	0,0006	40,2	0,0000	173,2
KV0055	0,0012	17,2	0,0002	23,8	0,0008	7,8	0,0001	16,7	0,0005	33,0	0,0001	12,8	-0,0004	17,3	0,0006	22,4	0,0000	94,4

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	**Dy163(LR)**		**Ho165(LR)**		**Er166(LR)**		**Tm169(LR)**		**Yb172(LR)**		**Lu175(LR)**		**Ta181(LR)**		**Hf178(LR)**		**Ir193(LR)**	
	µg/g	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**
KV0056	0,0398	4,2	0,0085	8,5	0,0265	4,1	0,0035	5,0	0,0211	3,1	0,0031	3,9	0,0004	5,1	0,0030	11,0	0,0000	24,7
KV0057	0,0060	8,3	0,0012	18,4	0,0035	11,7	0,0005	2,6	0,0027	2,3	0,0005	14,2	-0,0003	20,0	0,0019	6,8	0,0000	173,2
KV0059	0,0148	5,5	0,0028	3,1	0,0085	6,9	0,0012	5,4	0,0066	3,8	0,0010	4,1	0,0002	12,4	0,0039	9,2	0,0000	173,2
KV0060	0,0214	1,7	0,0041	6,1	0,0120	8,3	0,0017	5,5	0,0094	7,4	0,0014	6,1	0,0004	6,6	0,0033	15,3	0,0000	43,3
KV0061	0,0002	21,1	0,0001	15,6	0,0001	31,8	0,0000	91,7	0,0001	42,1	0,0000	75,3	0,0007	7,5	0,0021	152,5	0,0000	116,9
KV0062	0,0001	48,3	0,0000	25,8	0,0001	62,3	0,0000	75,6	0,0001	81,0	0,0000	41,7	0,0034	10,2	0,0002	33,8	0,0000	173,2
KV0063	0,0000	50,1	0,0000	91,7	0,0001	134,7	0,0000	100,0	0,0000	86,6	0,0000	106,4	-0,0004	14,9	0,0002	33,3	0,0000	173,2
KV0064	0,0000	94,4	0,0000	45,9	0,0000	32,8	0,0000	52,1	0,0000	100,0	0,0000	100,0	-0,0002	23,7	0,0001	75,9	0,0000	91,7
KV0065	0,0000	25,8	0,0000	54,1	0,0001	74,5	0,0000	0,0	0,0000	173,2	0,0000	10,8	-0,0005	13,4	0,0000	0,0	0,0000	75,8
KV0066	0,0003	25,5	0,0001	40,4	0,0002	39,4	0,0000	37,5	0,0003	26,3	0,0000	16,3	0,0011	3,8	0,0004	29,2	0,0000	173,2
KV0067	0,0000	62,4	0,0001	80,9	0,0001	98,0	0,0000	28,9	0,0000	67,8	0,0000	43,5	-0,0005	15,0	0,0001	59,3	0,0000	69,3
KV0068	0,0000	70,4	0,0000	23,2	0,0000	173,2	0,0000	89,2	0,0000	94,4	0,0000	122,6	-0,0004	31,7	0,0001	33,4	0,0000	0,0
KV0069	0,0001	42,7	0,0000	20,5	0,0000	88,2	0,0000	91,7	0,0000	94,4	0,0000	173,2	-0,0004	29,8	0,0001	28,2	0,0000	173,2
KV0070	0,0002	44,2	0,0001	32,5	0,0001	76,5	0,0000	82,3	0,0002	7,8	0,0000	110,5	0,0020	5,7	0,0003	13,3	0,0000	106,4
KV0071	0,0001	24,7	0,0000	60,2	0,0002	69,5	0,0000	48,6	0,0001	14,2	0,0000	19,9	0,0006	5,6	0,0003	30,6	0,0000	87,7
KV0072	0,0003	30,3	0,0001	39,5	0,0002	32,5	0,0000	25,0	0,0001	48,4	0,0000	24,8	-0,0002	6,9	0,0001	57,8	0,0001	51,9
KV0073	0,0001	74,3	0,0001	43,5	0,0001	79,6	0,0000	89,2	0,0001	63,5	0,0000	93,9	-0,0004	18,9	0,0001	35,7	0,0000	86,6
KV0074	0,0002	25,0	0,0000	22,3	0,0002	45,8	0,0000	68,2	0,0001	35,3	0,0000	88,1	0,0000	15,2	0,0001	13,8	0,0000	173,2
KV0075	0,0003	43,1	0,0001	16,3	0,0001	45,3	0,0000	12,2	0,0002	32,0	0,0000	90,6	-0,0003	9,4	0,0001	51,2	0,0000	86,6
KV0076	0,0014	15,2	0,0001	13,2	0,0004	33,4	0,0000	18,6	0,0002	51,5	0,0000	88,2	-0,0009	2,4	0,0001	87,0	0,0001	96,1
KV0077	0,0002	56,8	0,0000	33,4	0,0001	57,1	0,0000	130,1	0,0000	122,6	0,0000	131,0	-0,0006	17,0	0,0001	63,0	0,0000	173,2
KV0078	0,0001	66,6	0,0000	51,3	0,0001	43,6	0,0000	29,4	0,0000	37,8	0,0000	86,6	-0,0007	30,9	0,0001	33,4	0,0000	0,0
KV0079	0,0001	65,6	0,0000	67,1	0,0000	116,9	0,0000	173,2	0,0000	173,2	0,0000	173,2	-0,0005	29,6	0,0000	77,9	0,0000	0,0
KV0080	0,0002	8,0	0,0000	28,6	0,0000	76,0	0,0000	40,0	0,0000	173,2	0,0000	114,1	-0,0005	21,4	0,0001	60,5	0,0000	0,0

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Pt195(LR)		Au197(LR)		W182(LR)		Hg202(LR)		Tl205(LR)		Pb208(LR)		Bi209(LR)		Th232(LR)		U238(LR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0001	0,0002	33,8	0,0013	7,2	0,033	2,6	0,108	1,4	0,0116	3,6	19,719	2,1	0,0435	1,6	0,1480	2,7	0,2533	0,4
KV0002	0,0002	100,0	0,0003	16,1	0,063	3,2	0,231	0,4	0,0213	2,9	10,352	3,6	0,0104	3,1	0,0718	3,8	0,1458	2,7
KV0003	0,0002	11,5	0,0009	4,7	0,124	0,9	0,178	1,0	0,0080	11,2	11,245	2,2	0,0294	4,9	0,0727	4,2	0,4939	2,0
KV0004	0,0004	40,8	0,0005	14,7	0,009	7,2	0,081	1,2	0,0024	1,6	1,276	1,7	0,0050	5,9	0,1137	4,8	0,4209	1,2
KV0005	0,0002	92,1	0,0006	12,5	0,024	9,0	0,053	6,2	0,0038	5,6	3,630	2,3	0,0144	3,5	0,0634	6,3	0,3120	2,8
KV0006	0,0004	37,5	0,0009	10,6	0,664	1,2	0,083	3,4	0,0091	4,8	48,975	2,6	0,0225	5,5	0,1297	3,2	0,4410	1,0
KV0007	0,0002	8,6	0,0014	19,7	0,288	1,7	0,110	1,6	0,0255	2,7	27,651	2,4	0,0306	3,0	0,4741	1,3	0,8251	1,7
KV0008	0,0004	30,1	0,0011	15,8	0,145	2,4	0,271	0,5	0,0059	4,0	11,162	4,0	0,0168	4,0	0,2990	4,0	0,7918	2,4
KV0009	0,0003	42,1	0,0016	10,9	55,934	4,3	-0,005	3,4	0,0132	4,5	21,048	1,2	0,0218	2,8	0,0287	1,7	0,4292	1,2
KV0010	0,0028	10,8	0,0086	7,5	0,216	2,0	0,339	1,4	0,0847	6,9	67,745	2,2	0,9989	3,8	0,3537	1,4	0,7754	1,1
KV0011	0,0002	70,4	0,0003	27,0	0,275	0,8	0,009	5,2	0,0016	8,9	1,361	2,8	0,0094	3,3	0,0078	2,5	0,0236	1,5
KV0012	0,0002	45,4	0,0003	24,1	0,141	2,4	0,035	1,7	0,0040	8,1	0,915	3,0	0,0032	9,0	0,0088	0,7	0,0283	0,5
KV0013	0,0002	20,4	0,0008	5,0	0,020	6,2	0,013	3,0	0,0032	9,1	1,785	3,1	0,0143	0,8	0,0359	3,0	0,2662	2,0
KV0014	0,0001	43,7	0,0003	12,2	0,008	0,5	0,000	1,5	0,0001	32,4	0,197	1,0	0,0182	2,2	0,0003	3,8	0,0004	22,3
KV0015	0,0002	7,2	0,0007	3,7	0,697	3,0	1,499	1,4	0,0090	8,8	40,315	0,8	0,0248	3,8	0,0499	2,6	0,1315	2,3
KV0016	0,0003	23,3	0,0001	52,2	0,006	1,8	0,001	7,7	0,0002	34,4	0,209	1,3	0,0020	2,2	0,0064	4,8	0,0293	1,9
KV0017	0,0001	41,8	0,0004	12,7	0,029	2,4	0,010	8,7	0,0012	16,2	1,716	2,1	0,0074	9,8	0,0055	2,3	0,0370	1,2
KV0018	0,0001	22,1	0,0003	36,8	0,015	9,1	0,013	4,0	0,0153	10,6	2,798	3,5	0,0207	2,9	3,5786	1,3	0,9782	0,5
KV0019	0,0002	11,6	0,0003	23,6	0,030	4,1	0,010	1,3	0,0014	11,4	1,332	1,7	0,0115	3,5	0,0549	3,2	0,0253	3,2
KV0020	0,0005	8,6	0,0003	24,2	0,038	3,7	0,058	0,6	0,0281	2,8	3,096	1,8	0,0568	1,6	0,0534	1,9	0,0621	1,3
KV0021	0,0001	87,7	0,0002	24,5	6,339	2,0	0,437	2,6	0,2180	4,3	9,607	3,1	0,0111	2,6	0,0243	0,6	0,0404	3,7
KV0022	0,0001	87,0	0,0003	8,4	0,043	2,0	0,018	2,2	0,0021	12,3	12,262	0,8	0,0124	5,2	0,0117	6,0	0,0678	1,4
KV0023	0,0006	42,1	0,0008	8,1	56,199	2,9	0,028	2,0	0,0389	1,9	37,741	0,4	0,0240	0,8	0,0754	1,6	0,1419	2,8
KV0024	0,0002	65,8	0,0003	17,9	5,714	2,4	0,348	1,2	0,2953	0,3	5,361	1,9	0,0094	1,4	0,0179	3,7	0,0142	4,3
KV0025	0,0002	28,6	0,0007	9,4	0,563	2,5	0,110	2,6	0,0082	2,6	4,748	1,2	0,0088	2,7	0,0446	1,6	0,9025	3,2
KV0026	0,0001	66,7	0,0005	18,4	0,337	4,1	0,161	1,7	0,0071	5,6	8,146	3,9	0,0070	2,2	0,1160	3,6	0,2277	3,6
KV0027	0,0000	53,9	0,0001	42,5	0,259	1,5	-0,001	5,9	0,0000	44,7	0,011	2,2	0,0001	10,1	0,0009	10,7	0,0030	4,8
KV0028	0,0026	5,1	0,0013	6,7	0,204	1,6	0,049	2,7	0,0444	2,1	8,441	0,9	0,0212	3,8	2,1304	3,1	1,3197	0,8
KV0029	0,0001	64,6	0,0003	13,3	0,141	0,6	0,009	5,7	0,0035	9,7	1,872	1,2	0,0067	4,0	0,1095	3,5	0,1066	2,4
KV0030	0,0011	27,5	0,0020	4,8	1,055	1,6	0,620	0,7	0,0862	2,1	39,127	2,9	0,1327	2,0	0,0528	3,5	0,0933	2,6
KV0031	0,0001	68,6	0,0016	5,4	0,063	4,5	0,032	4,4	0,0091	2,5	4,579	1,4	0,0064	4,8	0,0134	3,3	0,1736	2,0
KV0032	0,0004	12,6	0,0006	12,4	0,051	2,1	0,061	2,1	0,0140	4,7	3,922	2,5	0,0116	4,5	0,2055	3,1	0,4534	1,9
KV0033	0,0004	39,5	0,0002	41,8	0,091	5,4	0,008	2,8	0,0023	5,8	2,551	2,4	0,0049	5,6	0,0273	4,1	0,1097	1,7
KV0034	0,0003	26,9	0,0004	13,5	0,049	3,0	0,069	3,4	0,0299	3,8	7,039	1,7	0,0350	1,4	0,7966	1,8	0,6704	3,2
KV0035	0,0003	23,2	0,0021	13,7	0,124	1,2	0,317	1,5	0,0142	5,4	47,227	3,6	0,0887	2,4	0,0356	3,3	0,1315	3,9

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Pt195(LR)		Au197(LR)		W182(LR)		Hg202(LR)		Tl205(LR)		Pb208(LR)		Bi209(LR)		Th232(LR)		U238(LR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0036	0,0001	61,9	0,0003	24,4	0,076	1,4	0,022	3,4	0,0038	3,5	3,975	2,1	0,0059	6,2	0,0064	2,7	0,0319	4,7
KV0037	0,0004	5,0	0,0002	24,8	0,025	4,2	0,048	2,3	0,0074	4,2	1,934	3,8	0,0059	2,8	0,0575	3,8	0,2252	4,3
KV0038	0,0002	34,6	0,0004	9,1	3,965	2,1	0,056	1,3	0,0060	4,3	27,633	2,2	0,0128	3,2	0,1280	1,3	0,5042	0,8
KV0039	0,0017	12,8	0,0006	6,9	0,111	0,3	0,154	0,9	0,0566	3,7	6,807	3,0	0,0821	2,7	0,1046	1,8	0,1990	2,9
KV0040	0,0002	47,7	0,0005	31,7	0,049	3,9	0,099	1,7	0,0107	2,7	2,831	1,4	0,0102	4,8	0,0427	1,1	0,0546	1,7
KV0041	0,0001	62,0	0,0009	2,4	0,055	4,3	0,036	1,2	0,0069	0,6	4,665	1,4	0,0103	0,4	0,2969	2,1	0,0535	1,4
KV0042	0,0002	39,8	0,0099	2,6	0,071	4,6	0,012	4,1	0,0008	9,3	0,631	1,8	0,0127	1,4	0,0138	2,6	0,0446	3,0
KV0043	0,0000	88,2	0,0005	8,7	0,075	7,3	0,163	1,3	0,0152	7,5	6,095	3,6	0,0473	0,9	0,1349	4,8	0,6068	1,2
KV0044	0,0001	24,8	0,0003	9,8	0,054	3,4	0,064	1,5	0,0108	3,0	159,685	0,6	0,0561	2,6	0,1231	3,0	0,5400	4,7
KV0045	0,0009	42,7	0,0005	13,4	0,128	2,9	0,493	0,2	0,1255	1,0	15,329	1,8	0,0174	1,9	0,1039	1,5	0,0717	2,6
KV0046	0,0002	10,4	0,0006	11,9	0,397	3,4	0,623	0,2	0,0204	3,2	6,040	2,9	0,0414	2,3	0,0448	1,5	0,7847	3,0
KV0047	0,0001	67,9	0,0001	34,9	0,000	6,6	0,007	6,9	0,0021	7,1	0,116	2,6	0,0008	9,1	0,0191	3,8	0,0234	2,8
KV0048	0,0001	59,9	0,0005	15,1	0,004	4,1	0,005	9,6	0,0009	16,8	0,101	3,6	0,0010	4,5	0,0070	5,0	0,0293	3,3
KV0049	0,0002	69,5	0,0002	20,8	0,006	1,0	0,005	9,8	0,0120	4,7	0,662	2,6	0,0159	2,1	0,2466	1,0	0,0531	1,4
KV0050	0,0002	58,1	0,0004	21,2	0,017	3,5	0,007	6,2	0,0058	2,1	17,752	5,0	0,0081	9,4	0,0401	1,9	0,0298	1,0
KV0051	0,0002	48,2	0,0003	18,9	0,002	5,8	0,004	6,5	0,0035	3,8	0,236	1,6	0,0038	8,1	0,0248	4,0	0,0165	4,3
KV0052	0,0003	48,6	0,0009	14,4	0,017	3,4	0,009	7,8	0,0131	7,2	2,621	5,7	0,0073	4,8	0,0255	2,2	0,3349	0,7
KV0053	0,0002	16,9	0,0003	39,2	0,022	3,1	0,001	14,2	0,0005	16,3	1,672	0,7	0,0018	11,4	0,0014	5,8	0,0036	2,6
KV0054	0,0001	89,7	0,0002	36,0	0,000	2,8	0,003	14,9	0,0002	18,1	0,143	2,4	0,0030	9,7	0,0015	4,9	0,0027	4,0
KV0055	0,0001	53,7	0,0002	38,7	0,021	6,2	0,002	4,7	0,0005	30,8	0,162	1,0	0,0026	8,3	0,0018	7,7	0,0031	5,5
KV0056	0,0002	43,6	0,0003	25,1	0,063	5,8	0,005	6,1	0,0029	12,2	0,508	1,8	0,0063	8,1	0,0095	3,2	0,0118	2,5
KV0057	0,0001	43,3	0,0002	43,4	0,002	2,2	0,004	10,7	0,0031	7,1	0,459	2,8	0,0046	4,8	0,0112	4,0	0,0069	2,3
KV0059	0,0002	98,3	0,0003	21,1	0,003	2,6	0,006	4,3	0,0021	7,2	0,520	1,9	0,0149	3,7	0,0161	2,3	0,0321	1,8
KV0060	0,0001	64,6	0,0002	18,3	0,007	1,7	0,002	3,9	0,0021	8,8	0,317	2,6	0,0052	6,5	0,0140	6,7	0,0140	2,3
KV0061	0,0001	86,6	0,0001	43,7	0,002	4,1	0,001	8,6	0,0001	16,9	0,044	4,7	0,0005	16,9	0,0002	25,2	0,0002	23,1
KV0062	0,0000	94,4	0,0001	31,5	0,008	7,1	0,000	8,0	0,0000	55,0	0,075	2,3	0,0008	4,5	0,0001	10,8	0,0001	23,3
KV0063	0,0001	50,6	0,0001	43,6	-0,001	5,6	0,011	12,4	0,0000	173,2	0,007	3,4	0,0001	22,7	0,0002	28,5	0,0000	102,3
KV0064	0,0001	173,2	0,0001	43,9	-0,005	5,0	0,001	12,1	0,0000	36,7	0,013	2,3	0,0001	30,0	0,0001	12,4	0,0001	9,5
KV0065	0,0000	86,6	0,0001	13,5	-0,003	5,2	0,001	19,3	0,0000	97,9	0,000	3,8	0,0000	16,6	0,0001	14,8	0,0000	24,3
KV0066	0,0000	0,0	0,0001	13,4	0,001	2,3	0,000	22,7	0,0001	45,9	0,017	2,5	0,0004	5,0	0,0005	16,4	0,0004	20,4
KV0067	0,0000	91,7	0,0000	51,3	0,001	6,8	0,012	4,3	0,0000	173,2	-0,006	2,6	0,0000	23,0	0,0001	40,6	0,0000	33,0
KV0068	0,0001	126,3	0,0001	25,9	0,020	2,6	0,003	7,9	0,0006	23,4	0,019	5,4	0,0002	8,5	0,0000	17,6	0,0000	41,5
KV0069	0,0000	0,0	0,0000	114,6	0,001	8,7	0,001	22,2	0,0000	100,0	0,006	3,2	0,0001	37,3	0,0001	35,5	0,0001	6,4
KV0070	0,0000	124,9	0,0001	35,5	0,004	5,3	0,011	5,6	0,0001	12,5	0,165	1,7	0,0018	5,8	0,0001	6,7	0,0003	3,4
KV0071	0,0001	121,3	0,0001	33,9	0,000	3,3	0,004	11,9	0,0001	58,5	0,185	1,1	0,0016	11,1	0,0001	26,6	0,0007	12,0

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Pt195(LR)		Au197(LR)		W182(LR)		Hg202(LR)		Tl205(LR)		Pb208(LR)		Bi209(LR)		Th232(LR)		U238(LR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0072	0,0008	23,5	0,0002	48,1	0,017	3,5	0,000	3,5	0,0001	32,9	0,133	1,3	0,0009	7,9	0,0002	25,3	0,0004	10,4
KV0073	0,0001	25,8	0,0001	11,6	-0,001	3,8	0,007	1,4	0,0001	17,6	0,009	2,3	0,0003	8,5	0,0000	48,7	0,0001	35,3
KV0074	0,0000	86,6	0,0001	34,8	-0,002	9,9	0,001	8,0	0,0002	15,4	0,075	2,6	0,0011	4,2	0,0000	10,3	0,0002	15,1
KV0075	0,0001	94,4	0,0001	9,2	0,001	0,8	0,000	9,3	0,0002	63,1	0,029	5,5	0,0005	11,4	0,0004	5,7	0,0002	1,5
KV0076	0,0001	91,7	0,0000	37,8	-0,009	2,6	0,000	15,0	0,0001	24,7	0,015	4,2	0,0003	8,9	0,0017	7,1	0,0002	13,8
KV0077	0,0000	106,4	0,0001	54,6	-0,004	2,8	0,000	11,2	0,0001	58,8	0,015	3,7	0,0001	65,6	0,0001	12,6	0,0000	28,3
KV0078	0,0000	87,7	0,0000	70,8	-0,002	2,5	0,007	8,9	0,0001	51,4	0,025	2,3	0,0004	9,7	0,0000	33,2	0,0001	22,0
KV0079	0,0000	173,2	0,0001	36,7	-0,003	1,4	0,000	7,8	0,0000	131,0	0,102	2,1	0,0002	14,2	0,0001	3,8	0,0001	6,7
KV0080	0,0000	110,3	0,0000	47,5	-0,003	2,3	0,001	7,8	0,0000	49,5	0,064	2,7	0,0003	14,6	0,0001	28,0	0,0001	23,6

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Na23(MR)		Mg24(MR)		Al27(MR)		Si29(MR)		P31(MR)		S34(MR)		K39(MR)		Ca44(MR)		Sc45(MR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0001	227	2,9	378,66	3,5	465,9	3,9	960	1,6	119,9	1,6	15 114	2,0	225,6	2,1	1 081	2,4	0,195	2,9
KV0002	597	5,2	754,32	5,1	176,7	7,1	226	4,7	132,1	3,9	20 660	5,3	155,3	5,6	1 926	3,7	0,044	4,0
KV0003	420	1,6	701,14	2,4	441,0	1,4	625	4,3	286,8	2,1	14 437	1,1	200,4	4,1	1 374	2,3	0,077	4,1
KV0004	1 057	3,0	772,34	2,1	214,9	3,9	689	3,0	215,7	1,1	33 170	1,3	221,6	4,0	1 607	3,9	0,057	1,2
KV0005	1 111	5,2	1 087,40	3,5	239,8	4,7	750	2,0	158,9	3,2	22 154	4,0	264,7	5,7	1 860	2,8	0,059	5,2
KV0006	806	3,3	743,98	2,6	553,0	2,6	773	4,2	216,1	1,4	23 720	1,3	218,8	4,4	1 341	4,2	0,089	3,9
KV0007	944	2,8	1 165,97	2,6	1 515,3	3,6	2 322	0,9	309,2	1,9	28 277	2,3	385,8	2,2	2 351	5,4	0,329	3,8
KV0008	625	4,8	508,48	6,5	293,9	3,1	686	5,0	186,7	1,0	46 249	6,3	135,2	1,2	886	2,8	0,113	3,3
KV0009	5 079	1,9	1 507,68	3,8	221,5	0,8	417	5,4	221,8	0,9	12 431	1,6	419,8	1,8	3 034	4,7	0,051	5,1
KV0010	1 356	1,6	2 638,09	0,8	1 677,2	4,1	3 945	2,1	533,2	1,6	40 959	1,3	553,9	0,6	20 424	0,9	0,289	2,0
KV0011	70	3,3	36,52	2,2	48,3	5,9	118	3,2	18,6	2,1	18 793	2,8	20,2	3,5	32	1,9	0,012	15,4
KV0012	892	2,4	133,17	3,0	86,5	0,9	218	0,5	10,8	1,0	16 514	3,7	57,2	0,8	167	3,4	0,009	4,5
KV0013	1 939	4,0	412,80	3,8	186,3	4,6	396	5,2	69,5	0,7	6 173	3,9	182,2	1,9	594	5,7	0,037	1,1
KV0014	14	2,9	2,28	6,1	4,5	2,3	-91	6,7	0,6	3,7	28 647	2,1	9,5	0,8	10	1,5	0,000	18,2
KV0015	1 948	5,2	641,91	3,3	427,9	4,2	909	1,8	121,4	1,6	8 619	3,9	292,0	1,2	1 206	1,4	0,076	3,2
KV0016	43	3,3	112,24	3,0	17,8	1,2	-6	4,7	11,6	3,0	7 681	1,7	23,2	1,7	14 633	2,3	0,032	3,7
KV0017	108	2,3	42,14	4,2	56,5	5,4	179	2,7	36,3	1,0	14 369	1,0	23,6	4,8	30	1,9	0,010	22,4
KV0018	379	5,6	1 265,10	3,3	1 672,2	4,9	2 795	3,1	143,6	2,8	2 229	1,0	499,5	8,9	2 654	4,2	0,992	4,6
KV0019	845	4,3	160,37	3,3	50,2	1,5	121	4,0	16,2	2,1	13 851	3,7	72,0	2,7	103	2,6	0,010	12,7
KV0020	1 619	1,4	481,68	7,0	406,6	4,5	859	2,8	67,4	0,6	18 086	4,5	204,5	2,7	313	1,0	0,147	3,9
KV0021	560	1,2	188,53	3,1	146,1	1,9	462	3,3	49,1	2,5	6 542	2,6	85,2	1,5	417	7,4	0,033	5,4

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Na23(MR)		Mg24(MR)		Al27(MR)		Si29(MR)		P31(MR)		S34(MR)		K39(MR)		Ca44(MR)		Sc45(MR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0022	336	2,6	181,39	4,1	118,7	3,3	444	1,1	55,3	0,8	15 992	1,9	48,8	1,5	277	4,5	0,023	8,5
KV0023	1 606	3,6	436,97	1,9	274,0	3,7	727	2,3	157,0	1,8	11 904	1,2	290,1	3,4	721	4,8	0,062	1,6
KV0024	1 555	3,9	243,46	2,0	104,9	4,9	286	3,2	24,3	2,5	6 784	3,4	89,6	2,9	415	4,2	0,019	6,3
KV0025	1 906	3,9	1 074,27	2,2	403,4	2,6	802	4,0	178,5	0,9	52 902	1,3	264,0	1,8	1 929	1,0	0,289	1,4
KV0026	319	3,3	625,73	3,7	265,7	3,5	525	2,5	122,7	0,2	17 741	3,4	128,1	3,2	1 216	2,0	0,071	1,6
KV0027	2 108	3,1	2,42	3,2	-0,1	0,9	138	2,9	2 745,1	2,3	13	0,8	23,5	4,3	12	1,1	0,001	31,0
KV0028	3 716	2,5	2 025,20	2,6	1 662,4	4,7	2 968	1,6	570,2	1,2	17 024	3,3	944,1	5,4	20 519	1,1	0,239	4,5
KV0029	4 129	7,3	741,19	3,8	339,3	3,8	887	2,3	42,1	2,2	13 864	4,6	267,2	1,8	1 597	6,2	0,076	5,2
KV0030	2 464	3,4	766,34	5,0	399,1	3,3	1 429	3,9	138,0	1,8	13 727	0,6	213,6	5,2	1 601	2,2	0,078	6,7
KV0031	5 043	2,9	1 004,85	2,2	79,6	1,8	643	0,8	512,9	1,5	21 170	1,1	278,1	2,2	1 796	2,2	0,020	10,8
KV0032	1 642	5,6	711,32	3,3	314,9	4,5	581	4,5	134,6	3,2	48 875	0,7	219,1	1,8	1 601	2,1	0,051	4,0
KV0033	2 469	2,0	557,93	2,8	160,8	2,5	312	3,5	44,7	2,3	32 541	1,5	149,1	1,2	789	3,8	0,028	5,3
KV0034	660	2,7	1 374,63	5,7	1 766,7	5,9	3 214	4,3	3 078,4	0,4	11 953	3,9	1 061,8	2,5	24 381	2,6	0,425	3,9
KV0035	255	2,4	188,90	5,2	197,6	3,7	283	3,2	77,8	1,3	47 725	3,6	92,1	3,0	3 487	1,8	0,042	2,4
KV0036	4 678	2,3	659,77	3,5	71,1	2,5	423	4,1	30,0	0,9	24 939	0,8	189,4	3,6	314	2,8	0,017	1,4
KV0037	4 272	1,0	645,72	4,1	395,8	0,9	715	3,4	73,9	2,9	16 775	2,8	262,8	2,4	1 461	1,8	0,035	3,7
KV0038	587	1,0	239,00	3,3	492,8	2,4	1 170	5,7	136,0	1,4	8 594	3,6	282,0	1,9	2 045	1,8	0,047	7,0
KV0039	1 942	2,7	1 005,25	3,3	850,1	5,5	1 619	1,6	124,0	0,8	28 846	2,8	342,7	2,4	2 043	2,9	0,129	2,0
KV0040	883	0,1	297,76	2,8	400,5	5,6	852	3,3	33,4	1,1	22 865	1,4	123,7	0,2	467	2,7	0,075	3,1
KV0041	263	2,2	141,05	1,7	783,5	5,0	2 349	1,5	53,9	2,6	9 020	2,0	95,1	2,9	351	4,6	0,053	1,1
KV0042	195	6,5	88,10	3,1	33,0	5,5	-20	4,0	20,6	0,8	17 055	1,0	36,9	4,5	144	4,7	0,006	10,8
KV0043	3 622	1,2	2 483,93	6,0	460,5	5,7	830	4,0	5 923,5	0,6	9 178	1,1	5 857,1	3,9	1 919	6,1	0,102	6,4
KV0044	2 016	1,8	1 142,78	1,4	736,4	6,6	1 426	4,9	186,6	2,2	23 570	1,2	467,1	3,1	2 922	2,8	0,177	4,5
KV0045	894	2,2	199,97	3,8	1 395,5	3,8	1 438	4,0	85,5	1,9	27 908	3,0	254,2	4,2	8 634	6,8	0,051	1,9
KV0046	3 469	4,9	1 441,08	4,7	250,1	3,0	461	3,7	205,9	0,6	27 994	1,8	346,2	2,9	5 831	5,8	0,051	0,6
KV0047	3 339	6,3	444,11	0,8	77,4	5,4	65	1,4	8,3	2,8	10 804	0,7	159,0	2,3	280	0,8	0,022	1,2
KV0048	3 352	2,8	427,51	1,0	40,1	2,9	-147	0,6	8,1	2,7	10 156	3,1	128,8	4,2	194	2,1	0,006	15,5
KV0049	2 713	4,5	713,19	2,9	928,7	3,1	1 723	3,8	51,8	1,9	17 057	1,8	535,1	2,5	850	6,0	0,235	5,8
KV0050	4 208	1,4	584,62	3,3	182,6	5,8	330	2,5	36,4	1,1	25 865	3,8	248,4	0,5	830	4,1	0,051	5,8
KV0051	4 291	4,3	777,70	3,4	230,3	3,7	411	2,7	35,1	2,3	15 564	1,8	273,8	3,9	570	1,5	0,070	5,4
KV0052	11 392	6,9	2 028,70	1,6	136,4	0,9	259	4,3	199,5	1,8	17 926	1,7	644,8	2,6	3 459	5,3	0,032	5,1
KV0053	7 023	2,4	792,82	7,8	270,0	3,5	-54	3,9	1,2	1,4	12 719	2,9	254,5	1,2	310	2,5	0,002	20,6
KV0054	6 459	4,1	776,68	5,5	57,0	4,5	8	3,4	1,1	2,7	11 305	3,9	230,9	3,8	287	3,7	0,002	5,1
KV0055	6 685	0,9	861,49	5,2	109,0	3,5	87	3,6	1,7	4,3	10 725	5,0	262,5	0,4	294	7,5	0,003	8,4

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Na23(MR)		Mg24(MR)		Al27(MR)		Si29(MR)		P31(MR)		S34(MR)		K39(MR)		Ca44(MR)		Sc45(MR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0056	6 888	2,7	918,52	3,1	315,8	5,1	521	2,0	60,5	2,8	11 138	3,1	411,8	4,3	643	2,8	0,049	6,8
KV0057	7 703	6,0	983,61	1,9	147,8	4,1	249	2,2	8,4	4,2	11 220	0,6	303,0	4,3	848	2,3	0,015	3,6
KV0059	6 593	3,3	900,83	0,7	567,7	2,5	194	6,5	21,9	4,0	9 756	1,2	364,6	3,0	418	5,4	0,021	3,5
KV0060	6 113	2,1	865,78	3,5	645,5	5,1	516	7,2	12,8	2,3	8 592	0,9	329,9	4,7	2 591	4,3	0,065	4,0
KV0061	11	7,2	0,55	6,4	-0,2	2,2	-44	1,5	0,2	2,9	2 194	2,5	4,2	6,3	61	2,0	0,001	42,1
KV0062	8	1,9	0,50	1,4	-0,2	5,5	-19	4,2	0,2	2,2	2 376	0,8	3,3	4,9	46	2,1	0,000	26,0
KV0063	1	3,7	0,00	6,1	-0,5	8,6	21	4,5	0,2	2,9	225	1,2	1,5	2,1	-5	3,6	0,000	16,7
KV0064	4	8,1	0,12	1,4	-0,4	3,3	123	1,7	0,1	5,0	5 551	1,0	1,2	3,2	9	5,0	0,000	66,7
KV0065	1	1,9	0,11	0,4	-0,2	1,2	161	3,4	0,1	2,3	1 352	0,6	37,0	2,1	-6	2,8	0,000	66,1
KV0066	12	5,3	0,53	1,3	12,9	2,0	55	3,5	0,2	5,1	1 204	2,6	111,1	2,7	2	4,7	0,001	24,2
KV0067	0	9,4	-0,10	7,3	-0,6	4,5	-9	1,4	0,1	5,0	702	5,5	-0,4	7,2	-9	7,9	0,000	19,9
KV0068	10	3,2	0,31	0,4	-0,5	1,1	-12	3,9	0,1	1,3	2 150	4,0	0,4	3,9	0	3,3	0,000	33,3
KV0069	0	5,7	-0,01	7,5	-0,6	5,3	25	3,1	0,2	0,3	286	0,2	-0,1	4,2	-4	0,6	0,000	85,4
KV0070	13	3,3	1,11	5,0	1,2	0,9	-64	3,7	0,5	2,5	3 155	2,4	6,8	1,1	72	4,7	0,000	24,1
KV0071	11	4,4	0,94	2,1	1,3	1,9	-61	4,9	0,4	1,0	3 471	1,8	7,9	1,9	54	3,9	0,001	27,6
KV0072	199	4,3	2,77	2,9	0,0	1,9	-74	2,5	0,4	1,1	17 074	3,3	34,0	2,9	26	1,8	0,000	11,2
KV0073	7	5,1	0,33	2,5	-0,3	1,9	-98	5,5	0,1	4,8	1 577	3,8	2,6	3,7	29	3,5	0,000	51,2
KV0074	18	2,4	1,50	4,5	1,0	1,7	16	4,7	0,3	1,8	1 634	2,7	8,8	2,5	107	8,1	0,000	54,3
KV0075	18	5,4	4,70	2,0	1,0	2,7	87	4,2	0,3	2,9	1 159	2,7	35,5	7,9	104	2,3	0,001	3,1
KV0076	6	1,6	0,47	2,6	-0,4	5,2	-220	6,7	0,1	2,7	4 507	2,0	1,5	2,8	20	6,3	0,000	46,6
KV0077	7	3,8	0,20	0,6	-0,5	2,1	-55	3,3	0,1	1,5	3 292	2,2	0,5	5,4	6	3,2	0,000	49,1
KV0078	5	3,8	0,39	4,1	0,0	5,6	70	5,4	0,1	2,9	190	0,7	5,0	3,7	26	0,9	0,000	16,7
KV0079	1	3,4	-0,06	5,1	-0,6	2,0	-107	4,1	0,1	1,0	844	4,9	-0,2	4,3	-1	1,9	0,000	68,6
KV0080	3	6,4	0,29	3,8	0,0	8,2	-82	6,9	0,1	0,6	742	1,5	2,2	1,5	26	2,0	0,000	34,6

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Ti49(MR)		V51(MR)		Cr52(MR)		Mn55(MR)		Fe56(MR)		Co59(MR)		Ni60(MR)		Cu63(MR)		Zn66(MR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0001	56,71	0,7	120,20	2,8	2,18	4,7	15,24	2,2	1 936,16	1,0	0,411	4,5	41,83	3,1	33,43	3,3	1 291,42	2,1
KV0002	16,57	3,8	210,28	4,0	24,98	1,1	5,10	2,1	573,02	4,0	0,675	4,3	33,63	2,0	24,67	3,2	45,56	0,5
KV0003	19,92	1,3	53,22	5,8	4,38	2,7	6,10	2,3	741,07	1,8	0,296	1,3	11,63	1,0	5,60	2,6	89,09	1,7
KV0004	16,88	2,9	246,30	3,2	1,05	2,1	3,87	3,0	297,13	2,8	0,319	3,3	78,94	2,9	3,64	2,4	17,58	1,1
KV0005	12,64	1,1	324,39	1,8	1,22	2,4	7,21	3,6	1 317,41	2,6	0,498	2,9	47,16	0,4	11,08	1,2	14,53	0,2
KV0006	32,77	1,4	173,20	4,3	8,17	1,9	6,29	2,7	876,51	4,4	0,852	1,9	35,94	0,5	11,99	2,3	25,05	2,1
KV0007	82,15	1,8	130,32	1,5	23,19	1,6	60,73	1,0	13 917,43	2,0	2,711	3,5	47,51	1,7	57,74	3,9	1 671,83	2,0
KV0008	60,44	1,6	1 070,66	3,8	3,39	2,9	53,01	2,3	12 093,65	2,5	2,502	2,4	115,92	1,9	13,69	2,7	14,56	1,4
KV0009	6,59	1,9	64,07	1,0	1,28	3,0	5,41	1,1	291,05	2,0	0,194	1,6	12,30	2,8	17,27	2,4	50,28	0,6
KV0010	109,68	2,8	3,34	2,2	15,63	1,7	21,76	2,7	1 258,39	0,9	1,375	2,3	16,96	1,3	18,33	3,2	20 116,91	1,8
KV0011	3,07	4,3	52,22	7,2	1,83	3,4	14,76	3,1	3 173,66	2,0	0,205	2,6	16,61	2,0	12,78	1,4	45,53	1,2
KV0012	2,83	1,2	52,95	2,5	5,59	2,6	12,77	2,3	1 656,73	3,4	0,718	2,8	18,74	3,2	191,06	1,7	81,32	1,4
KV0013	9,89	3,0	13,13	6,2	1,50	3,2	14,79	1,7	2 387,09	2,1	0,533	2,4	19,86	1,4	17,16	2,3	8,22	1,2
KV0014	0,23	6,4	518,69	1,2	0,35	1,9	0,12	2,3	9,43	2,4	0,542	1,9	65,21	2,3	0,17	3,7	0,96	1,2
KV0015	10,07	1,9	51,50	0,5	2,45	4,9	7,11	2,4	1 397,01	5,0	0,381	5,6	10,81	1,0	19,39	2,2	42,97	1,1
KV0016	0,79	3,6	0,12	1,3	0,53	1,1	2,32	3,2	24,76	2,4	0,024	11,8	0,28	0,8	0,36	1,7	92,38	2,2
KV0017	2,69	1,1	50,50	0,4	1,42	1,3	21,41	4,0	3 914,14	2,3	0,205	5,3	16,42	3,6	12,84	3,1	32,23	1,6
KV0018	523,96	4,4	13,54	3,2	3,23	2,0	53,88	2,1	3 174,15	3,0	1,233	7,2	2,97	3,9	1,19	5,2	63,60	2,0
KV0019	10,70	3,9	46,85	3,7	1,09	3,5	12,93	2,6	2 587,68	3,9	0,143	1,1	15,03	2,1	13,12	4,5	22,78	2,0
KV0020	35,35	2,9	127,09	3,8	3,36	3,9	73,02	0,5	11 026,27	3,6	0,855	3,7	50,62	5,5	47,30	4,0	27,80	0,6
KV0021	11,27	3,7	7,59	3,6	1,54	1,1	7,25	3,9	1 381,39	2,7	0,132	3,0	2,45	2,4	13,37	0,7	14,58	2,3
KV0022	6,41	1,7	54,35	3,1	2,19	0,3	30,13	3,6	6 377,90	2,6	0,411	1,8	18,37	1,5	13,53	2,3	26,24	2,0
KV0023	10,76	3,1	70,63	2,1	2,35	1,8	8,36	1,3	498,72	2,2	0,179	3,0	14,18	3,1	25,29	2,4	58,80	2,4
KV0024	3,74	4,1	7,81	1,7	1,24	2,8	6,37	1,5	950,90	3,6	0,102	1,8	2,28	3,9	8,77	0,9	15,82	3,4
KV0025	32,74	1,3	1 077,83	2,0	1,57	3,2	18,44	2,4	3 032,86	3,9	0,780	4,1	101,88	3,6	6,90	3,1	19,68	1,4
KV0026	21,85	2,8	42,69	3,7	1,91	2,7	8,01	4,7	1 188,48	3,6	1,213	4,0	19,62	0,8	7,64	1,5	47,47	2,8
KV0027	0,11	2,6	0,01	6,8	0,02	5,4	0,02	5,6	5,90	4,6	0,001	39,0	0,01	6,3	0,02	6,5	0,74	2,4
KV0028	109,06	0,8	60,28	3,2	3,70	2,7	21,34	2,1	2 639,69	4,4	1,184	2,7	23,33	2,9	79,86	4,2	82,57	1,8
KV0029	12,98	3,4	37,31	1,2	0,92	5,5	4,87	0,6	398,27	5,8	0,286	5,4	14,11	0,9	1,12	3,0	5,65	2,7
KV0030	16,51	2,7	45,06	4,9	7,08	3,5	39,26	2,0	2 094,68	1,5	21,304	2,4	19,99	2,1	77,70	5,2	148,73	1,0
KV0031	6,00	3,4	273,18	2,2	0,36	3,9	6,30	4,2	148,94	0,7	0,415	0,6	37,66	3,0	4,21	1,6	10,05	2,0
KV0032	12,02	3,0	1 004,22	5,2	1,10	1,4	6,02	3,4	1 095,76	2,9	0,347	2,8	90,80	3,7	8,11	2,8	24,44	2,7
KV0033	10,67	3,1	410,89	3,6	1,68	5,0	21,10	1,3	3 199,26	2,3	0,473	0,1	97,60	1,4	2,06	1,9	12,53	1,6
KV0034	126,90	1,1	45,93	4,3	2,40	3,6	66,75	2,2	1 753,67	5,6	0,873	0,4	22,65	2,9	6,24	2,9	54,53	2,0
KV0035	7,00	4,8	851,35	2,2	1,42	2,0	3,43	2,1	1 714,90	3,1	0,449	2,2	81,14	0,9	211,96	4,3	192,79	2,0

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Ti49(MR)		V51(MR)		Cr52(MR)		Mn55(MR)		Fe56(MR)		Co59(MR)		Ni60(MR)		Cu63(MR)		Zn66(MR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0036	7,00	2,8	382,73	2,6	0,86	5,7	1,83	3,8	178,24	4,4	0,433	4,2	52,19	4,3	4,89	3,5	5,81	1,9
KV0037	6,83	1,2	88,98	4,1	2,44	3,1	56,74	1,1	9 076,61	2,5	0,668	4,6	34,20	1,4	49,56	1,9	207,96	0,8
KV0038	10,63	3,8	11,52	2,0	0,51	4,8	4,19	1,4	272,83	8,1	1,240	2,5	32,71	1,6	6,09	4,8	23,50	1,2
KV0039	25,69	4,0	72,17	0,7	4,00	3,6	15,21	3,0	1 010,12	3,3	0,796	2,9	28,94	5,0	29,11	2,9	56,54	0,7
KV0040	14,10	5,6	88,88	5,2	3,46	2,2	36,49	4,8	6 000,97	7,0	1,146	2,8	27,13	2,4	14,99	3,0	19,35	1,9
KV0041	18,66	4,0	26,60	1,8	1,92	1,9	19,80	2,4	5 121,40	2,6	0,583	5,3	10,39	3,9	211,32	0,4	185,02	0,7
KV0042	1,94	9,6	183,92	2,4	0,35	4,4	0,91	6,1	136,30	4,9	0,435	1,3	75,49	1,0	0,87	1,5	4,46	1,3
KV0043	36,05	0,8	1,16	1,2	0,46	1,7	22,80	5,5	626,36	4,5	0,393	3,0	1,57	1,3	5,67	2,4	22,52	1,2
KV0044	18,98	1,4	441,07	2,9	3,78	2,8	16,56	0,9	1 000,82	3,6	0,755	2,1	57,64	2,0	9,72	2,2	152,31	1,8
KV0045	22,60	1,1	114,83	4,6	5,02	2,9	7,29	1,4	1 015,35	4,1	0,955	3,0	87,41	1,9	13,02	3,1	39,32	1,2
KV0046	8,39	2,2	312,99	2,8	2,41	1,4	11,41	3,8	2 103,87	3,6	0,865	1,7	46,23	1,0	59,50	2,0	97,42	2,3
KV0047	4,26	1,2	59,72	1,6	0,14	3,8	1,77	1,9	80,47	1,5	0,196	2,3	17,72	3,5	2,44	2,9	3,51	1,4
KV0048	1,24	1,3	52,99	4,2	0,17	2,3	0,79	3,1	42,44	0,5	0,173	1,7	15,82	1,8	0,77	3,2	2,28	2,3
KV0049	43,69	5,2	97,31	2,0	1,48	3,9	18,91	3,2	775,23	2,2	0,602	3,5	29,22	2,7	5,20	3,4	10,78	1,2
KV0050	18,65	2,3	145,39	2,3	5,37	3,1	4,15	2,2	216,59	2,2	0,481	2,9	44,39	3,3	38,46	3,0	29,78	1,3
KV0051	12,47	1,4	82,85	1,0	0,69	1,7	10,91	3,2	232,16	4,9	0,341	0,5	24,75	1,9	6,30	1,9	5,56	1,3
KV0052	6,61	3,5	73,12	1,1	1,18	1,5	6,93	1,8	296,81	0,7	0,372	2,1	21,46	4,5	4,30	2,6	18,48	1,9
KV0053	1,77	8,8	31,30	2,9	0,53	5,8	1,38	3,5	85,92	1,5	0,180	3,8	13,85	2,6	4,48	3,1	11,61	1,4
KV0054	0,88	3,6	31,14	3,9	0,18	4,2	0,38	1,2	24,19	2,8	0,180	3,8	13,97	3,0	0,88	3,7	4,33	1,7
KV0055	0,98	1,0	27,39	6,7	0,19	3,1	0,40	2,7	29,06	4,5	0,170	1,5	12,06	2,5	1,07	2,1	3,58	1,5
KV0056	29,12	2,7	29,99	0,6	0,93	1,7	9,38	4,0	186,23	2,2	0,260	6,6	14,37	2,5	2,18	1,1	67,56	1,9
KV0057	4,06	4,4	36,95	3,8	0,57	3,5	3,36	4,4	112,23	3,6	0,263	5,4	16,41	2,5	3,93	2,0	7,92	0,6
KV0059	6,95	3,8	35,65	1,0	0,88	1,1	3,569	0,9	131,55	2,9	0,235	3,3	15,40	3,2	3,69	7,0	18,32	2,0
KV0060	10,61	3,8	28,11	5,4	0,52	3,3	3,228	3,5	137,52	1,3	0,211	4,3	11,89	0,5	1,31	2,4	11,78	2,1
KV0061	0,01	8,7	1,655	2,1	0,02	5,5	0,015	8,8	0,24	1,7	0,012	15,6	0,58	4,9	0,04	2,9	1,54	1,5
KV0062	0,06	2,6	1,086	3,6	0,04	3,8	0,049	4,7	0,36	7,0	0,023	0,7	1,17	2,6	0,02	12,2	1,30	3,9
KV0063	0,05	12,9	-0,002	3,7	0,00	11,5	-0,003	6,2	-0,19	1,0	0,000	109,0	0,00	16,6	0,00	2,5	0,05	0,7
KV0064	0,05	5,4	5,778	6,4	0,00	1,0	0,001	13,7	0,04	5,2	0,029	4,9	1,82	1,4	0,03	12,8	0,49	1,5
KV0065	0,00	4,8	0,268	1,8	0,09	3,9	0,020	2,5	0,91	3,9	0,007	1,0	0,34	2,0	0,01	3,5	-0,07	5,0
KV0066	1,51	3,4	0,278	2,3	0,01	1,5	0,044	4,9	2,46	2,8	0,004	12,1	0,31	10,0	0,01	15,9	0,71	3,4
KV0067	-0,07	9,3	-0,002	16,0	-0,01	9,0	-0,002	9,9	-0,19	1,2	0,000	91,7	-0,01	23,9	0,00	8,3	-0,16	8,3
KV0068	-0,05	6,0	0,210	0,3	0,01	7,5	0,000	8,7	-0,10	4,3	0,010	3,0	0,94	4,1	0,03	6,7	0,31	8,0
KV0069	-0,07	10,7	-0,002	29,5	0,00	8,8	-0,002	16,1	-0,18	6,1	0,000	57,7	0,00	24,4	0,00	7,7	0,01	5,0
KV0070	0,14	2,0	0,012	2,2	0,14	1,9	0,046	4,4	1,30	0,8	0,008	4,2	0,35	2,7	0,04	1,9	3,96	1,9
KV0071	0,37	6,8	0,049	3,4	0,12	2,5	0,041	2,3	1,02	4,1	0,008	10,2	0,74	9,8	0,05	8,1	2,86	6,0

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Ti49(MR)		V51(MR)		Cr52(MR)		Mn55(MR)		Fe56(MR)		Co59(MR)		Ni60(MR)		Cu63(MR)		Zn66(MR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0072	0,03	11,7	36,869	2,2	0,24	2,4	0,076	5,4	4,70	1,6	0,881	2,2	34,71	1,4	13,74	2,1	1,87	1,0
KV0073	-0,09	13,9	0,000	20,3	0,03	2,3	0,048	2,1	4,85	2,0	0,003	16,3	0,09	12,5	0,02	5,5	0,49	1,0
KV0074	-0,08	9,8	0,546	2,1	0,06	4,3	0,029	3,5	1,48	0,6	0,214	6,2	2,14	0,4	0,02	4,7	2,45	3,2
KV0075	0,16	4,5	0,425	1,8	0,08	2,4	0,350	3,4	5,06	4,1	0,013	8,4	0,36	4,9	0,04	2,2	2,28	4,8
KV0076	-0,09	6,7	3,536	2,1	0,00	4,7	0,013	5,8	0,54	2,6	0,350	2,6	10,04	2,5	0,04	5,2	0,82	3,1
KV0077	-0,02	2,7	0,395	3,4	0,00	8,0	-0,002	1,8	0,21	4,1	0,018	8,0	1,60	2,4	0,04	2,4	0,24	2,1
KV0078	-0,02	11,2	0,001	10,6	0,01	3,8	0,018	5,8	0,07	6,8	0,003	11,3	0,04	2,0	0,07	7,7	1,41	3,7
KV0079	0,01	7,1	0,012	6,1	0,00	3,7	0,005	1,0	0,01	6,4	0,001	28,1	0,21	3,2	0,04	9,6	0,02	1,3
KV0080	0,03	6,0	0,001	6,1	0,03	5,0	0,010	5,9	0,07	4,0	0,002	16,4	0,07	7,4	0,01	8,4	1,01	3,7

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Ga69(MR)		Rb85(MR)		Sr88(MR)		Ag109(MR)		Sb121(MR)		Ba137(MR)		La139(MR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0001	0,289	1,4	0,828	2,4	27,72	0,9	0,031	7,2	0,226	2,6	58,506	2,3	1,079	0,6
KV0002	0,076	4,0	0,257	3,4	105,41	4,5	0,072	2,2	0,122	1,5	869,975	4,2	0,245	7,6
KV0003	0,144	5,3	0,742	2,9	29,39	2,5	0,039	4,5	0,207	1,4	184,980	0,8	1,220	1,4
KV0004	0,224	3,6	0,312	4,9	25,87	1,4	0,030	5,1	0,077	2,3	5,266	1,7	0,702	1,5
KV0005	0,116	4,5	0,413	2,4	43,52	1,6	0,021	12,3	0,167	3,5	22,552	1,8	0,472	2,0
KV0006	0,270	9,4	0,554	3,1	27,24	2,6	0,027	7,2	0,735	1,9	308,591	2,9	7,059	1,4
KV0007	0,807	2,8	1,856	4,7	34,68	0,9	0,081	4,6	0,722	3,2	24,296	2,2	3,246	1,1
KV0008	0,479	5,0	0,463	3,4	16,47	1,2	0,030	6,6	0,714	3,3	8,972	2,6	1,903	2,4
KV0009	0,071	6,8	0,462	2,9	95,81	1,5	0,031	8,8	0,073	4,0	895,375	2,0	0,213	2,5
KV0010	0,554	1,5	2,788	2,2	59,30	1,8	0,173	4,0	0,722	0,7	253,447	3,1	2,381	0,9
KV0011	0,080	7,6	0,057	2,7	0,60	0,8	0,008	36,8	0,098	1,6	2,091	1,5	0,079	3,6
KV0012	0,087	6,0	0,083	1,0	2,42	1,9	0,039	5,8	0,195	0,3	8,340	1,4	0,642	2,7
KV0013	0,121	3,5	0,266	3,6	9,45	1,8	0,010	9,9	0,127	6,2	1,822	1,5	0,230	2,0
KV0014	0,039	1,6	0,011	2,8	0,04	2,1	0,007	10,7	0,016	5,6	0,134	1,0	0,004	13,3
KV0015	0,148	3,9	0,799	3,3	22,72	0,6	0,070	4,3	1,218	2,9	233,087	1,9	0,380	2,1
KV0016	0,005	11,0	0,037	7,2	16,34	2,4	0,002	18,5	0,005	12,6	0,345	1,2	0,120	2,0
KV0017	0,086	8,0	0,080	7,5	0,88	0,6	0,015	19,1	0,076	3,0	2,318	3,6	0,040	10,4
KV0018	0,934	3,4	2,470	1,6	19,73	3,6	0,013	5,3	0,091	4,2	9,303	1,2	14,871	1,1
KV0019	0,072	5,5	0,090	6,8	1,70	2,2	0,007	16,0	0,087	3,7	1,369	1,9	0,172	1,2
KV0020	0,380	2,7	0,723	1,3	3,55	0,6	0,041	0,7	0,657	8,2	9,422	1,6	3,450	0,4
KV0021	0,052	7,7	0,177	7,0	28,24	5,7	0,016	14,1	0,179	2,3	901,726	1,0	0,160	2,4

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Ga69(MR)		Rb85(MR)		Sr88(MR)		Ag109(MR)		Sb121(MR)		Ba137(MR)		La139(MR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0022	0,153	2,4	0,169	5,3	4,88	1,3	0,008	21,0	0,152	5,3	1,432	4,8	0,098	4,9
KV0023	0,093	4,2	0,501	1,3	34,14	3,9	0,021	7,7	0,080	5,4	1 350,274	2,9	0,516	3,4
KV0024	0,033	6,8	0,144	2,1	19,86	2,1	0,009	14,0	0,053	2,6	638,754	5,4	0,093	2,5
KV0025	0,405	1,4	0,579	2,9	46,62	3,9	0,029	6,1	0,376	3,2	8,439	0,3	0,276	0,8
KV0026	0,141	3,7	0,351	3,2	31,47	0,6	0,031	10,2	0,114	0,8	6,870	0,8	1,136	2,5
KV0027	0,000	44,4	0,005	6,8	0,14	2,9	0,000	24,7	0,010	13,1	0,429	0,5	0,001	26,2
KV0028	0,671	2,0	4,697	3,4	121,81	2,5	0,096	1,9	1,220	4,0	20,904	0,6	17,816	2,5
KV0029	0,137	1,1	0,485	3,5	16,21	1,6	0,006	3,4	0,055	3,0	3,326	1,7	0,394	1,7
KV0030	0,155	3,9	0,508	0,7	84,13	2,4	0,118	3,5	1,340	0,9	1 290,330	1,2	1,329	0,4
KV0031	0,050	4,2	0,192	2,5	25,71	3,4	0,015	15,7	0,067	4,5	8,921	4,2	0,070	5,2
KV0032	0,296	3,6	0,530	2,2	22,62	3,4	0,030	6,6	0,373	4,0	8,766	0,7	0,321	2,9
KV0033	0,354	3,1	0,226	2,1	9,47	3,5	0,007	20,2	0,060	3,5	4,420	1,1	1,002	2,6
KV0034	0,635	2,7	4,179	1,7	133,55	4,3	0,219	1,5	0,072	4,0	13,515	3,2	4,014	2,4
KV0035	0,242	1,2	0,267	4,3	7,40	2,3	0,073	1,3	0,416	1,9	6,785	2,2	0,213	2,5
KV0036	0,056	8,1	0,101	0,5	5,20	4,5	0,004	24,0	0,072	2,2	11,205	1,4	0,031	3,9
KV0037	0,267	1,4	0,421	2,0	11,00	3,9	0,013	5,4	0,652	3,1	11,521	3,8	2,371	1,7
KV0038	0,153	4,3	0,899	1,6	14,58	2,7	0,018	9,2	1,724	2,9	107,847	1,1	0,373	3,5
KV0039	0,336	1,1	0,918	1,2	72,08	4,3	0,039	2,7	0,683	0,3	223,393	2,1	5,980	2,3
KV0040	0,320	3,7	0,466	2,1	7,35	2,2	0,007	13,1	0,466	1,5	6,208	1,0	0,218	3,8
KV0041	0,152	4,9	0,305	2,7	7,21	1,4	0,095	5,8	0,133	2,2	52,294	2,9	4,276	0,4
KV0042	0,070	4,2	0,057	2,1	3,89	4,2	0,004	13,1	0,036	7,4	0,853	2,2	0,061	3,6
KV0043	0,152	5,0	1,860	6,0	21,34	4,4	0,079	4,3	0,033	6,5	2,561	2,2	1,318	2,0
KV0044	0,299	3,9	1,408	2,5	38,84	0,8	0,038	11,3	1,001	3,2	172,140	1,2	0,668	2,3
KV0045	0,622	1,1	0,843	1,5	59,38	3,0	0,074	7,3	0,875	1,8	86,145	1,9	19,841	2,2
KV0046	0,115	4,2	0,432	1,1	63,68	2,8	0,050	4,2	0,695	2,2	98,328	1,4	3,708	0,4
KV0047	0,071	6,3	0,175	1,3	3,28	0,6	0,001	58,9	0,046	3,2	1,148	2,6	0,246	1,6
KV0048	0,045	2,5	0,067	0,8	3,45	2,7	0,003	7,9	0,038	8,0	1,562	1,8	0,144	4,0
KV0049	0,360	2,5	2,120	3,4	11,06	3,3	0,008	20,1	0,060	9,7	6,846	1,6	1,029	1,2
KV0050	0,162	5,7	0,395	5,2	5,65	5,3	0,009	4,1	0,120	1,2	6,740	3,7	0,555	2,6
KV0051	0,136	2,8	0,427	1,7	7,969	3,2	0,002	5,6	0,050	2,2	3,633	3,2	0,367	3,3
KV0052	0,090	6,6	0,394	4,0	127,384	5,8	0,017	16,4	0,341	2,9	4,434	1,0	0,334	1,7
KV0053	0,070	9,3	0,086	2,1	4,843	2,4	0,002	25,0	0,109	6,0	0,390	3,4	0,215	1,8
KV0054	0,037	4,1	0,077	7,4	4,497	1,3	0,001	31,1	0,084	2,8	0,349	5,3	0,206	2,2
KV0055	0,039	3,0	0,101	2,6	5,119	4,0	0,002	5,7	0,095	2,9	0,409	4,3	0,242	5,3
KV0056	0,086	2,4	0,417	2,1	7,965	2,4	0,003	33,1	0,096	3,2	3,840	1,5	0,382	0,8

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	**Ga69(MR)**		**Rb85(MR)**		**Sr88(MR)**		**Ag109(MR)**		**Sb121(MR)**		**Ba137(MR)**		**La139(MR)**	
	µg/g	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**	**µg/g**	**RSD %**
KV0057	0,064	6,4	0,205	2,5	9,158	2,9	0,003	25,2	0,106	6,9	1,115	2,7	0,369	3,1
KV0059	0,129	2,8	0,206	2,1	7,031	0,6	0,002	23,9	0,115	5,5	2,094	3,5	0,503	2,7
KV0060	0,139	5,9	0,430	4,3	20,213	2,7	0,002	26,7	0,115	4,3	3,536	0,2	0,429	4,5
KV0061	0,001	28,8	0,002	29,3	0,031	3,4	0,001	54,3	0,001	22,9	0,008	15,0	0,002	21,4
KV0062	0,009	11,9	0,002	4,5	0,023	3,5	0,000	62,4	0,003	17,6	0,014	24,9	0,001	52,6
KV0063	0,000	173,2	0,002	9,9	-0,009	21,5	0,000	100,0	0,001	25,0	0,001	40,0	0,000	46,6
KV0064	0,002	9,4	0,000	38,4	0,005	2,6	0,000	51,6	0,001	35,9	0,008	25,4	0,000	35,3
KV0065	0,001	13,9	0,004	6,9	0,015	5,9	0,000	86,2	0,001	7,7	0,166	2,2	0,000	43,7
KV0066	0,003	12,8	0,019	2,6	0,096	3,6	0,000	30,9	0,002	15,0	0,205	8,4	0,002	35,6
KV0067	0,000	51,7	0,000	25,0	-0,012	19,1	0,000	63,5	0,003	8,6	0,002	17,3	0,000	21,2
KV0068	0,000	66,7	0,001	25,8	0,042	1,3	0,001	30,1	0,001	13,9	0,025	28,6	0,000	92,4
KV0069	0,000	112,0	0,000	22,3	-0,009	2,2	0,000	91,7	0,004	27,4	-0,002	56,8	0,000	44,4
KV0070	0,000	12,4	0,008	7,8	0,056	7,1	0,001	42,9	0,003	15,6	0,135	6,2	0,001	24,2
KV0071	0,001	69,3	0,007	16,0	0,029	5,2	0,001	29,0	0,004	24,7	0,037	8,1	0,001	29,2
KV0072	0,512	5,4	0,005	8,7	0,244	2,6	0,001	32,7	0,005	12,4	0,180	6,1	0,001	21,7
KV0073	0,000	114,6	0,005	10,6	0,052	4,7	0,000	24,7	0,001	49,5	1,088	2,0	0,001	61,9
KV0074	0,001	37,7	0,013	8,5	0,093	3,2	0,001	45,4	0,001	26,1	0,027	14,9	0,001	27,7
KV0075	0,002	15,0	0,014	5,6	0,114	3,2	0,001	24,7	0,001	42,8	0,319	6,5	0,002	16,3
KV0076	0,003	6,7	0,002	38,7	0,005	8,5	0,000	17,3	0,000	33,3	0,022	31,0	0,007	13,9
KV0077	0,002	13,3	0,001	5,3	0,022	1,5	0,000	75,8	0,001	31,1	0,020	20,2	0,000	9,1
KV0078	0,000	86,6	0,003	17,6	0,017	3,3	0,001	46,6	0,000	49,5	0,095	3,4	0,000	39,8
KV0079	0,000	86,6	0,000	44,1	-0,004	11,4	0,000	56,8	0,001	24,1	0,001	38,8	0,000	66,1
KV0080	0,000	91,7	0,002	15,4	0,011	8,8	0,000	56,8	0,001	47,5	0,004	38,0	0,000	35,6

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Ge72(HR)		As75(HR)		Nb93(HR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0001	0,041	27,6	2,283	0,5	0,164	3,1
KV0002	0,063	17,0	1,370	1,6	0,058	43,9
KV0003	0,027	0,0	0,939	1,6	0,063	5,9
KV0004	0,024	10,8	0,972	3,4	0,032	3,0
KV0005	0,027	8,1	1,386	2,4	0,066	5,0
KV0006	0,044	15,4	0,898	2,2	0,146	3,6
KV0007	0,249	5,7	5,707	1,5	0,184	1,8
KV0008	0,077	8,4	5,864	2,7	0,122	2,7
KV0009	0,021	27,8	3,017	3,5	0,019	10,7
KV0010	0,165	6,6	4,175	1,4	0,390	3,6
KV0011	0,028	4,8	0,610	5,5	0,011	11,9
KV0012	0,013	36,5	0,263	2,9	0,110	2,9
KV0013	0,045	5,2	0,894	2,4	0,035	6,9
KV0014	0,003	60,4	0,094	2,0	0,002	11,3
KV0015	0,039	6,7	0,834	3,0	0,061	4,3
KV0016	0,002	78,4	0,051	2,7	0,014	12,2
KV0017	0,032	19,5	0,660	4,6	0,009	11,5
KV0018	0,077	24,0	0,643	0,5	0,735	1,6
KV0019	0,024	29,9	0,632	1,6	0,043	2,2
KV0020	0,100	3,6	0,690	3,5	0,083	4,2
KV0021	0,095	4,2	0,353	6,0	0,037	11,1
KV0022	0,057	15,9	0,936	1,1	0,016	13,9
KV0023	0,023	22,2	0,545	1,0	0,027	5,3
KV0024	0,065	10,3	0,140	5,8	0,026	6,9
KV0025	0,046	8,4	3,408	1,0	0,052	7,6
KV0026	0,019	12,3	1,909	3,1	0,057	6,2
KV0027	0,001	54,3	0,099	5,2	0,000	39,2
KV0028	0,049	7,8	4,196	0,5	0,118	1,6
KV0029	0,015	19,5	0,551	5,1	0,066	3,1
KV0030	0,122	15,0	2,009	2,5	0,066	2,5
KV0031	0,018	16,5	1,283	2,2	0,017	3,9
KV0032	0,037	22,8	1,925	1,5	0,034	11,1
KV0033	0,029	2,7	0,370	1,2	0,031	2,0
KV0034	0,044	20,4	2,082	2,0	0,216	6,3
KV0035	0,037	10,4	1,720	0,8	0,022	3,1
KV0036	0,014	16,2	0,482	2,0	0,015	7,8
KV0037	0,065	6,4	0,666	0,5	0,039	2,2
KV0038	0,013	29,8	0,202	4,0	0,164	7,0
KV0039	0,042	17,0	1,565	1,1	0,111	6,3
KV0040	0,086	11,3	2,533	2,2	0,059	4,2
KV0041	0,047	18,8	1,630	1,5	0,041	4,9
KV0042	0,010	34,8	0,467	3,6	0,012	9,9
KV0043	0,012	20,7	8,292	1,4	0,070	3,2
KV0044	0,061	3,6	1,362	1,3	0,059	5,2
KV0045	0,057	15,6	0,447	1,8	0,112	10,7
KV0046	0,043	4,7	3,252	3,5	0,088	2,3
KV0047	0,002	76,7	0,061	6,3	0,016	11,2
KV0048	0,003	32,7	0,050	9,8	0,007	9,6
KV0049	0,019	41,4	0,489	4,7	0,355	1,7
KV0050	0,008	35,5	0,184	7,8	0,095	5,3
KV0051	0,007	22,2	0,178	3,5	0,034	3,4
KV0052	0,009	58,9	2,006	0,5	0,039	20,9
KV0053	0,001	69,3	0,043	3,1	0,005	6,4
KV0054	0,001	86,6	0,027	6,3	0,004	39,6
KV0055	0,001	47,9	0,027	5,7	0,003	26,5
KV0056	0,006	68,1	0,251	3,3	0,066	5,0
KV0057	0,005	40,4	0,130	5,0	0,015	8,0
KV0059	0,004	12,3	0,158	2,3	0,034	2,4
KV0060	0,007	16,7	0,085	2,7	0,044	0,9
KV0061	0,001	69,3	0,003	32,4	0,001	41,8
KV0062	0,002	58,1	0,007	2,9	0,001	26,6
KV0063	0,000	86,6	0,001	73,2	0,000	56,8
KV0064	0,001	43,3	0,078	6,9	0,000	93,2
KV0065	0,001	43,3	0,001	21,7	0,001	13,1
KV0066	0,001	28,9	0,002	53,6	0,016	10,3
KV0067	0,001	69,9	0,001	65,9	0,000	41,9
KV0068	0,001	91,7	0,006	25,8	0,000	121,8
KV0069	0,000	173,2	0,001	21,8	0,000	42,5
KV0070	0,001	34,6	0,003	26,2	0,003	28,7
KV0071	0,000	0,0	0,002	27,7	0,003	20,6

Table 9: Cont. Metals analysed by ICP-MS, corrected for blanks and massbias. LR = Low Resolution, MR = Medium Resolution and HR = High Resolution.

Sample	Ge72(HR)		As75(HR)		Nb93(HR)	
	µg/g	RSD %	µg/g	RSD %	µg/g	RSD %
KV0072	0,001	57,7	0,084	3,3	0,001	49,7
KV0073	0,000	173,2	0,001	17,9	0,000	47,0
KV0074	0,002	79,0	0,001	33,8	0,002	16,8
KV0075	0,001	132,5	0,004	11,6	0,003	17,2
KV0076	0,000	173,2	0,009	28,2	0,000	50,3
KV0077	0,001	63,0	0,024	4,7	0,000	92,1
KV0078	0,000	100,0	0,001	48,5	0,001	30,3
KV0079	0,000	173,2	0,003	24,0	0,000	9,6
KV0080	0,000	91,7	0,000	42,1	0,000	173,2