

École polytechnique de Louvain

Study of the formation of metal oxalates and soaps in oil paintings from the Southern Netherlands using ToF-SIMs

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Abstract

This work consists of applying the SIMS technique to the analysis of works of art with the aim of their restoration or conservation, as a complementary method to the ones already used.

Indeed, this master thesis is carried out in collaboration with IRPA as part of an international project called Metox, which studies the formation of metal oxalates and soaps in oil paintings by Flemish primitive painters from the XV-XVIIth centuries. IRPA has already been able to achieve numerous analyses using several methods, and this thesis will attempt to confirm the results obtained and discover new ones.

The studies were not carried out directly on real samples but were much more progressive. Initially, the SIMS analysis focused only on pure powders, synthesised in the laboratory, chemical elements that would be sought in the final analyses. In order to obtain a signature of this elements and to be able to identify them during the analysis of the more complex original samples and to be able to interpret the results obtained with the original sections.

A pure linseed oil sample was also analysed for the same purpose as the analysis of pure powders, *i.e.* in order to facilitate its identification in more complexe samples thanks to its specific "fingerprint" spectrum.

After that, the analyses focused samples mixing oil with all the pure compounds previously analysed. This allowed us to highlight the distribution of the different compounds within the sample and therefore to develop an optimal analysis technique. This consisted of determining an 'optimal' depth where we could observe the most compounds that our work focuses on and then etching down to image the surface at that depth.

Finally, by analysing real samples, it was possible to confirm certain results obtained by IRPA. But we also obtain some disappointing results, as it was the case for the the previous samples, pointing to potential causes such as the matrix effect, probability of ionisation and detection limit for certain elements, sample preparation, sample processing,...

Some perspectives, among the many imaginable in this vast and exciting field of research, were also put forward to close this master thesis.

List of Abbreviations

AFM	Atomic Force Microscope
Ar-GCIB	Argon Gas Cluster Ion Beam
f.a.	fatty acid
HCB	High Current Bunched
IRPA	Institut Royal du Patrimoine Artistique
LbL	Layer by Layer
LMIG	Liquid Metal Ion Gun
PDMS	Polydiméthylsiloxane
PMMA	Poly(methyl methacrylate)
ToF-SIMS	Time of Flight Secondary Ion Mass Spectrometry
ToF	Time of Flight

Contents

Acknowledgments	ii
Abstract	iv
List of abbreviations	v
1 Introduction	1
1.1 Oil painting	1
1.1.1 Different layers and materials of a painting	1
1.1.2 Linseed oil	4
1.2 The chemistry of oxalates and soaps	11
1.2.1 Soaps	11
1.2.2 Oxalates	13
1.3 Context of the Metox Project	15
1.4 State of the art of study of paintings with ToF-SIMS	17
1.5 Time-of-flight Secondary ion mass spectrometry (ToF-SIMS)	19
1.5.1 Principle of SIMS (from ion source to analyzer)	20
1.5.2 The basic equation of SIMS	23
1.5.3 Different analysis modes of the SIMS technique	24
1.5.4 Advantages and drawbacks of the technique	27
1.6 Objectives of the thesis	28
2 Experimental Section	31
2.1 Samples of pure oxalates and carboxylates powders	32
2.1.1 The samples: origin and preparation before analysis	32
2.1.2 Experimental Settings of analysis	33
2.2 Sample of pure linseed oil	36
2.2.1 The sample: origin and preparation before analysis	36
2.2.2 Experimental Settings of analysis	36
2.3 Mock-ups	36
2.3.1 The samples: origin and preparation before analysis	36
2.3.2 Experimental Settings of analysis	37
2.4 Real samples	41
2.4.1 The samples: origin and preparation before analysis	41
2.4.2 Experimental Settings of analysis	43

3 Results and Discussion	44
3.1 Analysis of pure oxalates and soaps powders	44
3.1.1 The interest of isotopic abundance	44
3.1.2 Precise identification of the mass spectrum	45
3.1.3 Global summary of the results and its implications	46
3.2 Analysis of pure linseed oil	49
3.2.1 Characteristic Oil ion peaks observed 1 20	50
3.3 Analysis of mock-ups	52
3.3.1 Slides of oil mixed with oxalates and soaps	52
3.3.2 Cross-sections	59
3.4 Analysis of real samples	66
4 Conclusion	70
5 Perspectives	72
6 Annexes	81
6.1 Historical Context	81
6.2 Results of the analysis of pure oxalates and soaps powders	82
6.3 Results of the analysis of the mock-ups	85
6.3.1 Slides	85
6.3.2 Cross-sections	92
6.4 Results of the analysis of the real samples	96
6.4.1 Red Sample from the Mystic Lamb of van Eyck	96
6.4.2 Sample from the "Adam et Eve" painting of the master of the Mansi Magdalene	97

1 Introduction

1.1 Oil painting

1.1.1 Different layers and materials of a painting

The third art, more precisely painting, which has been the source of so much interest, fascination and work for centuries, will be at the centre of all the research carried out in this thesis. Therefore it seems interesting to dwell a little on what a painting is, what it contains and what changes may occur within a painting over time. Indeed, even though painting methods and techniques changed throughout the centuries, painting materials showed only slight variations, especially during the period on which this work will focus, which goes from the XVth to the XVIIth century.

There are four main parts to a painting.

First of all, there is the support, mainly wood or canvas. During the period of the Flemish masters of the Southern Netherlands, on which this work focuses, both types of supports were used. There was a gradual but definite shift from the panel, i.e. wooden supports which was widely used until the 16th century, to canvas. Its treatment is important to allow a good cohesion between the paint layer and the support.

Indeed, if the paint is applied directly to the support, several phenomena can take place, notably related to conservation-restoration issues and lead to decohesion. In addition, the oil produces acids during its drying process which can attack the support once the oil has been absorbed. [6]

The second part is therefore a preparation layer, generally composed of glue and chalk, chalk being composed of more than 90% calcium carbonate ($CaCO_3$) and clay for the rest or there is also pure chalk without clay. Depending on the artist, several preparation layers can be applied. Each time one is applied, it can be sanded as to make it really smooth. In order to reduce the absorption capacity a little more, this protective layer, once applied and dried, is frequently sanded and covered again with a thin layer of glue or varnish.

Thirdly, there is the paint layer, containing the pigments. It is at this stage that

the artist can really start to paint. He will therefore use paint, which is a subtle mixture of pigment and binder, possibly with additional fillers.

The pigments are the materials that give the colour to the mixture. They can be of natural or synthetic origin, organic or inorganic, and must be ground before dispersion in the binder.

A pigment has several properties which can be summarised in two main factors, a covering factor and a colouring factor. The covering factor is the opacity of the paint and depends on the way the pigment has been ground. The colour factor refers to the ability to stain or cover a surface. As far as the colour factor is concerned, there is a wide variety of different coloured pigments, each with its own purification or synthesis method and degradation mechanisms[8].

For the period on which this work focuses, it will therefore only be natural pigments. The raw materials from which these pigments are derived have hardly changed during this period and in the northern european region. Thus we can use the twenty or so pigments found in the Eyckian palette used for the *Ghent Altarpiece* to give examples of the main pigments that were used. Thus coal black, bistre, kermes lake, orpiment, bone white, white vitriol or colourless powdered glass were added to the existing list which included lead white, chalk, carbon black, azurite, ultramarine, indigo, verdigris, malachite, lead-tin yellow, yellow ochres, vermilion, red earth and red lead (minium) [15]. The performance of these pigments varies according to whether they are of mineral or organic origin. They are also known for their high covering power, always depending on the grinding. [5]

A final important parameter concerning pigments is their permanence. This character includes fixity, solidity and lightfastness. In fact, the UV rays of light can degrade the colour. Moreover, the binder (oil) and the pigment can interact over time, transforming the original materials in many ways. This parameter is all the more important as the paintings analysed in this project are several hundred years old. Particular emphasis will therefore be placed on the ageing and degradation over time of the various parts of a painting, which are being described, according to the conditions and environment in which the works of art were produced and conserved. Especially for pigments and binders, which are particularly complex subjects and for which many grey areas remain to be discovered.

However, in this work, only the ageing and degradation of oil-based binders will be studied in more depth.

Indeed oil is the characteristic binder of the flemish painters on which this work focuses, it is however necessary to define what a binder is.

A binder is a substance that fixes pigments and fillers to the support by drying. The oil coats the pigments and fillers to form a film, so a sufficient amount of oil

is required. Depending on the period and the school, there are many binders other than oil, and the oil itself can come from various sources, such as flax, walnut or poppy.

Other binders include egg yolk, which is known as egg tempera, distemper technique also exist that uses two immiscible liquids such as oil and water-based binder and the addition of a third agent is added to stabilise the emulsion, but many secrets still remains about this technique [10].

This third part of the painting, the paint layer, which is made up of the different layers of paint, can be created using two main techniques, *Alla prima* or layered. *Alla prima* means that all the colours are mixed not only on the palette but also on the painting, they are applied against and over each other. In the end, this forms only one layer of paint and it must be finished while the paint is still wet.

The layered technique, as the name suggests, consists of applying several layers on top of each other, with a mandatory waiting time between each one so that the previous one has time to dry. This requires following the "fat on lean" technique, which consists of increasing the concentration of oil in each successive layer. [3]

The fourth and final part, which is in direct contact with the environment, is the varnish layer. Historically, varnishes are made from the same materials as those used in paint. Their preparation consisted of boiling natural resins (such as sandarac, mastic or rosin) with drying oils (such as walnut or linseed oil) and to this could be added driers such as lead white or litharge, always with the aim of accelerating the drying process [4]. However, oil varnishes were progressively replaced, from the XVIth and more generally from the XVIIth century, by varnishes which were solutions of natural resins in a volatile solvent, usually oil of turpentine.

Its purpose is to protect the paint layer from its environment or to give a certain optical effect. Indeed varnish has a great influence on the appearance of a painting by producing a gloss and color saturation. It has been shown that the predominant factors in determining the optical properties of varnishes are molecular weight and refractive index and not surface tension and molecular composition which have a much smaller impact if it is considered that the varnishes of practical interest are all of relatively low polarity.

The research also mentions that van Eyck mixed varnish with oil colours which illuminated them so intensely that they themselves already gave so much brilliance that an additional layer of varnish was not necessary.



Figure 1.1: Example of stratigraphy of sample from the mystic lamb (Image from IRPA)

Figure 1.1 shows the stratigraphy of a sample analysed for this thesis from panel XVII of the Mystic Lamb taken from a red robe. There is a surface varnish (at the upper edge) and numerous layers of red paint interspersed with an internal varnish layer (the black band). However, the preparation layer is not present on this sample.

1.1.2 Linseed oil

Although the use of oil has been reported since Greek times, it was not until several centuries later that its application to works of art was found in dried form. Indeed, the first mentions appear in the Vth century with Aetius, but only for the purpose of protecting paintings, in the form of a surface layer [12]. It was not until the XIth century by the monk Theophilus that the usefulness of oil as a binder and the ease of painting that accompanied it were put forward. The main problem that arose was the slow drying process, which made the technique laborious and time-consuming. It was not until a few centuries later that the technique was perfected and developed. For a long time, van Eyck was credited with inventing oil painting in the XVth century. Although this myth was eventually deconstructed, the fact remains that van Eyck became a master in the field and made oil painting popular among artists of the time. In fact, over the next five centuries, oil painting became the preferred technique, to the detriment of the pre-existing water-based techniques.

This was mainly due to a great advantage of the slow drying process of oil, which is the possibility to retouch its work to a certain extent and to add certain details, which was not the case before. Another advantage is the enormous improvement that oil painting allows in the imitation of certain materials. Indeed, since the mixture in oil can make the pigments transparent, the artist has the ability to apply a colour in very thin layers, called glazes, bringing a lot of subtlety and detail, thus allowing to get closer to the reality of the depicted subject.

It is through the modern era of heritage science that it has been possible to approach the composition of the oil binder used by old masters. Through numerous tests and analyses (FTIR or GC-MS) it was clearly established that van Eyck as most of the flemish old masters used linseed oil as a binder (medium). Either pure or with the addition of additives (dirterpenoid resins).

Preparation

Linseed oil is extracted from flax seeds where it constitutes the energy reserve for germination. The seeds are harvested when ripe and then dried for several months. After dry storage, the extraction of the oil from the seeds is started via two possible methods, called expression and solvent extraction. In both cases, the seeds were first heated to between 90 and 115°C to facilitate the extraction of the crude oil. In effect this reduces its viscosity, coagulates the proteins and adjusts the moisture content to the desired level (3 to 5% depending on the type of seed). The most common process was expression, which consists of pressing the seeds with a screw or hydraulic press to release the oil and a small amount of water once the seed has been burst.

The stronger the extraction, the more oil is extracted but the less clear it is and with a lower acid number, which is an indicator of the proportion of free fatty acids, i.e. fatty acids released by hydrolysis of triglycerides. This highlights a disadvantage of linseed oil which is its slight natural colour, it is indeed not transparent which could be a disadvantage for its application in paint. However, it can be easily clarified in contact with sunlight. To prevent the oil from turning yellow, it should not be dried in a dark place [14].

A final step in the preparation of linseed oil is refining. The raw oil contains a large number of impurities which must be removed by various refining methods [13]: degumming, mucilage removal by flocculation (mucilage is a substance that swells on contact with water and forms a gelatinous mass), neutralisation with caustic soda (elimination of the fatty acids present and therefore reduction of the acid index) and decolourisation with absorbent earth or activated carbon.

However, even after refining, it is possible that impurities remain, such as dyes, waxes, vitamin E, sterols, traces of heavy metals,...

The painters of the time would also have often cooked the oil before using it, in order to obtain a higher viscosity, a brighter shine and better drying properties. Indeed, as will be detailed later, the oil network polymerises during the cooking of the oil, which accelerates its drying. They would also have added metallic salts to improve these drying properties. These added drying agents were generally based on lead, such as litharge (PbO) or lead white ($2PbCO_3PbOH_2$).

However, according to Xavier de Langlais ([14]) van Eyck would not have used this type of drying agent, which was widely used by the painters who followed him.

According to other, even more recent studies ([15] [17]), van Eyck used zinc-based drying agents, Zinc sulphate to be precise.

It is common for studies nowadays to investigate the chemistry behind these multi-

century paintings and all the complexity that this entails.

And what is certain is that if the artists of the time did not master all the complexity of the chemical reactions that took place before their eyes, they were already at the basis of totally brilliant scientific discoveries. For example, very recent studies have confirmed the impact of lead-based drying agents on drying and induction time [16].

Composition

Oil is composed of only one type of molecule, the triglycerides (or triacylglycerols). Figure 1.2 show the formation of these triglycerides, which are triesters resulting from an esterification reaction between a trialcohol, glycerol ($C_3H_8O_3$) on the left, and three carboxylic acids, the fatty acids. [18] [20]

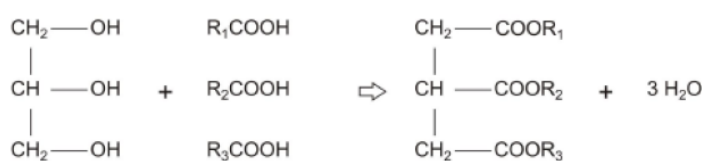


Figure 1.2: Formation of triglyceride by esterification [1]

A carboxylic acid is a molecule containing a carboxyl group ($-\text{COOH}$) which is a functional group composed of carbon atom linked by a double bond to an oxygen atom and linked by a simple bond to an hydroxyl group (OH). A fatty acid being a carboxylic acid with a hydrocarbon chain of 4 to 36 carbon atoms. The R_1, R_2, R_3 groups on the figure above represent these hydrocarbon chains. They are not identical, which is why several different types of fatty acids can be found in linseed oil triglycerides [19].

The main ones are 5 and are summarised in the figure 1.3 according to their relative concentration in the fresh oil and their chemical formula.

Compound	Relative concentration	Chemical formula
Linolenic acid (triply unsaturated)	48-60%	$\text{C}_{18}\text{H}_{30}\text{O}_2$
Linoleic acid (doubly unsaturated)	14-19%	$\text{C}_{18}\text{H}_{32}\text{O}_2$
Oleic acid (mono-unsaturated)	14-24%	$\text{C}_{18}\text{H}_{34}\text{O}_2$
Stearic acid (saturated)	3-6 %	$\text{C}_{18}\text{H}_{36}\text{O}_2$
Palmitic acid (saturated)	6-7%	$\text{C}_{16}\text{H}_{32}\text{O}_2$

Figure 1.3: Composition of linseed oil: principal fatty acids

Although all fatty acids are characterised by a hydroxyl group, or an ester if bound to the glycerol, attached to the end of a long hydrophobic aliphatic chain, they can be distinguished from each other by their number of carbon atoms, the number of double bonds they have and the spatial arrangement around these double bond (*cis* or *trans*). The presence or absence of double bonds in the carbon chain determines if it is a saturated or unsaturated fatty acid. This distinction has a strong influence on the polymeric network that is formed during the drying of the oil, as will be detailed in the next section. The proportion of saturated and unsaturated fatty acids depending on the nature of the drying oil. Indeed, as will be explained in the next section, the proportion of unsaturated fatty acids has a major influence on the drying properties of oils.

Based on table [1.3](#), it is clear that linseed oil contains a very high proportion of unsaturated fatty acids (f.a.), particularly in linolenic acid, and it is therefore understandable why linseed oil is highly valued for its drying properties, as it dries very quickly. It must be highlight that the values given in table [1.3](#) which have been measured by gas chromatography [\[19\]](#), refer to the f.a. present in the triglycerides and not to free fatty acids. Even though in fresh form, the oil contains almost none. Free fatty acids are those f.a. that have not undergone esterification with glycerol and are therefore freely present in the oil mass, having a high mobility and being able to bind to other compounds (such as metal ions as will be explained later).

The different combinations of fatty acids within the triglycerides also have an important impact on the drying of the oil. There are indeed preferential distribution of the f.a. that take place within the triglycerides. For example, 24% of triglycerides are composed of 3 linolenic acids, while 12% are composed of 2 linolenic acids and 1 stearic acid, etc. Linolenic acid being the most present in oil, it is therefore found in the vast majority of triglycerides.

Drying: auto-oxidation process (solidification)

The aim of this section is to outline the various phenomena behind the drying of oil.

The formation of an entangled and cross-linked 3D polymeric network is based on the reactivity of triglycerides. Indeed, the double bonds of unsaturated fatty acids are the source of reaction with oxygen from the air but also with other fatty acids to trigger the formation of an oily network. The study of auto-oxidation and hydrolysis processes is therefore the basis for understanding the ageing of oil. Indeed, during the first stages of drying, the two processes will be concomitant, but afterwards it is mainly hydrolysis that determines the structure of the aged oil.

It should be noted that the transition from a viscous liquid to a solid is a very

gradual process and also, as already mentioned, that the number of radical mechanisms that cause it is very important given the diversity of triglycerides found in the oil.

The fact that linseed oil is particularly rich in polyunsaturated fatty acids further underlines the complexity of this oil.

The first stage in the drying of the oil consists of a series of radical oxidation reactions. This takes place in 2 main phases.

Initiation: This stage consists of the production of a radical by the loss of a hydrogen atom (see figure 1.4). This step takes place on an unsaturated fatty acid and is most advantageous, energetically speaking, at a carbon located between two non-conjugated double bonds (i.e. separated by more than one single bond). Linolenic and linoleic acids are therefore those that allow this reaction. The resulting radical is stabilised by resonance.

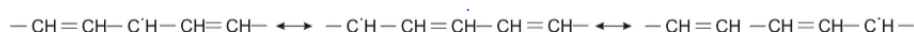


Figure 1.4: Resonance forms of the hydrocarbon chain after the loss of an hydrogen atom [20]

Then a peroxide is formed by reaction of the radical with oxygen from the air (see figure 1.5).

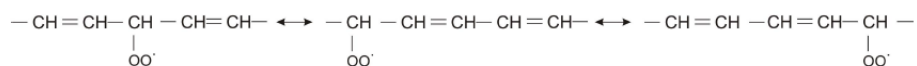


Figure 1.5: Formation of a peroxy radical after reaction with oxygen [20]

After this, the peroxide can react with a hydrogen atom of another chain and transfer its radical character to it. Hydroperoxides are then formed.

These three steps of the auto-oxidation process lead to the oxidation of the hydrocarbon chains and initiate the formation of the network, but the formation of a solid film cannot only be explained on the basis of these reactions, which only modify the triglycerides but do not make them connected with each other.

The hardening of the oil can therefore be explained by other reactions that occur after the formation of peroxide and hydroperoxide radicals.

Propagation: Indeed, the peroxide radical can also be added to the double bond of a neighbouring chain to create a branching between the two chains (see figure 1.6).

Again, the reaction will be energetically favoured on carbon atoms located between a double bond on one side and a single bond followed by a double bond on the other.

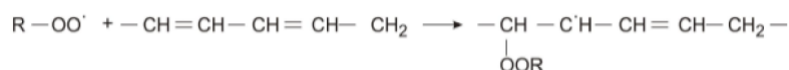


Figure 1.6: Addition of a peroxide radical on a double bound of a neighbouring chain[20]

Similarly, the O-O bond of peroxides and hydroperoxides is not very strong and can be easily broken by light or thermal energy. Thus forming two alkoxy radicals ready, in their turn, to react with a double bond, once again combining two chains (through an ester group).

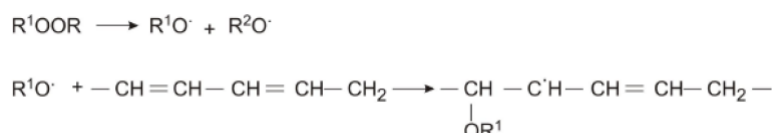


Figure 1.7: Addition of a alkoxy radical on a double bound of a neighbouring chain[20]

Whether via a peroxide or ether function, these two mechanisms therefore lead to the creation of links between chains.

Drying: degradation

In addition to the various constructive reactions which have just been detailed and which are at the origin of the formation of the polymeric oil network, there are destructive reactions that break the connectivity of this network.

Indeed, instead of initiating the formation of a polymeric network by connecting with another chain, the alkoxy radical (described above) can also split up. Depending on where the split occurs, two cases arise.

Either the formation of a free aldehyde and an alkyl radical remains bound to the glycerol skeleton, as shown on figure 1.8.

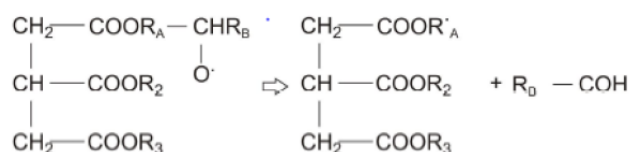


Figure 1.8: Formation of a free aldehyde and a alkyl radical linked to a glycerol[20]

Or the formation of a free alkyl radical and the formation of a dicarboxylic acid attached to the triglyceride in the form of a dicarboxylic acid ester, as shown on figure 1.9.

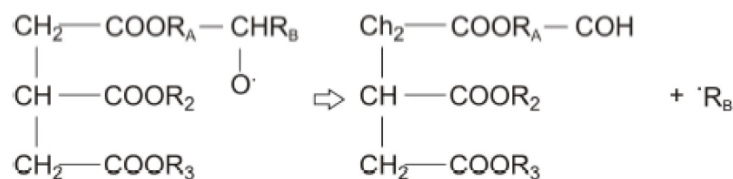


Figure 1.9: Formation of a free alkyl radical and a dicarboxylic esterlinked to a glycerol [20]

The length of the fatty acids formed by these reactions depends on where the auto-oxidation has taken place. This is often in the middle of the chain, producing fatty acids C_8 , C_9 or C_{10} . These di-carboxylic acids can therefore serve as evidence that destructive reactions have taken place. The acid that is most commonly used for this purpose because it is the most produced is azelaic acid ($C_9H_{16}O_4$) [24], which will be the subject of particular attention in the research for this work.

Another type of destructive reaction can take place under the action of temperature: a hydrolysis of the ester bonds of triglycerides and thus the production of free fatty acids (see figure 1.10). This is the exact opposite process of the formation of triglycerides from glycerol and fatty acids.

These free fatty acids formed will therefore be found in the dried oil, as well as dicarboxylic acids formed in the process mentioned above and acid-rich network oligomers.

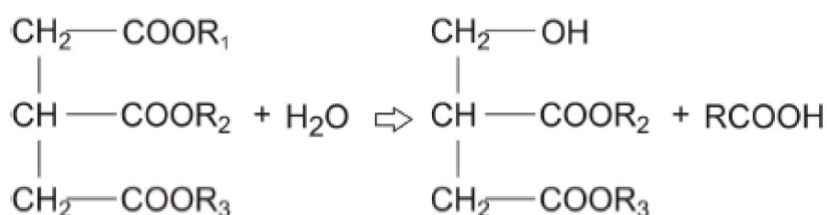


Figure 1.10: Hydrolysis of a triglyceride with formation of a free f.a. [20]

The study of all these reactions highlighted the key role of double bonds in the drying of an oil. And thus the direct link between the drying properties of an oil and its content of doubly or triply unsaturated fatty acids.

The ageing and degradation of the oil network is at the basis of the work and research carried out in this project. Since it is indeed on the grounds of what follows from this degradation that the formation of oxalates and soaps could be explained.

The following section will therefore describe what these soaps and oxalates are, before describing the research and discoveries that have already been made about them, and finally describing the context in which this work is carried out and its precise objectives.

1.2 The chemistry of oxalates and soaps

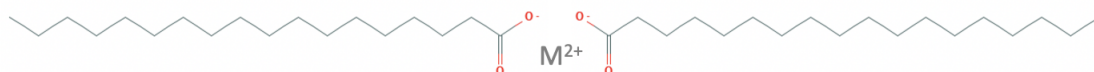
1.2.1 Soaps

From a historical point of view, the knowledge and use of metallic soaps dates back to antiquity but it is only from the middle of the XIXth century that the term metallic soap appears. Indeed, it was shortly before that that the process of saponification, which is the basis of the formation of metallic soaps, was described for the first time, in 1823 by the chemist M. Chevreul. It was also at this time that questions arose about the impact on paint degradation of lead white and, more generally, of lead-based driers. Subsequently, more researchers looked into this issue and observed what are called now lead soap aggregates. At the beginning of the XXth century, the German chemist A. Eibner questioned the role of lead soaps in the transparency phenomena observed in oil paints. But at the same time another chemist, A.P. Laurie, dismissed the idea of saponification of paints as a potential source of the transparency of many paints and argued that the reason was solely due to the increase in the refractive index of oil with time. This interpretation continued until the end of the XXth century, when new research supported what Eibner had argued. It was not until the very beginning of the XXIth century that the link between metallic soaps and the degradation observed in the various paint and preparation layers was clearly established. It was at this time that the first international conferences on metallic soaps took place, in 2005 in the Netherlands and in 2006 in the the United States. And finally, only 5 years ago, a new conference "Metal soaps in art" was held, which reviewed the state of knowledge on the subject and on which what is said here is partly based[34].

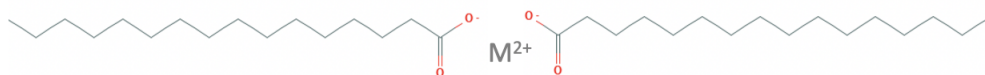
Metal soaps represent a specific form of metal carboxylates, as do metal oxalates which will be discussed in the next section. These are complexes that result from the interaction between the carboxylic groups ($-\text{COOH}$) of the free fatty acids present in the oil with metal ions from pigments or driers [34].

As shown Figure 1.11, the chemical structure of soaps is relatively simple. Palmittates and stearates are composed of two mono-carboxylic fatty acids, palmitic and stearic acid respectively, bound to the metal ion. Azelates, on the other hand, contain only one azelaic acid, since this one is di-carboxylic, linked to the metal [32].

Metal Stearate
($C_{36}H_{70}O_4M$):



Metal Palmitate
($C_{32}H_{62}O_4M$):



Metal Azelate
($C_9H_{16}O_4M$):

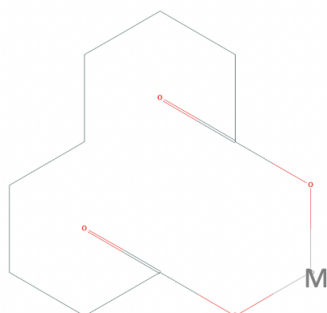


Figure 1.11: Chemical structure of metal soaps [30]

As introduced in the section 1.1.2 of the introduction, the formation of soaps only occurs in the case of oils that have begun their degradation process. This is because it is at this point that the fatty acids that make up the soaps are produced. As a reminder, the different acids used in soaps come from destructive reactions of the oil network, palmitic and stearic acids being the result of the hydrolysis of triglycerides and azelaic acid the result of the oxidation of unsaturated fatty acids. In order for metallic soaps to be formed, a significant proportion of the triglycerides must be hydrolysed.

Once there are enough free carboxylic acids, they will release a hydrogen H^+ from their hydroxyl group, become carboxylate ions and therefore become available to react with the metal ions present in the paint layers, which will act as a Lewis base. Indeed, they have an electron gap in their valence layer and are able to accept electron doublets from carboxylate ions in order to balance their charge. This is how coordination bonds are formed, resulting in the creation of a complex, the metal soap.

However, a distinction must be made between the chemical structure of a metallic soap, shown in Figure 1.11, and its crystalline form. Indeed, once soaps have been formed, if they meet they can crystallise and form what are called crystalline nuclei. A crystalline structure is defined as a structure in which the molecules are ordered periodically in three-dimensional space. This state is solid. In the case of metallic soaps, Van der Waals forces are responsible for crystallisation by allowing the alignment of the molecules [31].

This crystallisation process is cyclic, i.e. the more soaps crystallise the more other soaps appear and therefore the more potential new crystallisations can take place. Indeed, the more crystallisation takes place within the oil network, the more an imbalance appears. To counteract this, new fatty acids must be released from the binder and also metal ions, which can lead to a loss of pigments.

This gathering of metallic soaps is the basis for the formation of aggregates, called protrusions, which tend to migrate to the surface. This is one of the main consequences of soap degradation. These protrusions lead to the transparency of the paint. In fact, there is a loss of covering power of the pigments in this area, which have been strongly modified due to their role in the formation of soaps, supplying metal ions. And the resulting soaps modify the refractive index of the area, since their refractive index is much lower than that of the original pigments, close to that of oil.

Studies have been carried out to investigate their formation and it was found that only palmitates and stearates concentrate in protrusions and not azelates, this study having focused on lead soaps[33]. This would be explained by the greater mobility of lead monocarboxylates within an aged oil paint film, azelate being a bi-carboxylate.

An important point to emphasise concerns the catalytic action of a metal ion, i.e. its action on the oxidation of triglycerides, which therefore increases the drying rate. This is a function of its solubility and dissociation within the binder as well as the number of oxidation stages it presents. A certain concentration is therefore required for an effect to be observed. This can be achieved either by adding the ion directly to the oil (this is where the addition of litharge to the oil to increase its dryness comes from). Or by using a pigment that dissociates on contact with the oil. It is interesting to illustrate this with lead-based pigments, lead which has been the subject of much research in the field because it is frequently used as a drying agent. For example, lead tetraethyl does not dissociate in the oil binder because it has covalent bonds and therefore has no catalytic activity. While lead white dissociates easily in contact with oil, the rate of dissociation varies with the method of preparation. Lead white is one of the most widely used pigments in the history of painting.

1.2.2 Oxalates

Oxalates are composed of oxalic acid, the smallest of the di-carboxylic acids. Figure 1.12 shows the deprotonated form of oxalic acid, the oxalate anion, which coordinates

to the metallic cation in order to form a metal oxalate[37].

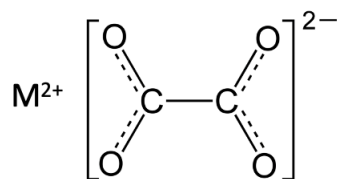


Figure 1.12: Chemical structure of metal oxalate (C_2O_4M)[29]

Next to a chemical origin, oxalates are also widely found in nature, in a number of vegetable and animal cells and are the major components of urinary calculi in man. But can also be produced by many organisms including bacteria, lichens, algae or fungi.

To highlight this, it is interesting to focus on one of the many studies that have already been conducted on the formation of oxalate on historical buildings, monuments and natural outcrops [28] mainly on the whewellite and weddellite, the mono- and dihydrates of calcium oxalate.

Since then, the origin of the formation of these oxalates as a layer on the surface of certain monuments has been proven. This occurs in the presence of lichens (or to a lesser extent other microorganisms such as algae or fungi) which provide the oxalic acid required to precipitate the calcium in the form of oxalates. Indeed the oxalic acid attack the surface which is carbonatic and the calcium carbonate reprecipitates as calcium oxalate. Thus the oxalate layer is formed gradually.

It is therefore a phenomenon, in the case of the monuments, that only takes place on the surface, the depth of formation of this oxalate layer simply depends on the depth of penetration of the micro-organisms, the thickness being therefore a few hundred microns. Moreover, studies also show that if this type of biological attack on monuments was among the most frequent in the past, this is no longer the case today in highly polluted sites. In fact, in the past, the quality of the atmosphere was more favourable to the support of lichen, whewellite and weddellite that can be found there is only a witness to past transformations. This highlights the importance of taking into account changing preservation conditions in understanding the ageing of works of art.

This formation of an oxalate patina can be seen as a protective layer of the rock (usually marble or limestone in the studies).

It has obviously been proven that the formation of oxalates is not due to artificial surface treatments since they are observed on natural outcrops and artifacts lacking in artistic merit.

Concerning the study of oxalates in paints, if there is no certainty and only a few of observations have been established, several hypotheses have already been put forward (within the Metox project, which will be described in the next section).

Indeed, the 3 hypotheses explaining the formation of metallic oxalates are :

- Because there are some oxalic acids in the dust. These oxalic acids and the calcium suspended in the air are thus found on the surface and then bind together.
- Due to microorganisms on the surface (hypothesis on the basis of the oxalates present on the rock)
- Or because of the pigment/binder interaction, *i.e.* oil/pigment interaction.

It has been shown that ageing leads to the formation of many coordination complexes due to pigment-binder interactions that alter the original composition of the painting material. But also the ageing would involve that the cation M^+ , previously bound to a grain of pigment, would be taken and put in solution by the oil, it would take them out of the pigment and would introduce them in the mass, *i.e.* the fatty acids of the oil.

1.3 Context of the Metox Project

The analysis of artworks with SIMS is a field of research which, despite the fact that it has been in existence for some years now, is still rather limited in terms of the applications already carried out. Especially with regard to the study of the formation of soaps and even more specifically that of oxalates.

It is in this context that the international Metox project was born a few years ago in 2016 and this master thesis takes part in this project.

This project, unites several major European museums around a common objective, which is the preservation of our artistic heritage, mainly that of the Flemish painters of the XVth-XVIIth centuries. Indeed, this project studies the correlations that may exist between degradation pathways of historical oil paints. More precisely those induced by metallic oxalates and soaps.

To do this, it studies the formation and migration of these soaps and oxalates and the different elements that can impact these processes such as environmental factors, cleaning and conservation treatments. These two degradation processes

are among the most common but for which much misunderstanding still remains. Thus this project goes beyond the state of the art in terms of topic, but also in terms of methodology by a multi-analytical characterisation at not only micro but also nanoscale and by developing a series of innovative model systems. Indeed, the project innovates in terms of methodology by using both conventional and more recently developed analytical methods and studies at the same time cross-sections of historical paintings, pioneering chemical model systems and mock-ups.

The findings of the project will therefore provide major advances for the world of heritage science and painting conservation as they will lead to new and improved ways of cleaning, restoring and conserving paintings. To enable future generations to continue to enjoy these magnificent traces of our artistic and cultural past.

Refer the annex [6.1](#) to learn more about the historical context of the XV-XVII period of the Southern Netherlands to allow you to realize all the more the precious and magnificent character of the works of this period. The context of the period also had a strong influence on the evolution of painting styles and worldviews.

If it is well proven that paintings are irreplaceable relics of our past, they are not however unalterable. It is indeed essential to always keep in mind that over time, a multitude of modifications are constantly taking place within a painting. It is far from being static from a physical-chemical point of view. The complexity of the composition of the raw materials leads to numerous possibilities of chemical reactions within the paint layers, and even with the canvas or panel or with the external environment. Indeed, throughout its life, a work of art will be transported, retouched, restored and will be confronted with many other traumas, both of human and non-human origin.

The interaction with the ambient air, the percentage of relative humidity or the exposure to light are other factors that can significantly influence the evolution of a work of art.

In conclusion, in addition to the fact that it is now well known that the complex chemical systems formed by oil paints (composed of organic and inorganic materials such as pigments, oil, fillers, driers) are constantly subject to chemical changes influenced by the material composition of the paint and by environmental factors. It has also been recognised that cleaning and conservation operations play a role in the delicate chemical environment formed by the various painting materials which can significantly impact on the weathering of oil paintings. However, these physico-chemical phenomena are not yet fully understood. And this is where the role of the Metox Project comes in to play in the struggle for the long-term conservation

of these artworks and at the same time all the historical, cultural, technological, social and aesthetic values they contain, through the preservation of their visual and material aspects. This is done through the study of the degradation pathways that accompany the formation and migration of oxalates and metallic soaps within paintings.

1.4 State of the art of study of paintings with ToF-SIMS

Through the various studies carried out with SIMS on paintings, similar broad approaches have been adopted in the analyses, allowing several major conclusions to be drawn regarding the understanding of their compositions and ageing.

First of all, many characteristic peaks are highlighted to identify the components of the different parts of a sample of painting. The *modus operandi* for establishing the different attributions (from ion detection to certain compounds) within the layers is quite similar and quite common. For example, to establish that the detection of certain ions, such as lead oxide ions, confirms the presence of lead white, they compare the mass spectra of a pure reference of lead white powder with those obtained from the analysis of a specific area where lead-containing ions have been detected, after imaging the area [42].

SIMS also makes it possible to observe, thanks to the superposition of images of several ionic species, interactions between neighbouring components. For example, it is frequently observed that lead white interacts with the lipids of the oily binder, which would lead to the formation of lead soaps that cause degradation of the works of art.

Other observations frequently made during these studies are applicable to most studies on paintings and could therefore be of interest to this thesis. For example, with regard to the embedding resin, the peak corresponding to the detection of K^+ (m/z 38.96) is generally chosen in positive and the $C_4H_5O_2^-$ peak (m/z 85.03), which is characteristic of PMMA, is chosen in negative. In the context of the analysis of a work of art of Rembrandt ([42]), the SIMS also allowed the observation of proteins, which could point to the origin of the paint, which would be dyed wool, or rather the manufacturing waste that resulted from it.

The SIMS analyses also made it possible to prove the type of binder that is used. Indeed, for example, for a work of Nicolas Poussin [40] it could be proved that it had not been painted "a guazzo", i.e. with a binding medium based on glue or egg, by detecting lipids and thus proving the oily nature of the binding medium. In another study [42] it was proved that linseed oil was used via a ratio of 1.35 between palmitic and stearic acid (i.e. between the air under the m/z 255.24 and 238.28

peak curve). It was also possible to prove the use of egg yolk in the paint layer thanks to the presence of phospholipid.

Surprising observations also occur. Indeed, thanks to the SIMS submicrometer study, very small structures were discovered in a Rembrandt painting, such as starch in the "second ground layer", which is surprising and completely new for a painting by this artist.

The study carried out on a work by Lambert Lombard [1] supported a hypothesis of particular interest for this thesis by putting forward the hypothesis of the degradation of smalt (a blue mineral pigment widely used by Flemish painters of the XVIth and XVIIth centuries, which is a silicate of potassium and cobalt) by the oily or protein binder, based on the observation of the systematic migration of potassium, the binder being the only common denominator - observed - to this migration. Underlining the significant impact of the smalt compositions, its level of impurities, the various possible environments, the type of binder on the degradation behaviours. A major conclusion of the study is the importance of sample preparation. Indeed, a careful and systematic preparation can provide information that is hidden in the case of an inappropriate preparation.

Before carrying out a SIMS analysis, which is a surface-sensitive analytical method, a major importance concerns the condition of the sample surface. Indeed, several sources of contamination may appear on the surface, exogenous lipids, hydrocarbons and/or silicones (mainly polydimethylsiloxane PDMS). These impurities will have the main negative consequence of masking the ion signal expected from the sample itself, as the ions detected will mainly come from these components which tend to ionise very well. In addition, irregularities in the surface (protruding grains, steps, porosity,...) significantly impact the mass spectrum. Since secondary ions are formed at different distances from the extractor, this widens the ion peaks, or may even lead to signal loss.

Thus, one study [41] used the GCIB beam, that will be detailed in the next section, to clean and flatten the surface of the samples and improve the image contrast. This is due to the heterogeneous layered structure of the samples, alternating organic and mineral compounds, which makes the analysis more complex. Indeed, GCIB allows a soft sputtering of the surface without damaging the underlying layers.

However, GCIB sputtering is not ideal in the case of complex paint samples that include inorganic particles of several tens of microns in size within an organic matrix, each compound and mixture having its own sputter yield, resulting in an irregular surface and leading to analytical artefacts.

Therefore the ultramicrotome is presented as the best solution to obtain high quality ion images and mass spectra. This is however a long and delicate step. It allows

very thin cuts to be produced using a diamond blade. (The method is described in detail by Mazel et al [46]).

It is also important to specify that throughout each study, they systematically resort to cross-sections. Ideal to allow the simultaneous analysis of all the pictorial layers.

In conclusion, they manage to determine layer by layer what is in the painting, the pigments and oil used, but also more surprising compounds such as starch as well as certain interactions, notably those concerning soaps, but nothing yet appears concerning oxalates.

Besides all of that, it is important to remember that the characterisation and distribution of the compounds within the layers of the work also allows for a better understanding of the painting techniques of the artist.

From a more experimental and analytical optimisation point of view, the various studies cited also highlight all the parameters that need to be adjusted for the analysis of paintings and the difficulties that come with it. Mainly related to the insulating character of these samples and the different permittivity of the layers (and thus the different values of surface potentials). It is therefore necessary to carry out charge compensations before each acquisition so that the analyser parameters can be set optimally. Sometimes it is even necessary to reduce the analysis area if the dielectric properties are really too changeable within the initial area.

1.5 Time-of-flight Secondary ion mass spectrometry (ToF-SIMS)

This entire section is heavily based on the book by Vickerman et al. [47], the book of Mahoney et al. [54] and their references.

Nanomaterials have been enjoying a golden age in the scientific community for some years now. Indeed, discoveries about the novel properties these can display compared to bulky materials have propelled them to the forefront of scientific researches. This has led to the development and design of a large number of new nanostructured materials. All of these advances were made against a backdrop of strong development of studies and characterisation of materials at the nanoscale. It is in this context that SIMS has been able to evolve so much and to be applied to a wide range of fields.

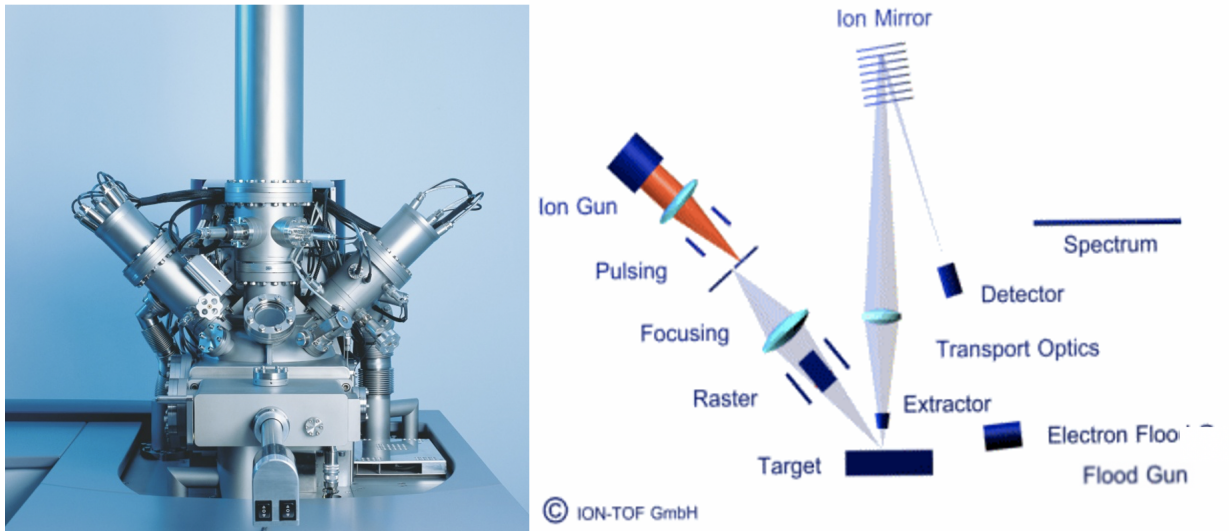


Figure 1.13: Time-of-flight secondary ion mass spectrometer [48] [49]

Secondary Ion Mass Spectrometry is an ultra high vacuum surface analysis technique based on the collection of ions that have been ejected from that surface by an energetic (of the order of the keV) focused primary ions beam, see figure 1.13. When the beam impacts the solid surface, a redistribution of energy takes place, through a collision cascade, causing the emission of elementary, molecular or intermediate fragment characteristic to the solid. The ionised part of these fragments is then channelled into a time-of-flight mass analyser which discriminates the particles according to their mass/charge ratio (m/z).

1.5.1 Principle of SIMS (from ion source to analyzer)

Primary ion source

First of all, a ion gun is used to send a pulsed beam of ions, called primary ions, focused with a certain energy on a specific area of the sample. The sources used for many years in SIMS are of the LMIG (Liquid Metal Ion Gun) type, ions being formed from a metal in a liquid state. These allow great focusing and therefore great spatial resolution. The spatial resolution offered by SIMS is nowadays of the order of a few hundred of nm.

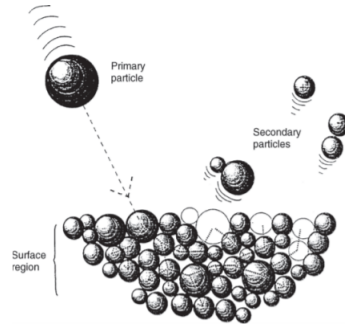


Figure 1.14: Representation of the billiard ball type collision cascade[47]

Once sent from the source, the primary ions will collide with the surface and transfer their kinetic energy via a cascade of collisions to the surface atoms of the bombarded material, as shown in Figure 1.14. Several types of analysis are possible with the Tof-SIMS, but the most common one is the static analysis. If SIMS is always sensitive to the top surface, in fact 95% of the secondary particles come from the 2 outermost layers of the solid. The static mode mainly concerns the dose of primary ions that is sent on the sample. Indeed, in static SIMS is sent a dose so low that the surface is almost not damaged. The maximum dose to remain in static mode, called static limit, is 10^{13} ions/cm². Therefore only about 1 atom in 1000 collides with an incident ion. Thus the collision cascade is initiated, after this first collision the target atom that has received energy from a primary ion through elastic collision, will in turn collide with its close neighbours and so on. This can lead to a sufficient transfer of energy and momentum to an atom, or a cluster of atoms, close to the surface to be ejected, provided that the energy transmitted to it exceeds its binding energy. Among these atoms or clusters of atoms emitted by the surface, only a small part is ionised, positively or negatively, about 1 in 100 is charged, the rest being neutrals. Ionisation appears on emission from the surface and can occur via several mechanisms such as electron exchange, proton transfer, adduct formation or finally via fragmentation. An important point that influences the ionisation processes is the chemical state of the surface. Indeed, the ionization probability of an element depends on its whole chemical environment, largely by the electronic state. This influence is referred as matrix effect. To underline this, an example can be given, if an element is in a metal or in its oxide it impacts by several orders of magnitude the ionic yield because of the effect of the electronegativity on the ionization process. Indeed, the oxygen atoms will attract the electrons of the metal atoms, in the case of the oxide form. Therefore, the metal atoms will be more easily sputtered as Me⁺ ions in the oxide than in the metal. The relative proportion of each of the sputtered ions is then highly influenced by this matrix effect.

Secondary ion information

The range of kinetic energy in which secondary particles are emitted is wide. Several parameters determine this energy distribution: the types of bonds that are on the surface, the number of bonds that need to be broken and the amount of energy that can be stored in the emitted species (*e.g.* by vibration or rotation). This distribution is also influenced by the primary ions, mainly by their nature, energies and angle of incidence.

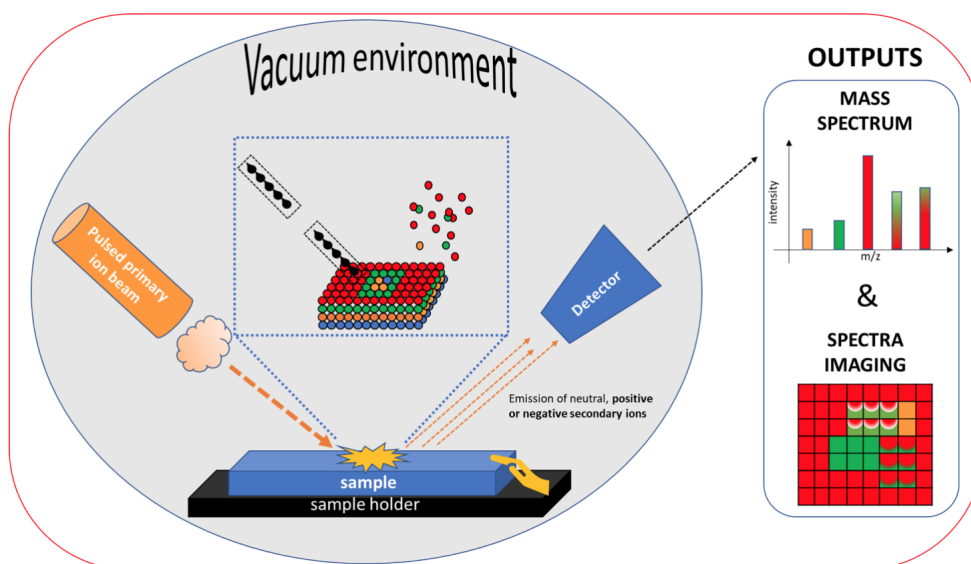


Figure 1.15: Material Sputtering in SIMS[50]

Mass analysis (ToF mass analyser)

After the ejection of material from the sample surface, the analysis phase of the secondary particles can start. For this purpose, the particles are channelled into the mass analyser, which in most cases (and in the case of the machine used in this project) is a time-of-flight analyser. This consists of matching a time of flight to the m/z ratio of the secondary ions. For this purpose, the primary ion beam is pulsed and thus the secondary ions arrive at the detector in pulse trains. In order to allow this discrimination according to the m/z ratio, it is necessary that the speed of these ions is dependent only on their mass. They are therefore accelerated via a constant potential to acquire a certain kinetic energy which depends only on the charge. This is done within a filled drift tube of known length. Knowing this distance travelled by the secondary ions to the detector, the time of flight of each ion allows to deduce each of the ion masses. It has to be specified that in SIMS the ions are monocharged ($z=1$). This allows a discrimination of particles only according to their mass (m) without having to take into account the number of charges they have. This is very practical as it is already very hard to ionise once in SIMS so being able to ionise these particles again would be very complicated.

The equation governing SIMS, presented in section [1.5.2](#), describes this secondary flux for each ions.

It should be noted that the damage inflicted on the surface is negligible, only in static mode, the ions emitted being therefore characteristic of the chemical composition of the bombarded surface. Indeed, the probability that 1 atom of the surface comes into contact with more than 1 incident ion is almost zero. It can therefore be considered that the surface from which the spectral information is removed can be considered undamaged.

1.5.2 The basic equation of SIMS

The equation governing SIMS describes the secondary flux of ionic species m and, in turn, the peak intensities in the spectrum:

$$I_m = I_p y_m \alpha^+ \theta_m \eta \quad (1.1)$$

Where:

- I_m is the secondary ion flux of species m^+
- I_p is the primary ion flux
- y_m is the sputter yield, *i.e.* the number of emitted species m , either neutral or ionised, per primary particle impact
- α^+ is the ionization probability to positive ions
- θ_m is the fractional concentration of m in the sample
- η is the transmission factor to the analyzer

A fundamental parameter is y_m , the yield of sputtered particles of species m (neutral or ionic) per primary particle impact. It increases with the primary flux, with the mass of the primary particle, its charge and its energy which is optimal between 5 and 50 keV and has a minimum threshold for sputtering between 20 and 40 eV. y_m also increases with the incident angle, which is optimal between 60° and 80° to the normal. In the case of atomic ions, the yield is also optimised as the mass of the primary particles increases, since the energy is deposited closer to the surface. This is not valid for bigger clusters since the penetration depth is proportional to momentum.

A second fundamental parameter of this equation describing the formation of the secondary ions is the ionisation probability. This parameter is significantly impacted

by the chemical state of the surface since it is highly influenced by the exchanges that take place between the surface and the departing species. The ionic yield of an element will vary for example by several orders of magnitude across the periodic table. It will also depend on whether that element is in a metal or its oxide as ionisation is strongly impacted by electronegativity.

Several types of secondary ions from organic materials can be formed depending on which mechanism takes place. Therefore, the formation of an odd electron ion M^+ is observed if the ejection of an electron happens; or the formation of $(M + H)^+$ $(M - H)^\pm$ ions if polar molecules undergo an acid-base reaction; or the cationisation or anionisation of neutral molecules and finally the fragmentation can also bring charges.

Collision-induced mechanisms would be at the origin of the ionisation of the different species, due to their direct interaction with the primary ion or energetic recoil atoms within the material. The precise location of ionisation is unknown but would take place on or just above the surface, at the so-called emission region.

1.5.3 Different analysis modes of the SIMS technique

SIMS exists in two different modes: static and dynamic. In fact, as already explained, the ionised part of the fragments is redirected to a time-of-flight mass analyser to discriminate the particles according to their mass/charge ratio. And depending on the particle flux of the incident beam, this technique can be used in dynamic mode, which consist in a profiling of the surface with a high ion flow (higher than 10^{14} ions/ cm^2). Or, as mentioned earlier, in static mode which consist in a analysis of the extreme surface, as already mentioned, with a low intensity flow (lower than 10^{13} ions/ cm^2). It allow to obtain a positive and negative spectra from a precise point of the surface. Therefore, what is interesting is that after analysing the extreme surface of a layer in static mode, it is possible to etch into the sample with a profiling beam to reach new underlying layers of the sample. It is not always necessary or desirable to dig to great depths, so sometimes the dynamic mode is used simply to refresh the surface, *i.e.* eliminate surface contamination, and not to dig into the sample.

With the ability to use an ion beam in either static or dynamic SIMS mode, it is possible to use two different primary ion beams and thus analyse the sample in several different ways. There are 4 main ways of analysis.

Surface Spectrometry

This is the most basic mode of analysis, in which a small area of the sample is scanned with the primary ion beam for a short time so that the analyser can generate

a spectrum after collecting the secondary ions. (The values generally used in this project are $250\mu m^2$ for the analysis area and 60s for the acquisition time).

Surface Imaging

This mode therefore consists of obtaining an image of the sample surface. To do so, the ion beam scans the surface which is divided into several small areas, each of which is briefly analysed. The data collected in this way is collated to provide a chemical map of the surface.

For a given mass, it is possible to track the intensity of secondary ions as a function of their position on the sample.

Depth profiling

It is for this mode that the interest of using 2 ion beams comes into play. The first is an analysis beam, of the LMIG type, identical to that used for the first two analysis modes. A frequently used element is Bismuth, in mono-atomic form or in small clusters of 3 or 5 atoms. The second, of the GCIB type, is used to dig into the surface. This allows the sample to be analysed in depth, a "layer by layer" analysis. In effect, the two beams are used alternately, to analyse and then dig to a new depth where a new analysis will be performed and so on. A frequently used element is Argon, in the form of large clusters of usually 1500 to 10000 atoms [60].

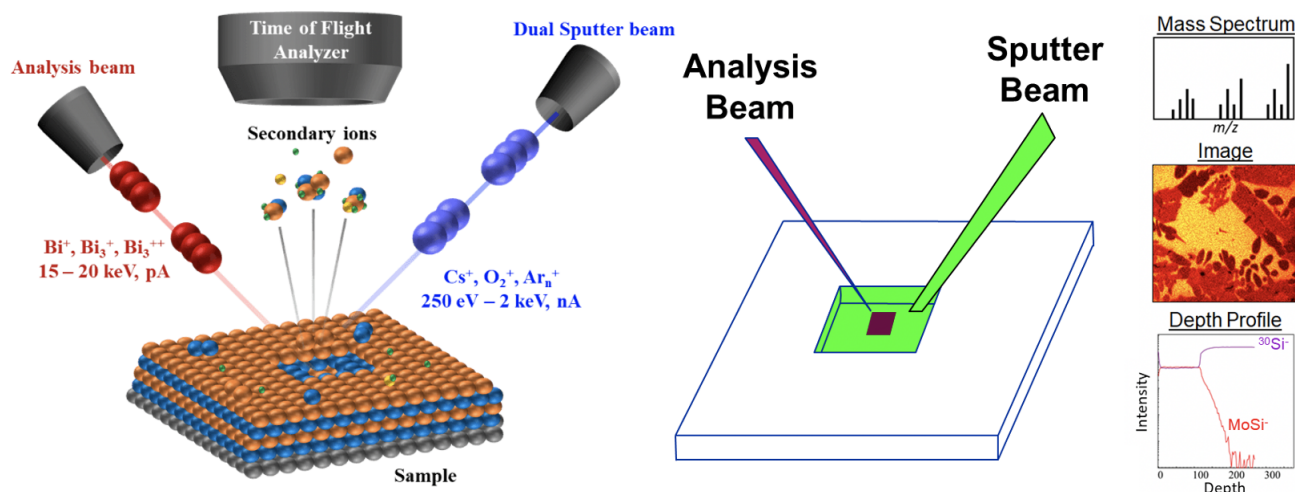


Figure 1.16: Depth profiling in SIMS [51] [52]

Concerning the different types and forms of primary ions that can be used for the primary beams, some important factors need to be raised.

As mentioned earlier, the distribution of energy in the material is influenced by the choice of the primary ions. Indeed the use of one type of primary ion in place of

another will have big impacts in term of energy distribution and thus modification of the surface. Its influenced mainly by their nature, energies and angle of incidence.

Over time, the types of primary ions used for profiling have evolved, passing through different types of mono-atomic, then by clusters, first of C_{60} and SF_5 then finally of argon and bismuth. Indeed, molecular profiling (without damage) works with Argon but also, to a lesser extent, with C_{60} or SF_5 . If there is an effect of cluster size, there is also one of mass matching for C_{60} and SF_5 , in fact, for organic profiling, the light atoms of C_{60} and SF_5 transfer their energy more easily and rapidly to the solid, this by Newtonian mechanics, the atomic masses being identical, the transfer of 100% of the energy is possible. These ions are then stopped very quickly in the solid and the damage created on the surface is pulverised and thus "cleaned" at each impact.

The great advantage of using Argon clusters, which range from 1500 to 10000 atoms, for profiling is that as there are many atoms in the cluster, the energy per atom is very low, which leads to few bond breaks and therefore a "soft" desorption of the surface.

On the contrary, for Bismuth the mass ratio is very unfavourable to energy transfer, they sink further into the solid and cause deep damage, this is well in the case of a large ions dose that would be used for profiling (in dynamic mode), which is not the case in static mode where the maximum dose is the static limit. It is therefore not possible to do molecular profiling with it.

On the other hand, the interest in using Bismuth clusters to compose the analytical ion beam lies in the fact that they have already been shown to have a high sputtering rate, thus allowing a large number of secondary species to be obtained. In addition, bismuth clusters are easy to manipulate, allowing for highly focused bismuth ion beams, which is of great use for the precise analysis of chemical compositions of a sample. It is this very precise focusing of the Bi beam that allows to obtain the very high spatial resolution that SIMS has today.

Thanks to the fact that the sources have evolved, this has allowed to significantly increase the analysis performance of the SIMS.

It is therefore to this GCIB beam that the SIMS technique owes its micro-destructive character. Indeed, this beam operates in dynamic mode, as described above, and thus the surface of the sample is eroded. On the other hand it is important to note that the layers below the eroded surface are not modified. There is only a loss of material that is operated but no modification of it.

Complete 3D analysis

3D analysis allows more complex samples to be studied by combining the previous modes. In effect, surface imaging and profiling are carried out in succession. First the analysis beam performs a 2D image of the surface after which the GCIB beam digs into the sample to obtain a 3D map. The features and defects of the sample can thus be clearly visualised in terms of their position, composition and shape.

1.5.4 Advantages and drawbacks of the technique

SIMS is a widely used method for its ability to determine the chemical composition of materials, as diverse as they are, whether homogeneous or inhomogeneous and whether inorganic or organic or a mixture of the two, and this with a very high sensitivity (until the ppm range) so very few elements are needed to detect them but also with a high lateral resolution. However, the analysis is not the same for each of the different types of materials. Indeed, the most accurate results are obtained by analysing inorganic, conductive and homogeneous materials. The performance of this technique depends on several factors. It depends on the nature of the sample analysed and its structure, the nature of the primary ions as well as their initial kinetic energies or the impact angles with respect to the target.

A disadvantage of the SIMS technique is that it is micro-destructive in dynamic mode, it is therefore neither a non-invasive method that does not require taking a sample, nor a non-destructive method that does not damage the sample taken. However, only a very small area of the sample is damaged by the ion beams, so it is often possible to re-use the sample for further analysis, depending on its size. Otherwise, a simple surface treatment, such as polishing, may be sufficient to allow further analysis, depending on the mode used.

Referring to the section [1.5.3](#) describing the static and dynamic modes, it is therefore understandable why after using the dynamic mode with a significant digging depth, a new sample will be required and a simple surface treatment will not be sufficient.

A second disadvantage of the technique that needs to be taken into account when preparing the samples is the vacuum compatibility of the samples, as the analyses are carried out at ultra high vacuum in a special chamber at about 10^{-9} mbar. Indeed, the whole process is carried out under ultra-high vacuum in order to avoid non-specific collisions with the gaseous molecules which could induce further fragmentation [\[58\]](#). First the sample is introduced in a decompression chamber (called a loadlock) where, depending on the sample, it can remain for several hours before reaching vacuum and entering the analysis chamber. Working under vacuum

can therefore have an impact on the surface of the sample because the longer it takes to reach sufficient pressure values, the more of the sample can be pumped out, depending on the volatility of the molecules on the surface (because if these molecules detach from the material they will increase the pressure and therefore the pumps will have to work harder to decrease this pressure).

Vacuum damage must therefore also be taken into account when re-using a sample.

It should also be noted that even with a sample that does not pose a problem at this level, there are frequently other problems that will appear during the analysis due to the sensitivity of the results to sample irregularities. But also to the contaminations which can have taken place on the sample and which occur very frequently, as already mentioned the peaks corresponding to these contaminations (mainly PDMS) might disrupt significantly the spectrum of the sample.

A problematic phenomenon that occurs when bombarding an insulating or even semiconducting sample is the increase of the surface potential due to the positive charge coming from the cation beam and the emission of secondary electrons. This accumulation of charge on the surface can deflect the primary beam and even modify the kinetic energy of the secondary ions, thus affecting the mass resolution. Indeed, this increase in kinetic energy can be so great that it exceeds the acceptance window of the analyser, resulting in a loss of the SIMS spectrum. In this case, it is therefore essential to use an electron floodgun, this consists of another gun which will bombard the surface with a weak current of electrons at low energies to avoid any damage to the surface but to compensate for the charges on it. However, the primary ion beam is frequently in pulsed form, the electrons must therefore be sent in a pulse train between the primary ion pulses.

Another aspect of the SIMS technique is its semi-quantitative nature. Indeed, since the probability of ionisation is strongly influenced by the matrix. It cannot immediately be concluded from the fact that the yield of a particular ion is greater than that of another, that this species is more present in the surface of the sample.

1.6 Objectives of the thesis

It has already been observed, through numerous studies notably mentioned in the section [1.2.1](#) and [1.4](#), that the interaction of the binder with pigments leads to changes in the original composition of the materials in the paint layers. Including the detachment of metal ions from the pigments that are introduced into the oil binder.

Although many studies have already been done to explain the formation of soaps following these observations, many new studies and confirmations are still needed.

Concerning oxalates, nothing has been done yet.

But it is also on the basis of these observations that the hypothesis put forward by the Metox project of pigment/binder interaction as the source of their formation, mentioned in section [1.2.2](#), was formulated. Thus this hypothesis is the one favoured for the moment in this project because it seems to be the most likely.

The objective now is to prove it, and try to determine where they form and what kind of oxalates and soaps form where. The spatial localisation is then very important. In order to do that, this work will try to determine the optimal analysis conditions to be able to detect what is being looked for. For example, how much etching is needed to detect what is being searched for, is it more optimal to do it in positive mode or in negative.

Concerning oxalates, an important aspect of this localisation is that it makes it possible to rule out the hypothesis of microorganisms. Indeed, although calcium oxalates are systematically found at the surface, other types of oxalates (copper oxalates for example) have been observed in depth and one hypothesis would therefore be that these oxalates are formed in depth but that there is a migration towards the surface. Indeed, thermodynamically speaking, calcium oxalate is very stable compared to others that may be observed. So there will be ion exchange mechanisms that will make the oxalate pass through different forms until it reaches the most stable form on the surface, which is calcium. This migration could be explained by the cleaning of the works of art, the solvents entering and leaving would carry with them numerous compounds during their passage in the pictorial layer.

It could also be explained by variations in humidity, as oxalate is very ionic it is attracted to water and can be solvated. So changes in humidity would cause the anion to gradually migrate and once on the surface it would come into contact with calcium, complex and stay there.

So to summarise, there would be the formation of copper/potassium oxalate etc in the lower layers as a result of pigment/binder interaction which comes up during restorations and changes in humidity which turns into calcium oxalate and remains on the surface as it is a very stable oxalate.

This highlights the difficulty of the restoration work as well as its validity, since it could be the origin of the mechanisms that trigger the formation of oxalate crusts on the surface. These could therefore be a natural protective layer. All these questions have not yet been answered, as this is the first project on the subject.

It is important to note that a great deal of analysis and research has already been carried out in this project by the various partners, using a number of techniques, each with its own strengths and weaknesses. Tof-SIMS is therefore one method among

others that attempts to provide as much interesting information as possible on the formation of these chemical compounds, using all the advantages and possibilities that are described in this work.

To cite the techniques that are currently working to detect oxalates and soaps in this project, there are: XRPD (in Synchrotron radiation or in reflection mode) which works only to detect crystalline metal oxalates and micro ATR-FTIR which allows to detect different types of crystalline and amorphous metal oxalates in paint samples and if cross-sections are used, to visualize their spatial distribution.

Tof-SIMS therefore represents the main contribution of UCLouvain as a partner in this vast project. This technique has many important advantages. Indeed, it allows to obtain both chemical, molecular and positional information. In fact, identification is made possible by a substance-specific "fingerprint" spectrum and the position is obtained thanks to the very good lateral resolution of the technique compared to other chemical analysis technique. Moreover, it is sensitive to both organic and inorganic compounds, which is a major contribution to the study of paints, which are mixtures of oils (organic compounds) and pigments (inorganic). Finally, the extreme sensitivity of the technique allows compounds, even present in very small concentrations (in the ppm or ppb range) to be measured.

SIMS is therefore an interesting additional tool to be able to confirm certain things that can be observed via the other methods, or to discover new ones.

2 Experimental Section

The experimental research carried out in this work can be separated into several distinct stages. Indeed, it is easy to understand that in order to be able to recognise what makes up the pictorial layers of a real painting, with all the complexities that it entails, and to be able to draw conclusions about the interactions between the different components, a progressive study seemed necessary.

Before starting to analyse samples of real paintings, a systematic and methodical study has been carried out for each of the main components of interest and then for different mixtures between them.

Firstly, pure powders of all the oxalates and soaps on which the project focuses were analysed. These were oxalates of copper, lead, zinc, potassium, calcium and cobalt. As well as the soaps corresponding to the same metal ions. The three soaps being stearate, palmitate and azelate.

In a second step, we analysed pure linseed oil. The choice of linseed oil was already explained in the introduction. This is the most commonly used oil at the time on which this work focuses and is found in each of the actual samples that were analysed.

After that we analysed mixtures between linseed oil and the different oxalates and soaps, called mock-ups.

Finally, three real samples were analysed, so that we could compare all our research with a concrete case.

It has already been observed in previous research (conducted by C.Poleunis, UCLouvain) that when pure compounds are analysed, very different observations are made depending on the metal ion concerned. For example, the mass spectrum obtained during the analysis of lead oxalate powders shows clear and distinct peaks for the oxalate in question, whereas in the spectrum of calcium oxalate, the peaks are hardly, if not at all, perceptible.

Since it has also been observed that as soon as this is mixed/dispersed in oil, the

results are strongly altered. Indeed, for example, in some cases only oxalate anions were observed and not the whole molecule.

As stated in section 1.6, this work will try to determine the optimal analysis conditions to be able to detect what is being looked for. For example, how much digging is needed to detect what is being searched for, is it more optimal to do it in positive ion mode or in negative, etc.

Once this will be determined for the mock-ups, the work will focus on real samples to see if it works as well or not, i.e. if our parameters are, to a certain extent, transposable from mock-ups to real samples.

2.1 Samples of pure oxalates and carboxylates powders

2.1.1 The samples: origin and preparation before analysis

All the materials analysed in this work come from the Royal Institute for Cultural Heritage of Belgium (KIK-IRPA). Their synthesis was therefore entirely directed within IRPA. The preparation steps required at the UCLouvain therefore only consisted of setting up the best way to introduce them into the machine.

Given that there were three different types of soaps: the stearates, the palmitates and the azelates, and also the oxalates. With six different metal ions for each. The number of powders to be analysed was supposed to be 24, but the cobalt azelate powder was missing from IRPA's supply, so the exact number was 23.

The preparation of the samples in UCLouvain consisted simply of spreading a small quantity of powder on a post-it and placing it between two polyacetal cylinders. Then the two cylinders were compressed using a hydraulic press to make the material adhere to the post-it as much as possible in order to limit its volatility during its handling and analysis.

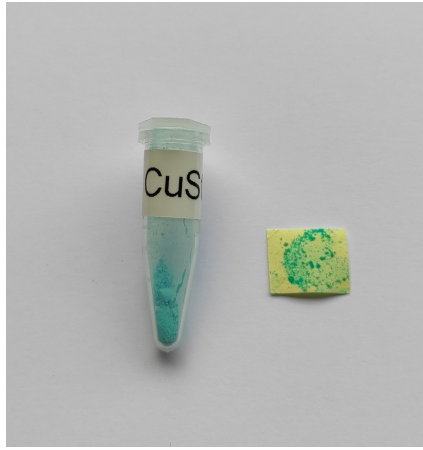


Figure 2.1: Images of pure powder samples

All these preparations were done with gloves, the handling of the post it with tweezers and the application of the powder with a tip. The tip and tweezers were cleaned with Isopropanol ($CH_3CHOHCH_3$) between each type of powder. The cylinders were also cleaned with Isopropanol between each powder. All this to avoid contamination as much as possible.

2.1.2 Experimental Settings of analysis

Before starting the analysis of any sample, it is essential to start by calculating the current of the different sources, at this stage only that of Bismuth. To do this, a Faraday cage is used and allows to directly analyze the ionic currents. The objective is to recover the electrons which are emitted by the surface to calculate only the current of Bismuth sent. Given that $I_{primary} = I_{Bi} + I_{e^-} + I_{photons}$, it is therefore necessary to turn off the light and the floodgun and to measure only the positive ions.

As shown on figure [2.2](#) the Faraday cage consists of an opening on the surface of the sample holder to allow the ions to enter and a closed cylinder in this hole. By applying a difference between the surface and the cylinder, secondary electrons are trapped[\[61\]](#).

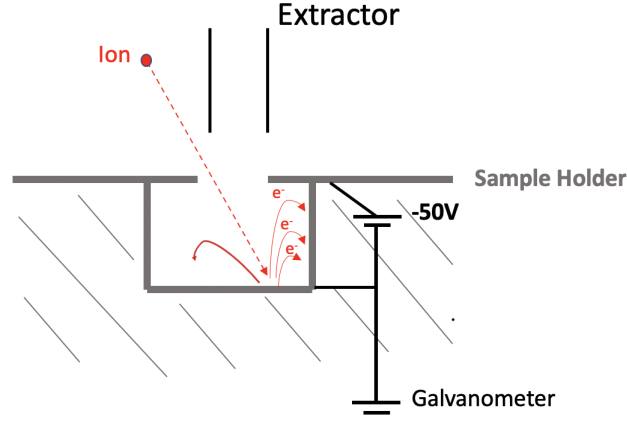


Figure 2.2: Figure of a Faraday cage

For the powder analysis, the as-prepared samples were placed in the Backmount sample holder and each sample was cleaned with a nitrogen gun. At this stage of the project, only the LMIG analysis beam is required for the analysis of these samples, so no profiling or imaging is required. The primary ion beam chosen is a Bismuth beam, it can be composed of ions or ion clusters. Indeed, there are several possibilities between Bi , Bi_3^+ , Bi_3^{++} or even Bi_5^+ and this was defined with the help of a temporal mass filter in the gun. The beam energy is 60 keV for the Bi_3^{++} beam and 30 keV for the others. If the choice of using Bismuth has already been explained in the section [1.5.3](#) of the introduction, the choice of beam (Bi_3^{++}) and the corresponding beam energy (60keV) is dictated by the achievable lateral resolution it offers, which is better with 60 keV than with 30 keV because the beam is much better focused. This is therefore very valuable in the context of imaging, which is particularly important for this work as many images of mock-ups and historical sections will be made to try to locate oxalates and soaps in our samples as best as possible. Indeed the reason behind this choice is not related to the fragmentation of the material or to a more or less soft analysis implied by the amount of energy transported per atom since whether the energy is 10 keV or 20 keV this energy always remains thousands of times higher than the binding energies within the material. However, this will not really be the case with Argon beams for profiling, as will be explained in the dedicated section [2.4](#).

Within the framework of this project, the choice was made to work with Bi_3^{++} throughout all the analyses in order to maintain consistency in the results obtained.

It is important to mention that the analysis of each of the powders was carried out in 3 different locations to confirm the results obtained. Which undoubtedly increased the total analysis time but ensured the validity of the results obtained, which was essential for the future.

It was also necessary to use the Floodgun because of the very insulating nature of the powders to allow compensation of the charges on the surface and to keep a desired potential difference. The voltage applied to the reflectors never remained constant throughout the measurements as each of the powders have different compositions and therefore different insulating behaviour. This is one of the reasons why the analysis of the powders was very time consuming, as not only was it necessary to adjust the charge compensation between each sample but also between each analysis, each sample being analysed in 3 different places. The thickness of the samples also varied, so the height of the sample holder had to be adjusted in relation to the surface between each analysis. When switching from one polarity to the other, it was necessary to be careful not to do this above the powders, by positioning oneself above the sample holder, as an electrostatic effect could suck particles from the sample. This would cause serious damage to the extractor.

All the SIMS experimental parameters of importance used in the analysis of pure oxalate and soaps powders are summarised in the table [2.1](#).

Table 2.1: Experimental conditions and settings for the ToF-SIMS measurements of powders

Primary ion gun	LMIG Bi_3^{++}
Primary beam energy	60 keV
Gun mode	HCB (High current bunched)
Primary ion current	Around 0.2-0.3 pA
PIDD (Primary Ion Dose Density)	Around 7.10^{10} (ions/ cm^2)
Analysed area	Generally $250 \mu m \times 250 \mu m$ or $300 \mu m \times 300 \mu m$ depending on the surface
Raster Size	128 by 128 pixels
Cycle time	100 μs
Angle of incidence	45°
Reflector Voltage	Between 200 and 500 V depending of the insulating nature of each powder
Flood gun energy	20 eV
Total acquisition time	60 seconds (interlaced mode)

In which the the primary ion dose density (PIDD) is calculated by:

$$PIDD = \frac{I_{(FC)} * t}{e * S_a} \quad (2.1)$$

Where:

- $I_{(FC)}$ = Current in the Faraday Cage

- t = time [s]
- $e = 1,6 \cdot 10^{-19}$ [A.s], the elementary charge
- S = Analyzed surface [cm^2]

2.2 Sample of pure linseed oil

2.2.1 The sample: origin and preparation before analysis

The preparation of the oil sample used as a signature for future analysis consisted simply of applying a free-standing film of linseed oil (Standoil 73200, Kremer Pigmente, Germany) on plexiglass.

2.2.2 Experimental Settings of analysis

From this stage on, the production of profiles began. As a reminder, the profiles consist of alternately digging and analysing the sample with two different ion beams. To obtain the evolution of the composition of the sample as a function of depth. So in order to dig into the sample, this requires the use of the Argon beam, called GCIB, in two different possible modes. Either to refresh the surface used during images taking between each analysis or to etch it in order to reach new layers of the sample used during profiling. As well as two LMIG modes Burst to send a high current during the profile for optimal identification but less good spatial resolution and HCB with a lower current for imaging, to increase the lateral resolution and keep a good mass resolution. This two modes will be detailed in the next section.

All the SIMS experimental parameters used in the obtaining of profiles and images of the sample of pure linseed oil are the same as those used for mock-ups and are thus summarised in Tables [2.2](#) and [2.2](#) in the following section.

2.3 Mock-ups

2.3.1 The samples: origin and preparation before analysis

Two types of mock-up samples were analyzed: (i) free-standing films applied on plexiglass, which will be called slides in the rest of this work; and (ii) cross-sections produced with fragments of these films (see Figure [2.3](#)). In both cases, sample preparation was performed at KIK-IRPA.



Figure 2.3: Images of a slide (on the left) and the corresponding cross-section (on the right)

In order to produce mock-up samples of type (i), pure oxalate and metal soaps powders were dispersed in linseed oil (Standoil 73200, Kremer Pigmente, Germany). The powder and oil were mixed together in a small agate mortar and applied on 5 pieces of square-cut plexiglass lined up in a row and fastened on a glass slide with double sided tape. Samples dried in open air for about 6 weeks in the dark. This form allows only one layer of the sample to be analysed at a time, the surface layer but it also offers a very large analysis surface and therefore the possibility of repeating the analysis to confirm the results.

Afterwards, in order to produce type (ii) mock-up samples, small pieces of the dried films were embedded with Technovit 2000® LC resin (Kulzer, Germany) and polished in order to produce cross-sections.

This form allow not only the study of the structure of the layers but also the characterisation of the components of each layer. However, the difficulty lies in the limited analysis space available, as the depth of the slides, the width of the cross-sections, is a few hundred of μm .

This makes as many mock-ups as twice the number of oxalates and soaps analysed in the form of pure powders, i.e. 46.

2.3.2 Experimental Settings of analysis

All the SIMS experimental parameters used in the obtaining of profiles of mock-ups are summarised in the table [2.2](#).

Table 2.2: Experimental conditions and settings for the ToF-SIMS measurements of mock-ups

Primary ion gun of analysis	LMIG Bi_3^{++}
Primary ion gun of sputtering	GCIB Ar_{3000}^+
Primary analysis beam energy	60 keV
Primary sputtering beam energy	10 keV
Gun mode	HCB (High current bunched)
LMIG primary ion current	Around 0.12 pA
GCIB primary ion current	Around 5 nA
PIDD of LMIG	Around 2.10^{11} (ions/ cm^2)
PIDD of GCIB	very variable between 1.10^{10} and 5.10^{15} (ions/ cm^2)
Analysed area	$200\mu m \times 200\mu m$
Sputtered area	$600\mu m \times 600\mu m$
Raster size	128 by 128 pixels
Cycle time	$200 \mu s$
Angle of incidence	45°
Reflector Voltage	Between 200 and 500 V depending of the insulating nature of each powder
Flood gun energy	20 eV
Total acquisition time	15s (non-interlaced mode)

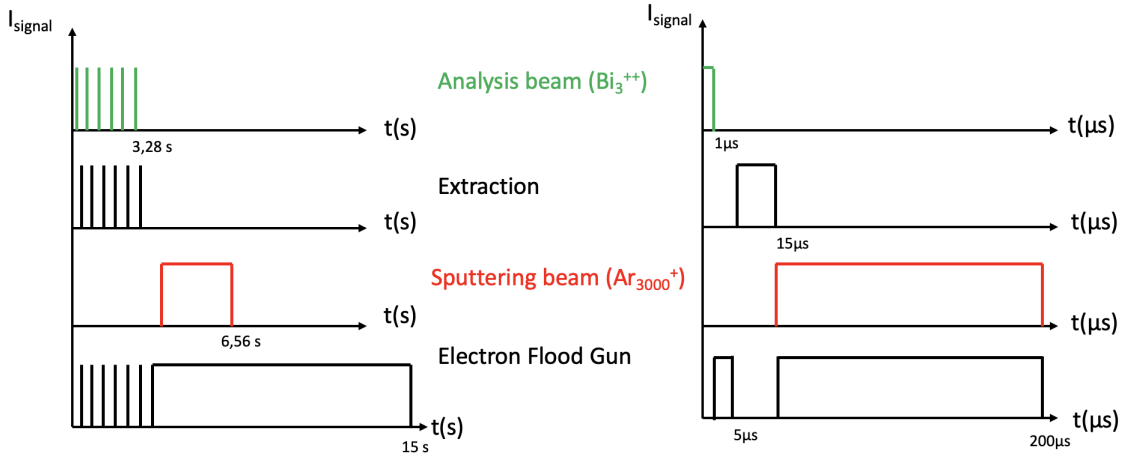


Figure 2.4: Non-interlaced (on the left) and interlaced (on the right) modes for profiling

Once working in the dynamic mode using two primary ion beams, one for analysis and one for sputtering, there are two different modes that allow to choose the best use of these two beams. The first and most commonly used mode is the non-interlaced mode, which consists of first analysing the surface with the pulsed LMIG, then digging with the GCIB, each for the same amount of time, after which the electron

gun is triggered to bring the surface potential back to its desired value. In the case of the different profiles carried out in this work, the duration of each phase remained unchanged, with the values as shown in the figure [2.4](#). However, one sample was an exception during the analyses, its insulating behaviour was too different from the others, so the duration of the electron gun phase had to be extended, alongside the total acquisition time.

In the imaging mode, the non-interlaced mode was also employed. However, the total acquisition times were much longer since imaging requires a much longer analysis time and thus, a much longer charge compensation time. The sputtering time is then the same as the analysis time, but with a much lower sputtering current, so it is just a simple refresh of the surface and no etching.

The second mode consists almost exclusively of the use of the GCIB, with the aim of digging very quickly to reach a certain depth in the sample. With this mode, problems of charges will appear (since our samples are insulating). And a non-representative spectrum is obtained, with peaks that are always shifted because the voltage at the reflector is not good since the electron gun is always used at the same time as the surface is bombarded with the GCIB and never alone, as shown on figure [2.4](#), and the voltage at the surface therefore does not have time to stabilise.

This mode is therefore interesting to use after having carried out a first analysis in non-interlaced mode, thanks to which it will be possible to obtain a very precise spectrum at each sputtering layer and thus be able to determine at what depth the conditions of interest are met. Then on another part of the sample, with the interlaced mode, it is possible to dig very quickly to this predefined depth and carry out the desired analyses.

It was therefore initially decided to use this interlaced mode in this work but, as will be presented in the results section, the optimal depth in the samples at which the images were taken was not very deep. In the interests of efficiency, it was therefore decided that it was not useful to use this mode as it would have saved very little time in reaching the desired depth and on the other hand would have wasted more time in moving from one mode to the other.

All the SIMS experimental parameters used in the obtaining of images of mock-ups are summarised in the table [2.3](#).

Table 2.3: Experimental conditions and settings for the ToF-SIMS measurements of mock-ups

Primary ion gun of analysis	LMIG Bi_3^{++}
Primary ion gun of sputtering	GCIB Ar_{3000}^+
Primary analysis beam energy	60 keV
Primary sputtering beam energy	10 keV
Gun mode	Burst alignment mode
LMIG primary ion current	Around 0.001 pA
GCIB primary ion current	Around 5 pA
PIDD of LMIG	Around $2 \cdot 10^{10}$ (ions/ cm^2)
PIDD of GCIB	between $8 \cdot 10^{11}$ and $2 \cdot 10^{13}$ (ions/ cm^2)
Analysed area	200 μm x 200 μm
Sputtered area	600 μm x 600 μm
Raster size	1024 by 1024 pixels
Cycle time	100 μs
Angle of incidence	45°
Reflector Voltage	Between 200 and 500 V depending of the insulating nature of each powder
Flood gun energy	20 eV
Total acquisition time	116.58s (non-interlaced mode)

The HCB and Burst modes mentioned above refer to the two different ion source operating modes used for imaging and profiling. HCB refers to 'High Current Bunched mode', which is a mode that provides moderate 1-2 μm focusing of the primary ion beam and high mass resolution due to ion pulses of less than 1ns (the Bi_3^{++} primary ion pulse current being about 3 pA for powders and 12 pA for the rest at a frequency of 10kHz). For more details, Publication [\[45\]](#) describes in detail the mass calibration and the accuracy of a few ppm obtained.

The important point is that due to this high mass resolution this mode allows accurate identification of compounds.

Next to this, the Burst alignment mode provides high spatial resolution at the expense of mass resolution. The focus of the primary ion beam is about 400 nm due to the much longer pulse duration of about 30 ns. Indeed the longer the pulse duration the lower the mass resolution (the Bi_3^{++} current used in the analyses is 0.001pA at a frequency of 10kHz). The lateral resolution has therefore increased from a few micrometers to several hundred nanometers, this operating mode is used to locate components with precision.

These explanations allow us to understand why the Burst mode is chosen to make

the most precise images of the sample and why the HCB mode is used to characterise the sample as best as possible during the profiles to determine the precise evolution of each compounds.

Concerning the analysis of the powders, imaging was not of interest and therefore only the HCB mode was used to allow a good characterisation of the spectrum and thus to identify precisely the samples that would serve as signature for future analysis.

Concerning the use of Argon for the GCIB beam, contrary to what has been seen regarding the choice of the Bi analysis beam, the energy per atom dictates the choice of Ar clusters for sputtering/depth profiling, in order to manage the desired etching rate. Since effectively depending on the beam energy and the number of atoms in the cluster (varying from 1500 to 10000) the energy per atom will vary significantly and this will lead to a more or less "soft" desorption of the surface.

2.4 Real samples

2.4.1 The samples: origin and preparation before analysis

Historical cross-section sample preparation was performed at KIK-IRPA. Micrometric historical samples were taken from the selected paintings using a scalpel. They were then embedded in a resin (Technovit 2000® LC resin, Kulzer, Germany) and polished in order to produce cross-sections.

The number of historical cross-sections provided by IRPA is 5, corresponding to four different paintings by different masters and from different periods. Firstly, two samples comes from the polyptych of the "Adoration of the Mystic Lamb" by Hubert and Jan van Eyck, that can be seen on Figure [2.5](#) completed in 1432.



Figure 2.5: Image of the painting from which two historical samples were taken [\[43\]](#)

Secondly, it is a work of art by the master of the Mansi Magdalene, entitled "Adam and Eve" and completed in 1520, as shown on Figure [2.6](#).



Figure 2.6: Image of the painting from which one historical sample was taken [\[44\]](#)

Thirdly, a sample of the painting "Les sept joies de la vierge" by Blondeel, completed in 1540.

And lastly, a sample of a painting by Jacob Jordaens, "Deploration of Christ", completed in the XVIIth century, between 1620 and 1623.

These 4 paintings cover the 3 centuries on which the Metox project focuses.

Each of these samples was chosen by IRPA because they were able to detect soaps or oxalates in them. Mainly Calcium oxalates as they are the ones they most frequently detect but also to a lesser extent some Copper soaps and oxalates.

Concerning photos of the samples that will be presented in the section [3.4](#) of the results. Optical microscopy, under polarized light and ultraviolet radiation, was performed by Martina Stillhammerova at KIK-IRPA using an Axio Imager M1 optical microscope (Zeiss, Oberkochen, Germany) under white polarized light and UV illumination (excitation band-pass filter from 390-420 nm) with magnification up to 500 x.

2.4.2 Experimental Settings of analysis

The experimental SIMS parameters used to obtain the profiles and images of the historical cross-sections are the same as those used for the mock-ups presented in the previous section summarised in Tables [2.2](#) and [2.3](#).

Except for the area analysed of one of the samples from the mystic lamb, the results of which are presented in section [3.4](#) of the results section. The area analysed had to be reduced to $150 \times 150 \mu m^2$ due to the limited space available on this sample, as detailed in section [3.4](#).

3 Results and Discussion

3.1 Analysis of pure oxalates and soaps powders

3.1.1 The interest of isotopic abundance

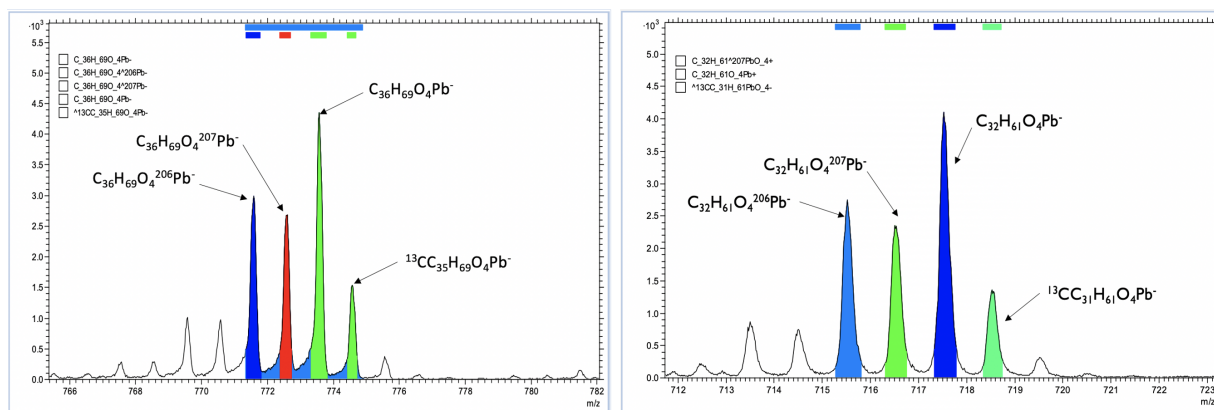


Figure 3.1: Peaks of Lead Stearate($C_{32}H_{62}O_4Pb$) and Lead Palmitate ($C_{36}H_{70}O_4Pb$) in negative ion mode

To begin with, it is interesting to highlight some of the most interesting and representative parts of the spectra obtained from the analysis of all the powders mentioned in the experimental section [2.1](#). Thus, the peaks selected in the figures [3.1](#) and [3.2](#) are representing compounds containing lead and copper. Indeed, the shape of these peaks is characteristic of lead and copper based compounds. The presence of the different isotopes of the metal ion in question, as well as that of Carbon, can be seen.

This highlights the great interest of isotopic abundance, which lies in the ease with which peaks can be associated with great certainty with the compound to which they appear to correspond. Indeed, there is a large number of possible molecules that can produce each of the different m/z peaks observed in a typical ToF-SIMS spectrum.

Isotopic abundance therefore makes it much easier to recognise the areas that have a characteristic appearance when analysing a spectrum, and thus to be able to

carry out the most detailed and precise characterisation of our sample.

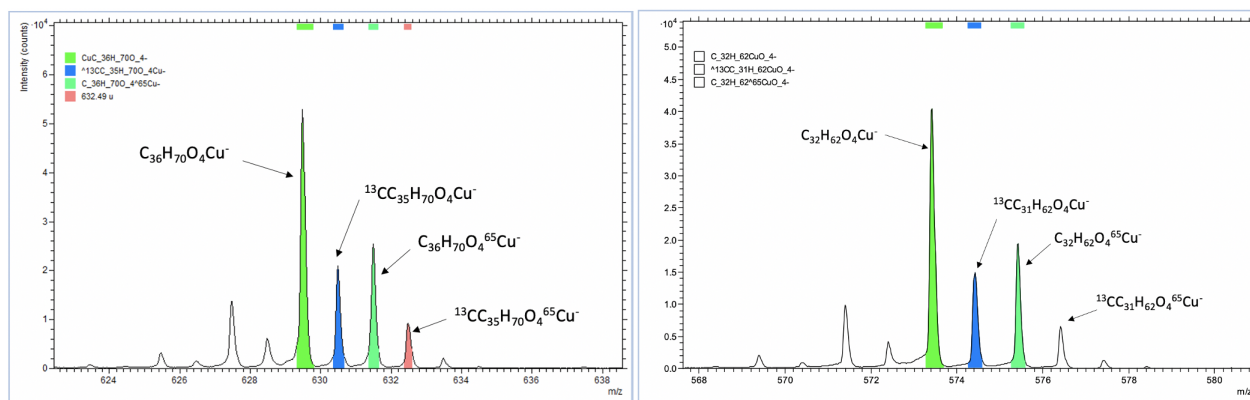


Figure 3.2: Peaks of Copper Stearate($C_{36}H_{70}O_4Cu$) and Copper Palmitate ($C_{32}H_{62}O_4Cu$) in negative ion mode

Table 3.1 shows the isotopes that were considered in the results for copper and lead, as well as for other metal ions. These are the isotopes that have a significant impact on the results, cobalt being monoisotopic.

Table 3.1: Main isotopes of the different metal ions

Lead	Zinc	Copper	Potassium	Calcium	Cobalt
206	64	63	39	40	60
207	66	65	41		
208	68				

3.1.2 Precise identification of the mass spectrum

Accurate identification of the mass spectra of pure powders is of great value in understanding the fragmentation pattern of oxalates and soaps in order to use them as guides for the analysis of fragments of more complex samples, both in positive and negative modes. Indeed, the observation of certain patterns in pure powders makes it possible to predict in which form they are likely to be found once dispersed in an oil matrix, such as found in the mock-up or historical samples. For example, for oxalate powders in the negative mode it was observed that oxalate is always found as an anion, i.e. $C_2O_4H^-$, and moreover with a peak intensity generally higher than that of the complete oxalate peak. On the other hand, in the positive mode, oxalates are almost not observed. The peaks that can be assumed to correspond are of very low intensity and are the peaks of the complete form $C_2O_4M^+$ and with one less oxygen for Pb and Cu, $C_2O_3M^+$. Concerning soaps, as already mentioned in the previous point, it is the deprotonated form of the compounds that is mostly

found in negative mode and the protonated one in positive mode. As well as the corresponding single fatty acid, thus in deprotonated form, following the dissociation of the metal ion with the fatty acids attached to it.

3.1.3 Global summary of the results and its implications

Overview Tables (of the entire compound)							
Stéarates	I/Itot	Azélates	I/Itot	Palmitates	I/Itot	Oxalates	I/Itot
CaSt	/	CaAz	0.08%	CaPal	/	CaOx	0.06%
CoSt	0.14%	CoAz	Unknown	CoPal	0.52%	CoOx	0.02%
CuSt	4.69%	CuAz	0.53%	CuPal	3.7%	CuOx	0.20%
KSt	/	KAz	7.84%	KPal	0.4%	KOx	0.16%
PbSt	0.59%	PbAz	0.79%	PbPal	0.71%	PbOx	7.24%
ZnSt	0.08%	ZnAz	0.07%	ZnPal	0.12%	ZnOx	0.15%

Figure 3.3: Summary of the results of analysis of pure powders of oxalates/soaps in the negative ion mode for the full compound

Table 3.3 shows the intensity values of the peaks corresponding to the full compound (metal ion + organic anion) in the negative mode, so in the deprotonated form, of the different oxalates and soaps for each of the powders. The intensities being normalized to the total intensity of the spectrum. The values therefore represent the total part of the spectrum represented by the whole oxalate or soap molecule.

These results confirm what had already been observed during analyses carried out by C.Poleunis. The analysis of pure compounds highlights the strong differences that exist in the detection of the various oxalates and soaps. For example, while those containing lead are generally well observed, those containing calcium are much less easily, if at all, observed by SIMS analysis.

This could be due to the ionisation probability of the different metal ions or of the whole molecules or to the strength of the fatty acid/metal ion interactions which vary according to the metal ion concerned.

As with the previous summary table, the isotopic abundance has been taken into account, at least for the main isotopes, which have a significant impact on the final values obtained.

The table 3.2 aims to show that metal ions alone are very well detected by SIMS in pure samples, in order to try to understand why they are not as well detected in

Table 3.2: Summary of the results of analysis of pure powders of oxalates/soaps in the positive ion mode for the metal ions

	I/Itot			
	Stearates	Azelates	Palmitates	Oxalates
Ca^+	4.53%	18%	5.82%	19.14%
Co^+	1.75%		3.14%	8.56%
Cu^+	1.50%	6.14%	2.2%	8.19%
K^+	25.34%	10.2%	24.58%	20.92%
Pb^+	9.64%	15.29%	9.47%	12.47%
Zn^+	0.55%	2.88%	0.73%	9.53%

the mock-ups. Indeed two main reasons seem to be possible: the low concentration (of the compounds of interest) in the sample and the interference of the mixing of the compounds with the oil on the ionisation probability of the compound, *i.e.* the matrix effect already discussed in the section 1.5.1. Since it is certain that its behaviour is totally modified after interaction with the oil because of the very complex behaviour of the oil, due to the large number of parameters that influence the hydrolysis and oxidation of the oil during its use and ageing, as discussed in the section 1.1.2 of the introduction.

What is also fairly straightforward from the table 3.2 is the big difference between the detection of calcium alone which is very good and the corresponding oxalate and soaps which are very bad. As far as zinc is concerned, it was already the weakest metal ion detected so it could be expected that the corresponding oxalate and soaps would be equally poorly detected. Besides this, there are examples of copper and lead which are well detected on their own and in the same way they are detected when attached to a fatty acid.

Finally, it was on the basis of the analysis of these pure powders that we were able to decide which samples to continue working with. Since it was impossible to analyse all the samples provided by IRPA. Because of the availability of the machine and the number of days that the first analyses have already taken.

Thus, taking into account all the results obtained for the 4 types of samples presented in the figure 3.3, the interest of the analysis of the Lead samples appeared to be obvious, with a marked interest for the Lead oxalates. After that, Copper also appeared promising for all 4 results, with less interest this time for Copper oxalates. Then, even though the Calcium powders showed weak or non-existent pseudomolecular peaks and therefore not very promising, it was decided to further analyse the mock-ups containing Calcium. The reason for this was IRPA's interest in these oxalates, which are very frequently observed using ATR-FTIR in a large majority of paintings (mainly at the surface as already mentioned).

Finally, the intensities corresponding to the samples containing cobalt, potassium and zinc were quite comparable and all of them was of great interest to IRPA. However, a choice had to be made and it was zinc which is currently of very high interest for two reasons. Firstly for future experiments of the MetOx project in which zinc white (a pigment) will be used given it quickly reacts to forms soaps and oxalates under particular ageing conditions (as presented in [15]). Secondly because of current research interests at IRPA concerning the use of zinc driers in the early oil paintings from the Flemish primitives, especially Van Eyck ([15]). Indeed the original zinc driers have transformed into zinc soaps and oxalates. Furthermore, zinc was chosen because one of the data for cobalt was missing (Cobalt Azelate) and Potassium Stearate gave no results.

It was also decided to focus on the oxalates and two of the three soaps samples, leaving out the palmitates samples. However, in the end, the complete analysis for the 4 selected metal ions was only performed for oxalates and stearates. For azelates, only lead azelate could be analysed. Due to lack of availability of the machine.

An important question that needs to be answered concerns the appropriateness of the contribution of positive ion-mode analysis. Since the main compounds of interest that are observed are in negative mode (most often deprotonated) and that avoiding positive mode analysis would save half the analysis time. But even if the contribution of the positive mode is much less important than that of the negative mode, it is essential to be able to clearly observe the positively charged metal ions. And this will continue to be the case for all the analyses in the project, as the localisation of these cations is important in trying to understand the changes that take place within the samples.

To access all the results obtained from the analysis of the different powders, please refer to section [6.2](#) of the annexes.

3.2 Analysis of pure linseed oil

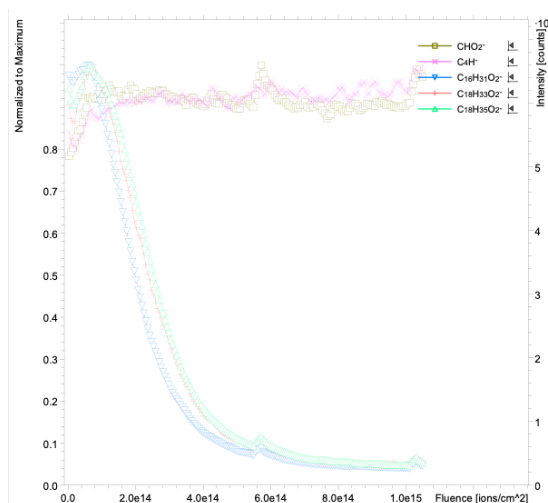


Figure 3.4: Profile of pure refined linseed oil in negative mode

Figure 3.4 shows the evolution of the chemical composition of the pure oil sample as a function of depth. In reality, the units used for the abscissa axis are not units of depth (μm) but of fluence (ions/cm^2). Indeed, for all the profiles carried out in the framework of this thesis, it was not possible to linearly transform the fluence into a depth scale since the samples analysed are not homogeneous, the etching rate was therefore not linear since each layer of the sample has a different composition. In the case of this pure oil sample this could have been considered but for consistency and comparison with the rest of the work the same units were kept.

As can be seen on Figure 3.4, there is a drastic drop in the signal intensity for different constituent acids of the oil. The intensity of the characteristic oil peaks drops by a factor of 10 with depth before reaching a plateau. This is particularly noticeable when compared with oil fragments (such as COOH^- and C_4H^-) which maintain a constant concentration with depth. The same trends are observed in the positive mode.

The disappearance of complete fatty acids from the oil with depth is a phenomenon that will continue to be observed throughout the analysis of samples containing oil. The explanation seems to be that the oily polymeric network is formed in depth and that the free fatty acids, not crosslinked to the network or resulting from the degradation reactions of this network migrate towards the surface, due to their high mobility, their low molecular weight and the rigidity of the oily network which expels them.

With regard to the fatty acids represented in the above profile, a choice had to be made for the sake of clarity of the graph, but other fatty acid peaks characteristic

of the oil were indeed measured in the analyses. The peaks shown in this profile are those with the greatest intensity and therefore for which there is the greatest certainty of identification.

Indeed, below is the complete list of all these peaks, which had already been established during Batardy's research ([1]) and which was also confirmed during the analysis of the spectra in the framework of this thesis. As is directly observable, the number of characteristic peaks is much greater in the positive ion mode but much less intense in general.

3.2.1 Characteristic Oil ion peaks observed [1] [20]

In positive ion mode:

The large number of hydrocarbon fragments observed at small masses (below m/z 100), derived from larger molecules present in the oil are not specific enough to be meaningful. Fatty acids are visible in the positive ion spectrum through two different types of fragments: a protonated form (through the addition of a hydrogen atom $[RCOOH + H]^+$) and a acylium ion form (trough the substraction of OH $[RCOOH - OH]^+$). Following fragments have been observed:

- acylium ions of the dicarboxylic suberic ($C_8H_{13}O_3^+$), azelaic ($C_9H_{15}O_3^+$) and sebacic ($C_{10}H_{17}O_3^+$) acids (at m/z 157, 171 and 185),
- acylium ions of the saturated palmitic ($C_{16}H_{31}O^+$) and stearic ($C_{18}H_{35}O^+$) acids (at m/z 239 and 267),
- protonated ions of the saturated palmitic ($C_{16}H_{33}O_2^+$) and stearic ($C_{18}H_{37}O_2^+$) acids (at m/z 257 and 285),
- acylium ions of unsaturated linoleic ($C_{18}H_{31}O^+$), linolenic ($C_{18}H_{29}O^+$) and oleic ($C_{18}H_{33}O^+$) acids (at m/z 263, 261 and 265),
- protonated ions of unsaturated linolenic ($C_{18}H_{31}O_2^+$), linoleic ($C_{18}H_{33}O_2^+$) and oleic ($C_{18}H_{35}O_2^+$) acids (at m/z 279, 281 and 283),
- acylium ions of monoglycerides (or monoacylglycerols) of azelaic ($C_{12}H_{21}O_5^+$), palmitoleic ($C_{19}H_{35}O_3^+$), palmitic ($C_{19}H_{37}O_3^+$), linoleic ($C_{21}H_{37}O_3^+$), oleic ($C_{21}H_{39}O_3^+$) and stearic($C_{21}H_{41}O_3^+$) acid (at m/z 245, 311, 313, 337, 339 and 341),
- acylium ions of diglycerides (or diacylglycerols) of palmitic acid on one branch and suberic ($C_{27}H_{49}O_6^+$), azelaic ($C_{28}H_{51}O_6^+$), sebacic ($C_{29}H_{53}O_6^+$), palmitic ($C_{35}H_{67}O_4^+$), linoleic ($C_{37}H_{67}O_4^+$), oleic ($C_{37}H_{69}O_4^+$) and stearic ($C_{37}H_{71}O_4^+$) acid on the other (at m/z 469, 483, 497, 551.5, 575.5, 577.5, 579.5),

- acylium ions of diglycerides of stearic acid on one branch and suberic ($C_{29}H_{53}O_6^+$), azelaic ($C_{30}H_{55}O_6^+$), linolenic ($C_{39}H_{69}O_4^+$), linoleic ($C_{39}H_{71}O_4^+$), oleic ($C_{39}H_{73}O_4^+$) and stearic ($C_{39}H_{75}O_4^+$) acid on the other (at m/z 497, 511, 601.5, 603.5, 605.5 and 607.5),
- acylium ions of diglycerides with linolenic acid on one branch and linolenic ($C_{39}H_{63}O_4^+$) and oleic ($C_{39}H_{67}O_4^+$) acid on the other (at m/z 595.5 and 599.5),
- acylium ions of diglyceride with linoleic acids on both branches ($C_{39}H_{67}O_4^+$) (at m/z 599.5)

In negative ion mode:

Fatty acids are visible in the negative ion spectrum through two different types of fragments: a deprotonated form (through the loss of a hydrogen atom: $[RCOOH - H]^-$) and aliphatic chain fragments, which are visible in ions of the type $C_2H_3(CH_2)_xCOO^-$. Following fragments have been observed:

- deprotonated ions of octanoic ($C_8H_{16}O_2$), nonanoic ($C_9H_{18}O_2$) and decanoic acid ($C_{10}H_{20}O_2$) ($C_8H_{15}O_2^-$, $C_9H_{17}O_2^-$ and $C_{10}H_{19}O_2^-$ at m/z 143, 157 and 171). These short chains are products of oxidation and degradation processes, but these could also correspond to larger molecules that have fragmented during the ionisation process,
- deprotonated ions of aliphatic chain fragments of fatty acids from the type $C_2H_3(CH_2)_xCOO^-$, separated by 14 amu. We observed fragments for x ranging from 0 to 12 (at m/z 71, 85, 99, 113, 127, 141, 155, 169, 183, 197, 211, 225 and 239),
- deprotonated ions of dicarboxylic suberic ($C_8H_{13}O_4^-$) and azelaic ($C_9H_{15}O_4^-$) acids (at m/z 173 and 187),
- deprotonated ions of saturated palmitic ($C_{16}H_{31}O_2^-$) and stearic ($C_{18}H_{35}O_2^-$) acids (at m/z 255 and 283),
- deprotonated ions of unsaturated palmitoleic ($C_{16}H_{29}O_2^-$), linolenic ($C_{18}H_{29}O_2^-$), linoleic ($C_{18}H_{31}O_2^-$) and oleic ($C_{18}H_{33}O_2^-$) acids (at m/z 253, 277, 279 and 281).

If all the characteristic fatty acids of the oil described above were taken into account in the profiles, this would result in unreadable profiles, as is the case in Figure [3.5](#). Therefore, only a few main peaks will be presented in the profiles in the following pages.

In addition to this concern for clarity, the profiles have the same evolutions and those with the smallest drops correspond to the rarest forms of the fatty acids.

The most abundant forms that will be represented in the profiles are the protonated forms of palmitic, stearic and oleic acids.

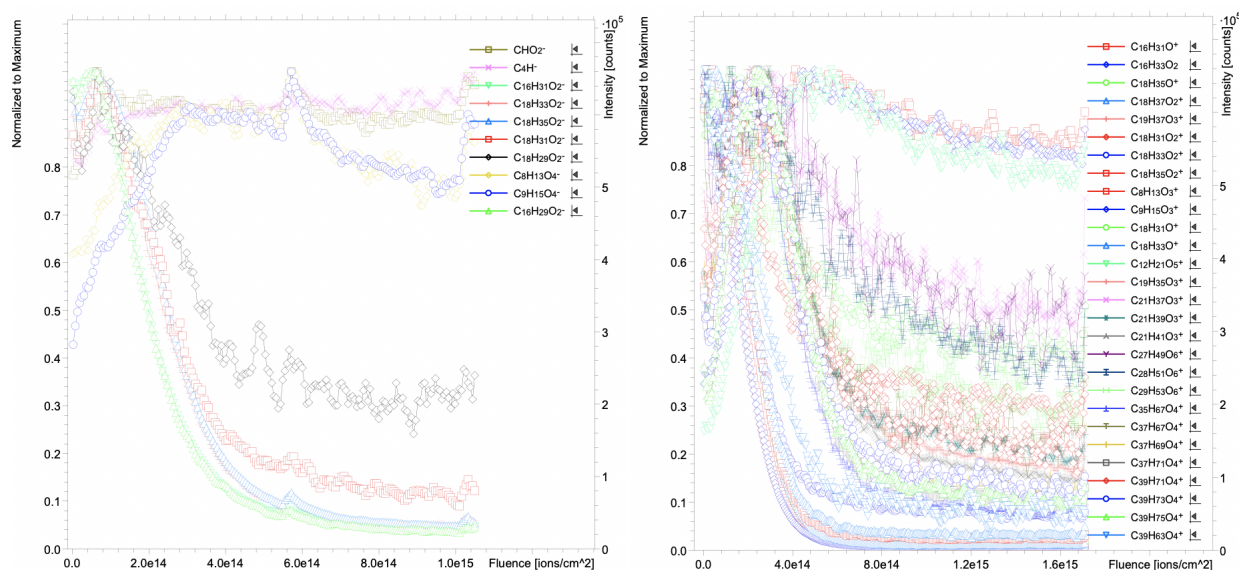


Figure 3.5: Overloaded profile of pure refined linseed oil in negative mode (on the left) and positive mode (on the right)

3.3 Analysis of mock-ups

This section will present only the most interesting and conclusive results. However, most of the results obtained in this thesis can be found in the section [6.3](#) of the annexes.

3.3.1 Slides of oil mixed with oxalates and soaps

For the analysis of the mock-ups, given that a significant drop in oil signals was observed with depth for the pure oil samples, it was first decided to analyse all our samples at the surface.

Indeed, the analyses that had been carried out previously by C. Poleunis had been done very deep in the samples where no oil signals were observed. C.Poleunis' objective was to etch deep enough to avoid being disturbed by the presence of PMMA dust which, during the polishing process, enters the cracks present on the surface of the samples, either naturally induced or induced by the vacuum damage suffered after previous SIMS analyses. This did not seem ideal in the context of this work, which is looking for links between the degradation of oil and the formation of certain chemical compounds that result from it.

It took several analyses to realise that while the oil signals were very well observed on the surface, the rest of the compounds of interest were only slightly observed.

A different analytical approach was therefore developed from this point onwards and for further analysis. It consisted in digging slightly into the sample to reach the maximum intensity value of the different compounds of interest (oxalates, soaps or metal ions), which are more or less the same, while allowing to keep a certain intensity of the fatty acids characteristic of the oil (however much lower than on the surface obviously). This can be observed in Figure 3.7 for the mock-up of lead azelate for which the total profile is presented in Figure 3.6. Indeed Figure 3.7 represents what will be called a "limited profile", which therefore represents how far it was excavated to reach the depth that seemed ideal for the analyses in the sample.

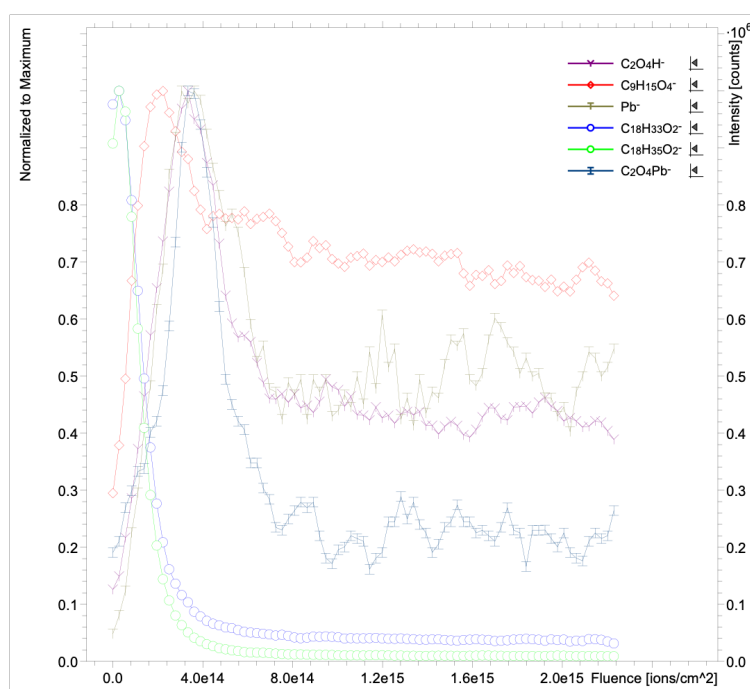


Figure 3.6: Profile of Slide of oil mixed with Lead Azelate in Negative mode

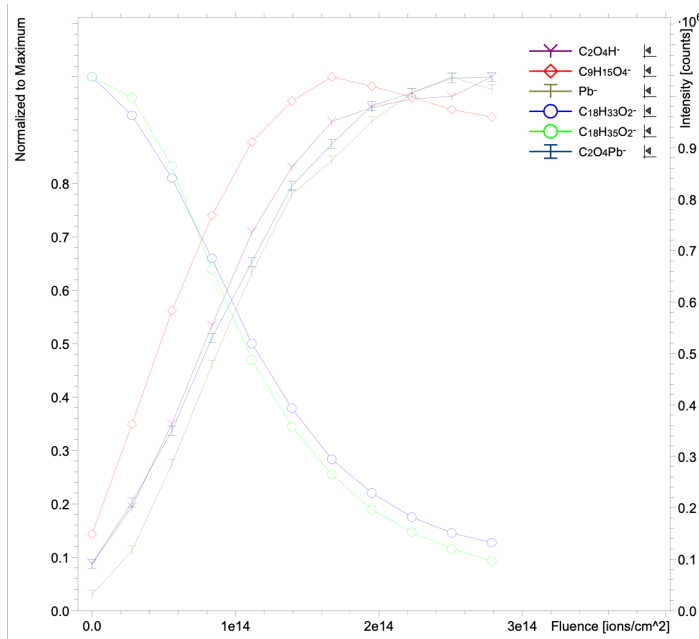


Figure 3.7: Limited profile of Slide of oil mixed with Lead Azelate in Negative mode

The number of scans (i.e. the number of etching intervals according to the non-interlaced mode described in the experimental part section 2.4) required to dig to the "optimal" depth was obviously not the same for each sample, so a profile was always done before images were taken in a sample. To be precise, for each of the analyses carried out on the slides, 3 profiles were carried out at different places to confirm the accuracy of the results obtained and to make sure not to have fallen on a particular zone not representative of the sample. After that, the limited profile could be made and then the images taken.

Another example is the profile of the lead stearate slide, shown in figure 3.8, where again a sharp drop in the oil signals and a peak in the characteristic oxalate, azelate and metal ion signals can be seen. The difference is that for the first example both palmitic and stearic acid drop drastically, whereas for the lead stearate slide stearic acid reached a plateau at much higher values. These stearic acids are therefore either derived from the degradation of the oily polymer and are about to associate with a metal ion or possibly from the dissociation of a metal stearate and are about to reach the surface.

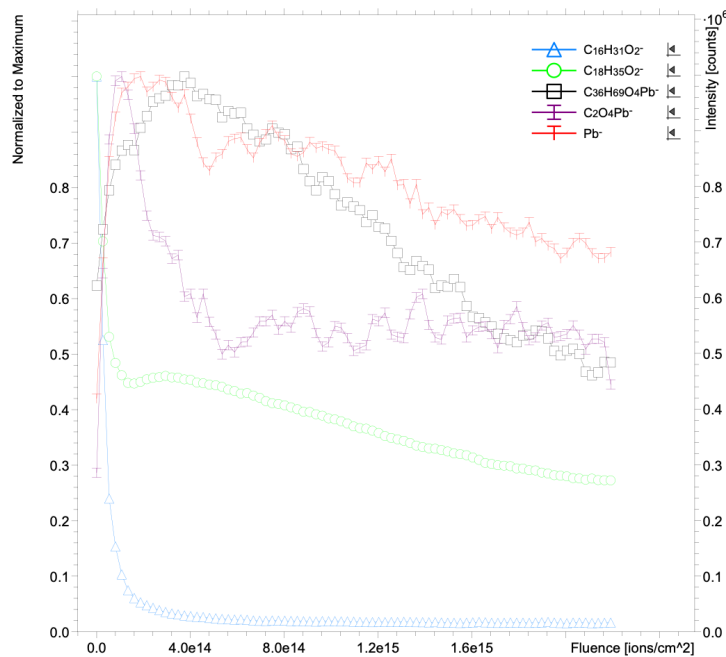


Figure 3.8: Profile of Slide of oil mixed with Lead Stearate in Negative mode

The images taken from this slide, as can be seen in Figure 3.9, show the quality of the results obtained by adopting the approach of etching to an optimal depth. Indeed, comparing this with the images obtained from the surface, as shown in Figure 3.10 for the slide of lead azelate, confirms that this is a better method of analysis.

Indeed, Figure 3.9 allows to highlight several interesting observations. First of all, stearic acid, complete lead stearate, the metal ion lead (in its different isotopes and even in the form of agglomerates) and lead oxalates are all observed and are all colocalised. The weak intensity of the lead is not surprising as it ionises much more in positive mode, but it already allows to localise it.

In addition to confirming the presence of oxalates, this could support the hypothesis that oxalates are degradation products of soap. Indeed, these zones would be the place of separation of stearic acid and the metal ion and the formation of oxalates. As stearic acids are not colocalised with palmitic acids (characteristic of the oil) but with metal ions and complete stearates, this supports the hypothesis that they come from stearates and not directly from the degradation of the oil. Another important reason for this is the fact that no oxalate was detected in the analysis of pure lead stearate powders. The formation of oxalates is therefore induced by the interaction with the environment over time and not by fragmentation of stearic acids during analysis with SIMS.

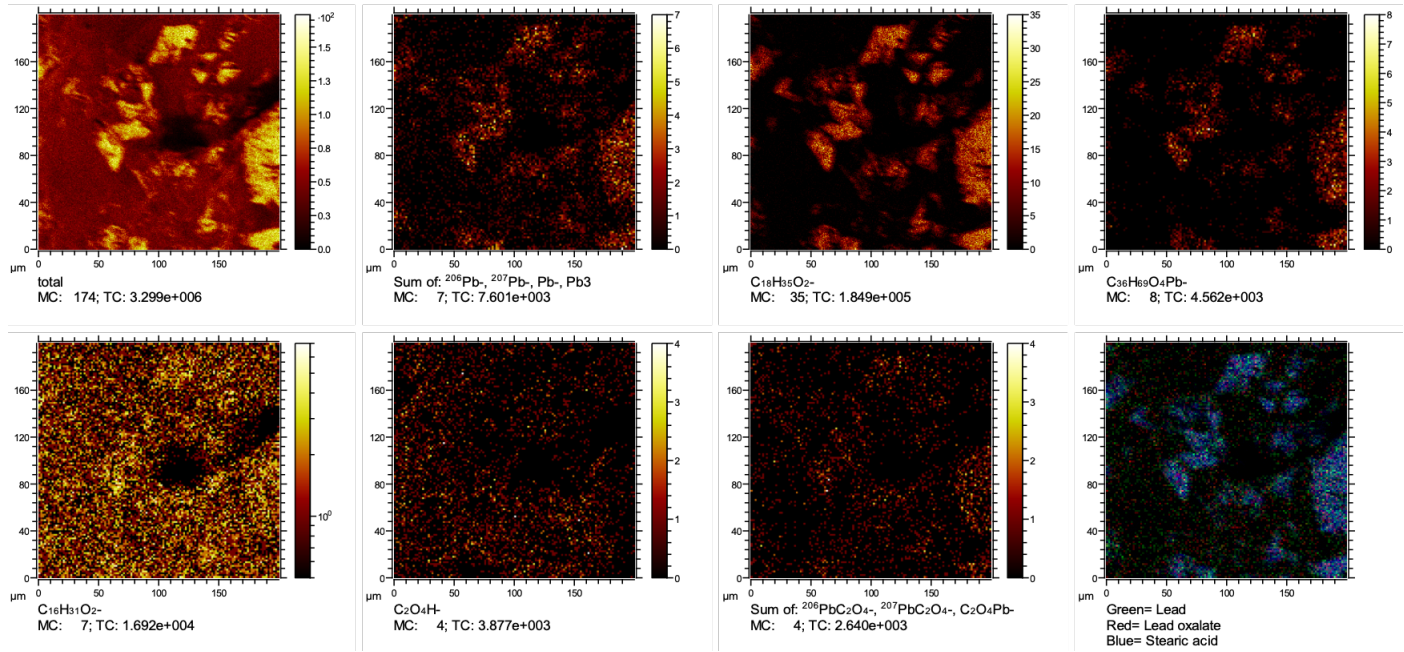


Figure 3.9: Slide of oil mixed with lead Stearate in negative mode: Images taken at the bottom of the cratter

By comparing with Figure [3.10](#), it is directly apparent that no signal is obtained on the surface other than those of the characteristic fatty acids of the oil.

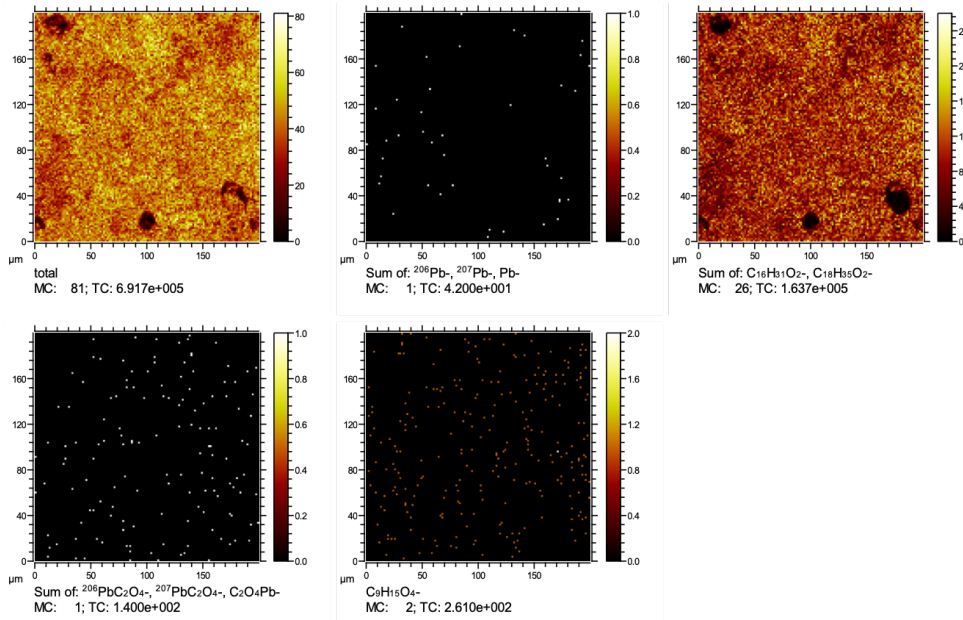


Figure 3.10: Slide of oil mixed with lead Azelate in negative mode: Images taken at the surface

As the results obtained in negative mode from the lead stearate sample were the most promising, two additional profiles in negative mode were carried out and an

image taken and the results obtained are fully consistent with what was observed in the first analysis, the results of which are presented in Figures 3.8 and 3.9.

Regarding the images, it should be noted that it is unfortunately impossible to perform image superposition between the two polarities. This is due to the fact that when using the double beam, the ion images in negative and positive mode show slight differences in stigmatism. During the measurement, the negative image was found to be dilated by about 3% along one axis compared to the positive image. An approximate translation of the sample was nevertheless carried out each time before starting the analysis in the other polarity to allow a maximum of coherence for the images obtained but the computer program does not enable anyway the superposition between the 2 polarities.

Another point concerning the images is the meaning of MC and TC, which are each mentioned below the image. For all the images that will be presented in this section, MC refers to maximal counts and TC to total counts. Thus MC represents the maximum number of secondary ion hits that there are at a single location on the detector. This represents the colour scale of the images in which yellow represents the areas of the sample with the highest intensity detected for the ion in question, i.e. where there were the most impacts at the same location. TC represents the total number of secondary ion impacts on the surface being analysed, which as indicated by the image axes will vary from $200 \times 200 \mu m^2$ to $250 \times 250 \mu m^2$.

Figure 3.11 and 3.12 provide an overview of the results obtained from the entire slides analysis, adopting the previously described analysis method of performing a limited profile before imaging.

The legend below is used to interpret them.

The use of orange is also made to mark a difference between compounds that are very well detected and those that are only slightly detected (less than 1% of the total spectrum) for which the certainty of identification is therefore much less.

Legend:	
✓	Organic acid moiety+ metallic cation
●	Organic acid moiety
✗	Not observed

What emerges directly from the two tables 3.11 and 3.12 confirms that the interest of the analysis in positive ion mode concerns mainly the detection of metal ions alone. Mainly concerning Calcium and Zinc which are not observed at all in negative mode. Zinc keeping very low values, as it was predicted during the analysis of pure powders. Indeed, apart from that, this mode does not bring any additional discovery in the analysis of the samples.

The Oil Matrix column refers to the set of fatty acid peaks characteristic of the oil, detailed in section 3.2.1 on the study of pure oil samples. The table therefore confirms the interest of the approach adopted in the analyses carried out in this work since the oil is still well detected even after etching into the sample. And in the same time many other compounds are detected.

The column Oil products designates the most observed oil degradation products, namely hydrocarbon fragments such as $COOH$, $C_2H_3O_2$, $C_3H_3O_2$.

Concerning the azelate column, described at length in the introduction, it could have been integrated into the column of degradation products since it comes from the auto-oxidation of unsaturated fatty acid, but a column was attributed to it in order to keep a detailed follow-up of this compound through this work.

In Negative	Metal ion	Stearate	Oxalate	Azelate	Oil Matrix	Oil products
CaSt	✗	✓	●	●	●	●
ZnSt	✗	●	✓	●	●	●
PbSt	✓	✓	✓	●	●	●
CuSt	✓	✓	●	●	●	●

In Positive	Metal ion	Stearate	Oxalate	Azelate	Oil Matrix	Oil products
CaSt	✓	✓	✗	●	●	●
ZnSt	✓	●	✗	●	●	●
PbSt	✓	●	✗	●	●	●
CuSt	✓	●	✗	●	●	●

Figure 3.11: Summary table of the slides of oil mixed with stearates

One of the major observations from Table 3.11 is that oxalates are always observed (in negative polarity) whereas this is a sample that initially contains only stearates, allowing to emit the hypothesis that oxalates are formed from stearates. However, most of the time it is the oxalate anion ($C_2O_4H^-$) and not the complete metal oxalate. In fact, only the lead-based slide allows identification of the corresponding oxalates with a sufficient degree of certainty, thanks to the observation of the different lead isotopes. In addition to the results just presented in figure 3.9, the lead stearate sample therefore stands out as the sample providing the most convincing results and the most promising sample to try to explain the formation of oxalates.

Concerning Table 3.12, oxalate anions are as most of the time well observed but surprisingly here complete oxalates were never observed. Furthermore, the stearate column could be assimilated to the oil matrix column since it is the characteristic stearic acids of the oil, the absence of complete stearate making total sense, as was the case for the azelate column in the previous table.

In Negative	Metal ion	Stearate	Oxalate	Azelate	Oil Matrix	Oil products
CaOx	✗	●	●	●	●	●
ZnOx	✗	●	●	●	●	●
PbOx	✗	●	●	●	●	●
CuOx	✓	●	●	●	●	●

In Positive	Metal ion	Stearate	Oxalate	Azelate	Oil Matrix	Oil products
CaOx	✓	●	✗	●	●	●
ZnOx	✗	●	✗	●	●	●
PbOx	✓	●	✗	●	●	●
CuOx	✓	●	✗	●	●	●

Figure 3.12: Summary table of the slides of oil mixed with oxalates

3.3.2 Cross-sections

The principle of cross-sections is to allow the study of all the pictorial layers in one analysis. For example, by comparing the same mixture of oil with lead azelate (see figure 3.10) and still on the surface, but in the form of cross-sections, we can already observe different things other than the oil, which was not the case for the slides. The example presented in Figure 3.13 show a sample for which the boundary between the sample and the matrix is clearly visible, which will definitely not always be the case. It is thanks to the negative peaks of oil and $C_4H_5O_2^-$ (m/z 85) characteristic of the PMMA. And in the positive polarity, $C_2H_3O_2^+$ (m/z 59) is chosen to represent the embedding resin but we can also clearly see the lead within the sample and not outside.

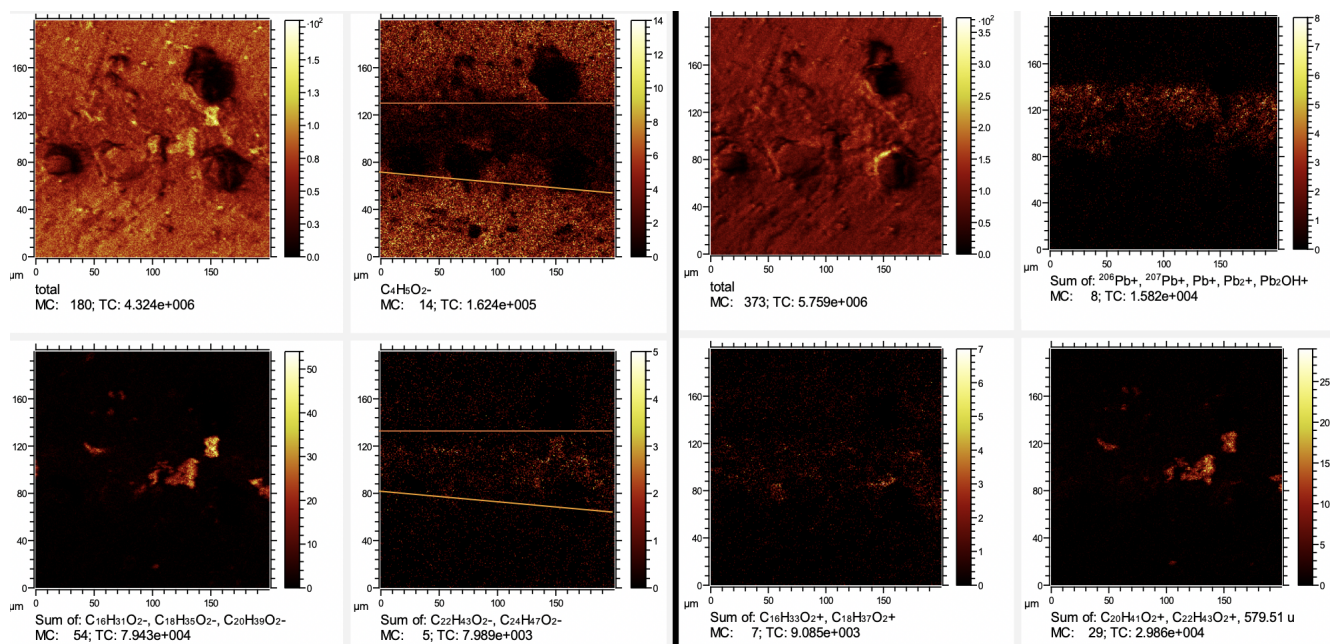


Figure 3.13: Images from the cross-section of oil mixed with lead Azelate in negative mode (on the left) and in positive mode (on the right): Images taken at the surface

However, analysis at the surface is not optimal even in the case of cross-sections due to contaminations that lies on the surface, such as polydimethylsiloxane (PDMS) which may mask ion signals expected from the sample itself. The approach detailed in the previous section, which consists of profiling to determine an optimal depth at which to go to analyse and take images, was therefore also applied for all cross-sections.

Furthermore, as can be seen in Figure 3.14, PMMA can be found on the surface of the sample itself, which decreases with depth as can be seen from the curve corresponding to the $C_4H_5O_2^-$ peak. This could be due to the polishing that was carried out on these samples before our analyses, as this could scatter all the components on the surface and thus strongly modify the surface chemical distribution. Even if, as explained before, some of this PMMA appears by infiltration of the matrix in the sample, it is therefore logical to find some of it still in depth.

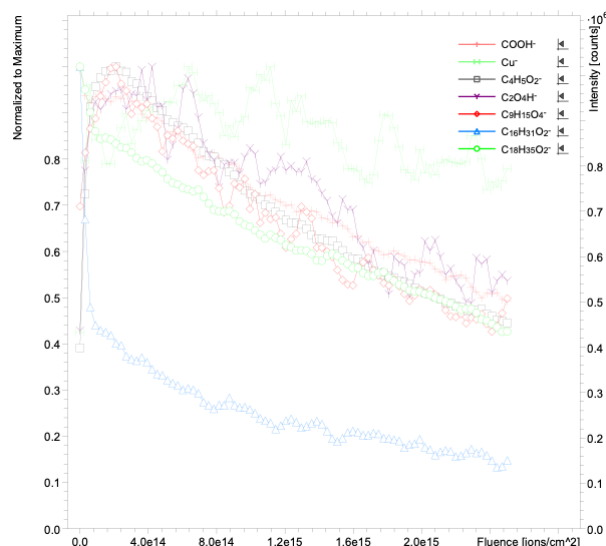


Figure 3.14: Profil of the cross-section of Copper Stearate in negative mode

A first difficulty, already introduced, in analysing the cross-sections is to localise the boundaries between the sample and the resin/polymer neck matrix in which it is embedded. To do this, it is therefore necessary to start an analysis to try to distinguish between the areas where the PPMA is observed ($C_4H_5O_2^-$ at mass 85 in negative mode) and the areas that are much more devoid of it and which will therefore represent the sample. In order to adjust the raster size (the bismuth analysis area) according to the distance covered by the sample and to be sure to analyse the whole thickness of the sample to be able to compare the different analyses that are carried out on it as judiciously as possible.

But a second main difficulty in analysing the cross-sections is the limited space available for analysis. In addition to the limited length of the cross-sections, several samples had already been analysed by C.Poleunis in certain places, with his technique of digging very deep mentioned earlier, which prevented any subsequent analysis.

The main negative consequence is that it is therefore difficult to confirm results obtained due to lack of reproducibility and that it can be confusing if some anomalous results are obtained which could simply be from a non-representative area of the sample.

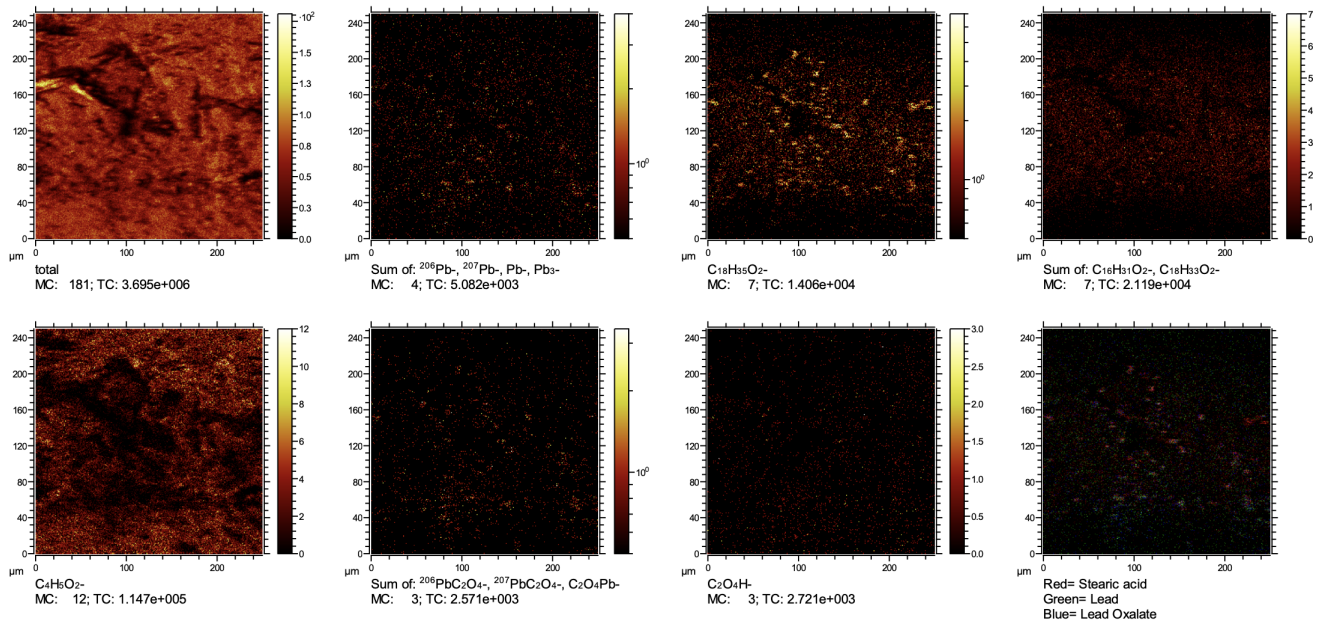


Figure 3.15: Images from the cross-section of oil mixed with lead stearates in negative mode: Images taken at the bottom of the crater

The results obtained for the lead stearate cross-section are the most interesting and allow some parallels with those observed on the corresponding slides. Indeed, once the limits of the sample have been established, not without difficulty, thanks to the less marked presence of PMMA in the central band, we find several elements of interest that had been observed in the slide. Indeed, as can be seen in Figure 3.15 lead, stearic acid and lead oxalates are detected in the sample. However, no real stratigraphy can be observed within the sample, all the compounds are uniformly distributed. It would seem, however, that they may be co-located at certain points, although this cannot be as clearly established as it was for the slide. But it is undeniable that there are some points with higher concentrations of these compounds, for example when comparing with the palmitic ($C_{16}H_{31}O_2^-$) and oleic acids ($C_{18}H_{33}O_2^-$) in the oil. As for lead, this is, as always, much more clearly visible in the positive mode, as shown Figure 3.16.

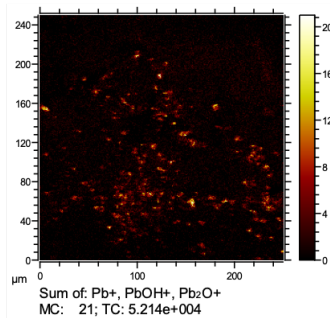


Figure 3.16: Image from the cross-section of oil mixed with lead Stearate in positive mode: Images taken at the bottom of the crater

Figure 3.17 and 3.18 provide an overview of the results obtained from the entire cross-sections analysis, adopting the previously described analysis method of performing a limited profile before imaging.

The organisation of the tables is exactly the same as those presented previously for the analysis of the slides. Each column refers to the same compounds and the legend useful for reading the tables also remains applicable.

A general remark concerning cross-sections is that they allow fewer observations, or similar observations but at lower intensity compared to the corresponding slides. This is easily understandable since if a compound is located on a layer of the sample, by analysing a cross-section which includes all the layers of the material, very little information will come from this compound whereas by analysing perpendicularly (as it is the case for the slides) the analysis concerns one and the same layer and thus the information is much more present and the intensity of the sought peak also. For example, the various fatty acids characteristic of the oil and their fragments are still observed but at lower intensities, which seems logical since all the layers are observed simultaneously, whereas they are known to be located near the surface. Moreover, most of the observations are again made in negative mode except for the metal ions which are always better observed in positive polarity.

Besides, a recurrent problem in the case of the cross-sections concerns the difficulty of observing the oxalates. Indeed, the oxalate anion ($\text{C}_2\text{O}_4\text{H}^-$) observed each time on the slides is not only much less intense but also interferes with other peaks. It is therefore very difficult to confirm with certainty that it is well oxalate, but the shape of the peak or the presence of a shoulder on it makes it possible to assume that it is indeed the case. Since if the whole spectrum has abnormally wide peaks, a problem of charge compensation or roughness of the surface is certainly in question and it is not possible to argue that several peaks come out at very close masses. But if this is not the case, *i.e.* if the spectrum does not show abnormally broad peaks, it is easier to distinguish two peaks at similar masses, *i.e.* even in the presence of interferences.

A major consequence of these interferences concerning oxalates is that the corresponding images are not representative of the real localisation of oxalates. Indeed the signal is noisy so the image obtained shows a homogeneous distribution over the whole analysis area (both in the sample and in the resin), in addition to the low intensity of the signals.

Again this phenomenon of interference which is very present for oxalates represents a rather general trend for cross-sections, since many layers are analysed at the same time a large number of compounds are present and are potential sources of

interference.

It can also be noted for all the cross-sections, the difficulty of observing the oil in positive mode.

In Negative	Metal ion	Stearate	Oxalate	Azelate	Oil Matrix	Oil products
CaSt	✗	●	✗	●	●	●
ZnSt	✗	●	●	●	●	●
PbSt	✓	●	●	●	●	●
CuSt	✓	✓	●	✓	●	●

In Positive	Metal ion	Stearate	Oxalate	Azelate	Oil Matrix	Oil products
CaSt	✓	✗	✗	●	✗	
ZnSt	✓	✗	✗	●	✗	
PbSt	✓	✗	✗	●	✗	
CuSt	✓	●	✗	●	●	

Figure 3.17: Summary table of the cross-sections of oil mixed with stearates

Of course the problem of interference for the peak of $\text{C}_2\text{O}_4\text{H}^-$ varies from sample to sample, for example lead oxalate stood out much better than other peaks present at very close masses, which is in line with what has been observed since the beginning, lead oxalate is the likely to be detected. And again in the line with what has already been observed, calcium oxalate is particularly poorly detected. These observations concern the stearate-based cross-sections presented in figure 3.17.

It is also surprising to observe almost no complete stearates, especially the lead stearate which stood out best in the slides, both in the positive and negative modes. Only, in negative mode, copper stearate seems to be detected, more surprisingly copper azelate is observed, although this was never the case. This is however difficult to confirm with certainty since it had not yet been observed and by lack of confirmation with another analysis which could have been carried out on another zone of the sample. Due to the lack of surface area available on the cross-section, as mentioned at the beginning of the section.

In Negative	Metal ion	Stearate	Oxalate	Azelate	Oil Matrix	Oil products
CaO _x	✗	●	✗	●	●	●
ZnO _x	✗	●	✓	●	●	●
PbO _x	✗	●	●	●	●	●
CuO _x	✓	●	●	●	●	●

In Positive	Metal ion	Stearate	Oxalate	Azelate	Oil Matrix	Oil products
CaO _x	✓	✗	✗	●	✗	
ZnO _x	✓	✗	✗	●	✗	
PbO _x	✓	✗	✗	●	●	
CuO _x						

Figure 3.18: Summary table of the cross-sections of oil mixed with oxalates

Table 3.18 shows similar observations to those obtained for the stearate-containing cross-sections. The oxalate anion still presents some interference with other peaks, but this time with the very weak observation of zinc oxalates. The oxalate anion was again most clearly observed for the lead sample, but no full lead oxalate was observed. And no calcium oxalate is detected.

The results for the positive copper oxalates do not appear because they could not be analysed. Except, of course, during the first analyses which were carried out on the surface but during which, as a reminder, only the oil was observed but nothing else, not even the copper ion.

The oil products column was not presented in positive mode as the peaks of the characteristic fatty acids of the oil are not clearly observed. This is because they are usually used to try to prove that they are their fragments. Since these small fragments could also be from PMMA or be compounds such as acetate, formiate,... But collocalising them with the oil would confirm their origin, which is no longer possible if the f.a. themselves are not observed

An important point to emphasize concerning all the mock-ups provided by IRPA is that the precise proportions of compounds within the samples are not known, even though, as it was said in section 1.4 of the introduction, the preparation of the samples has a major influence on the results obtained. Indeed, some information can be totally hidden if the preparation was inappropriate, such as too low proportions that would not allow to reach the detection limit of the technique. This could be the basis of misunderstanding of certain results and explain why certain things were

not observed despite the fact that it seemed more than expected.

The polishing that was done on the samples before performing our analyses could also have a significant impact. Indeed, as discussed in section 1.4, it can have negative impacts such as scattering and mixing of compounds present on the surface, disrupting the spatial organization of the surface. However, the ultramicrotome solution presented in section 1.4 was not feasible because there is no longer a person in charge of this at UCLouvain.

This already adds to the difficulty inherent to this type of sample to obtain a good homogeneity within them. Even if the impact of this aspect could be strongly limited by repeating several times the analyses in different places on the sample to confirm each of the results, if there is sufficient space, which is often not the case for cross-sections as already mentioned.

3.4 Analysis of real samples

The section 2.4 of the experimental part presents five historical samples from real paintings. However, it was only possible to analyse three of them in the framework of this thesis, the two from the Mystic Lamb polyptych and the one from the Adam and Eve painting.

Of these three samples, the results will only be presented in detail for one of the two from the Mystic Lamb. This is the only one for which conclusive results have been obtained. The images of this sample under polarised light and UV light are shown in figure 3.19. This sample was chosen by IRPA because many compounds are observed in it. Indeed, they detected the concentrated presence of Calcium oxalates in the varnish layer, i.e. at the upper end of the sample, as well as the presence of copper soaps and copper oxalates in several lower layers of the sample. They also noted the presence of lead white in several layers.

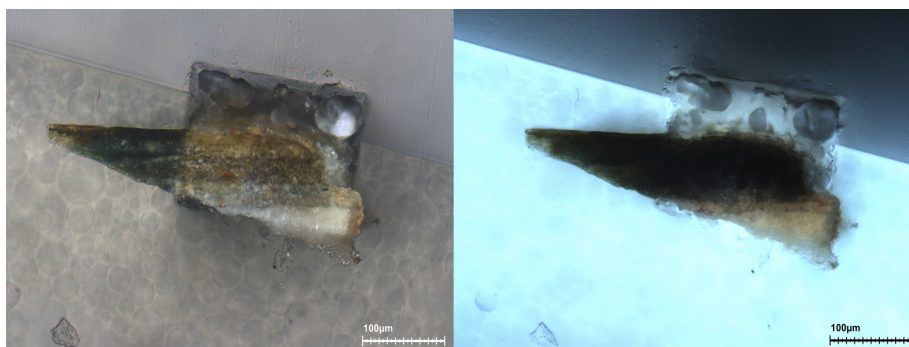


Figure 3.19: Images of the green sample from the mystic lamb under polarized light (on the left) and UV radiation (on the right)

The main problem encountered when studying real samples is the available analysis area. Indeed, these samples are available in very small quantities and have often

already been subjected to other, sometimes destructive, analyses. This is the case for the sample of the mystic lamb presented in figure 3.19, which was analysed in the framework of this master thesis. Indeed, the whole of the right-hand area of the sample was burnt after synchrotron analysis by other researchers. These destructive analyses impacted the entire depth of the sample, even after a profile no information could be derived from this part of the sample.

As the available sample area was not more than $150\text{ }\mu\text{m}$ long, as shown by the scale in the figure 3.19, the analysis area used was reduced to $150 \times 150\text{ }\mu\text{m}^2$, allowing the entire sample to be studied.

Despite the small area available, interesting results were obtained. First of all, as there was no room for error or going back, images were taken at the surface, where some interesting observations were already visible but with low intensities. It was therefore decided to carry out a limited profile, in the continuity of what had been done for the previous analyses and as there was no room to carry out a complete profile alongside. This allowed the intensity of the main compounds of interest to be increased, as can be seen in Figure 3.20, and therefore to carry out an even more conclusive imaging.

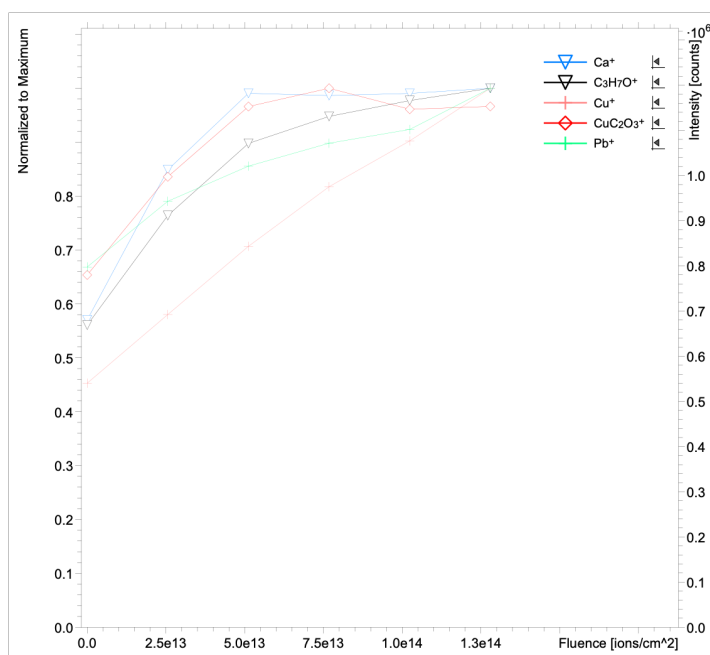


Figure 3.20: Limited profil of the mystic Lamb in positive polarity

After this profile, which allowed the removal of surface impurities and possible modifications caused by the polishing, the images taken at the "optimal depth" confirmed what had been assumed during the analysis at the surface and allowed the discovery of even more.

Figures 3.21 and 3.22 show these observations in negative and in positive polar-

ities respectively.

The first reason for satisfaction is the clear distinction between the sample and the embedding resin, as well as the damaged area. The PMMA is clearly visible outside the sample and the desired compounds clearly visible in the sample area. This was less the case for the surface images, where the information was less concentrated in such specific areas.

Then, Copper oxalates are clearly observed throughout the paint sample, with particularly high intensities compared to those obtained from oxalates with the mock-ups, apart from the extreme surface. Surprisingly, this time the oxalate anions are hardly detected. Perhaps, this is related to the age of these samples of almost 600 years, compared to the very recent mock-ups for which the complete oxalates would not have had much time to form.

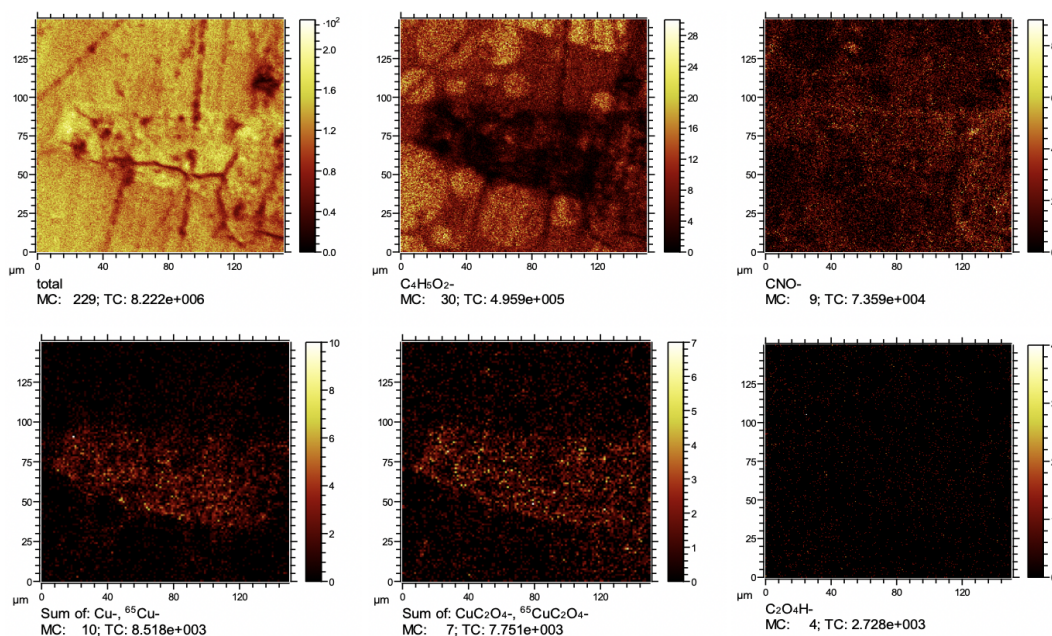


Figure 3.21: Images of the mystic Lamb in negative mode taken at the bottom of the crater

Finally, the metal ions, already visible in the negative polarity, are, as always, clearly identified and located in the positive polarity. Thus copper is found almost everywhere in the sample except on the surface, where calcium is concentrated. This is consistent with the hypothesis that the more stable calcium oxalates are found at the surface, while those at depth from which they would come are other oxalates such as the copper one. There are also some areas of lead in the sample, which may have come from drying agents added to the oil such as lead white or litharge.

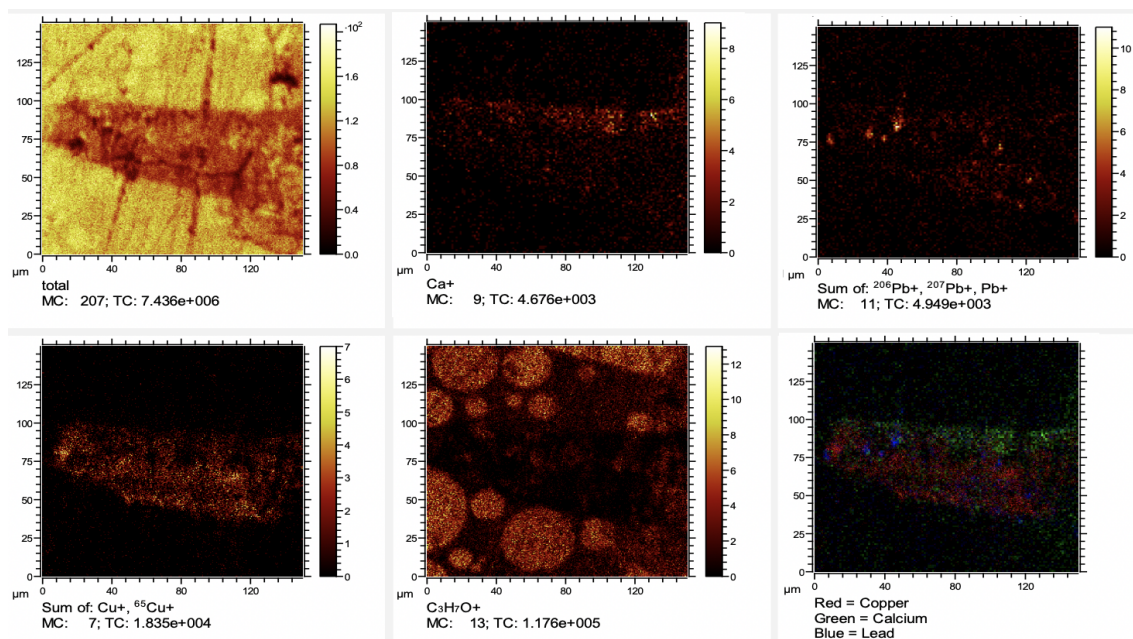


Figure 3.22: Images of the mystic Lamb in positive mode taken at the bottom of the crater

The results obtained in the analysis of this sample supports the interest of the SIMS technique in the framework of the Metox project. Indeed, they correspond with those obtained by IRPA, which also observed copper oxalates in the lower layers of the sample and calcium oxalates on the surface. Even if our analysis does not detect full calcium oxalates but only Calcium, it still gives hope since these complete oxalates have never been observed with SIMS so it could be a good indication of the presence of the calcium oxalates. While waiting to discover the cause of this non-detection.

No soaps could be detected in the sample analysis although this was the case for copper soaps at IRPA and no conclusion can be drawn from stearic acid as it is almost not detected. This quasi non-detection of oil f.a. is perhaps due to the strong cross-linking of the oily polymeric network with time and the already well advanced formation of oxalates derived from the soaps.

The results of the other two real samples analysed are not presented here because the signal intensities are very low, the only compounds represented because they could be clearly identified are metal ions and they do not allow interesting observations either. It is not even clear where the sample is. However, these results are available in section [6.4](#) of the annexes.

4 Conclusion

The research carried out within the framework of this thesis allowed the application of the SIMS technique to the field of art conservation, more precisely to study the formation of oxalates and metallic soaps within oil paintings from the Southern Netherlands from the XVth to the XVIIth centuries.

A first part focused on the study of pure powders of the compounds that would be the object of future research within more complex samples. In order to obtain spectra of these materials to serve as a signature in the analysis of the more complex samples, to facilitate and confirm their detection. This part was very successful in determining how well each compound was detected, at least in the negative mode. And for some of these analyses, those on oxalates, which had already been carried out by C. Poleunis before, the results are quite similar and concordant, which makes it possible to further ensure their validity. Some broad outlines had already been drawn from them, mainly the fact that lead and copper-based compounds are best detected by SIMS.

In a second step, the technique was applied to mixtures of each of the previously analysed compounds (actually only a part) with linseed oil, called mock-ups. Each mock-up came in two forms, slide and cross-section, allowing analysis from two different angles.

The most conclusive results, and the most hopeful for our research, were found on the mock-ups made with lead stearates. These have yielded observations that allow several conclusions to be drawn in support of previously formulated hypotheses. Indeed, the presence of lead and stearic acids, but also of lead stearates and oxalates, is clearly observed in certain distinct zones. While palmitic acid is uniformly distributed over the surface of the sample, characterising the oil. This not only proves the presence of oxalates, but also supports the hypothesis that the formation of oxalates and stearates is due to pigment-binder interaction. But beyond that, the colocalisation of lead oxalates and stearates would suggest that oxalates are derived from stearates.

These observations could be made mainly on the basis of the corresponding slide and to a lesser extent thanks to the cross-section. The limited contribution of the cross-sections was also observed for the majority of the samples.

What should be noted about the cross-sections is that they offer much lower signal intensities but, since they include all the layers of the sample, they allow the observation of a much greater number of compounds and their distribution within the strata.

These lower intensities can be explained by the fact that much less information will come from a compound present within a layer in the case of a cross-section that includes the whole stratigraphy of the sample than in the case of the analysis of a single layer in which this compound would be found. This obviously concerns mainly minority compounds that are found in only a few layers, such as oxalates and soaps, and not compounds present in large quantities in the sample.

This is also accompanied by interference problems, as more elements are detected and it is more likely that several will emerge at very close masses, which makes it difficult to identify certain peaks accurately. In addition to these interference problems, peak broadening due to higher surface roughness of the cross-sections can also occur, further complicating the identification of the spectrum.

A negative consequence of these interferences and difficulties of identification is that the resulting images may no longer be truly representative of the location of the compound, thus limiting the interest of the cross-sections.

Finally, the analysis of a sample from the Mystic Lamb allowed to observe copper oxalates distributed in the lower layers of the sample in a new way. While the presence of concentrated calcium at the extreme surface of the sample might suggest that these are calcium oxalates. To add to the excitement, these observations are in line with those obtained by IRPA for the same sample.

Alongside these few encouraging observations, there are however the vast majority of samples for which no conclusive observations could be obtained and the large number of misunderstandings that accompany them. With no precise and certain explanation yet put forward but only the hypotheses of the matrix effects of the binder and the strong reactivity of the copper and lead based compounds with it in contrast to those based on calcium or zinc.

5 Perspectives

This section presents some ideas that could answer questions raised during the writing of this thesis. Finally, some ideas that are outside the scope of this thesis will be presented.

First of all, a point that should have been clarified in this work is the quantification of the depth at which the oil, i.e. the low molecular weight free fatty acids, are no longer observed. As a reminder, no depth scale (in μm) was used to work during our analyses. It should be noted that the exact depth of the samples was not known either. However, it would be interesting to try to quantify this depth as much as possible.

To do this, a profile should be made to the depth at which the plateau of the different f.a. characteristic of the oil, observed in each of the profiles obtained, appears. And then measure this depth with a profilometer, present in the IMCN laboratory .

After that, a very interesting thing would be to study real samples in which lead soaps and oxalates are present. Since these are the compounds that gave the most promising results in mock-ups, and before that in pure powders, especially lead oxalate, which was detected with 10 times more intensity than the other types of oxalates. In order to confirm these trends and try to identify general behaviours related to these compounds.

To try to understand why certain compounds are sometimes observed, sometimes not, several avenues could be explored. Firstly, to study a large number of additional real samples to allow more points of comparison and also increase the chance of observing certain compounds that are sometimes hidden for as yet unknown reasons, potentially matrix effects specific to certain samples. Secondly and above all, to analyse mock-ups for which the concentrations are known precisely. To allow more reliable comparisons between the observations made on different mock-ups. Indeed, to conclude that one oxalate is less well detected than another when its concentration is perhaps much lower than the other is not necessarily correct. And similarly to try to establish conclusions on the detection limit of the various elements sought. This analysis of mock-ups with well-monitored concentrations had also been envisaged in the framework of this thesis since all the samples in question in this work are being remanufactured within IRPA with very precise concentrations. But

as their production is long and complex, they could not be completed in time and it was therefore unfortunately not possible to analyse them.

Another point that has already been discussed in detail in this thesis is the use of an ultramicrotome to obtain the smoothest possible sample surfaces and to improve the results obtained from the cross-sections.

Several studies also mention the use of egg yolk within the pictorial layers (notably [1]). The analysis of such samples would potentially allow new discoveries as it would certainly modify the matrix effect and therefore allow a modified detection of compounds within the sample, and thus potentially of soaps and oxalates.

There are also complex samples developed in the laboratory which aim to reproduce a real sample as closely as possible, while at the same time providing precise knowledge of the compositions and concentrations of each of the compounds and the ageing conditions applied to the material. This type of sample would therefore be a possible solution to allow all the above-mentioned future analysis proposals to be carried out. A sample of this type was analysed in the framework of this thesis but since it was composed, in term of oxalates, only of calcium oxalates no significant observations were made.

However a crucial question concerns the relevance of the SIMS technique to the Metox Project. Since the question of calcium oxalates remains a major problem, as these are the oxalates most frequently observed with ATR-FTIR but for which no formal trace could be observed with SIMS. Despite the fact that the SIMS technique, through the observations concerning lead stearates and oxalates supporting the hypothesis of pigment/binder interaction as the source of oxalate formation and the detection of various oxalates, mainly copper oxalates in a real sample, provides important confirmations for the Metox project. Nevertheless, these are not new discoveries but only some confirmations of things already observed...

If this concerns the intervention of the SIMS technique in the study of the formation of soaps and oxalates in paints, SIMS remains a very appreciable tool for the molecular information it allows as well as the very good spatial resolution that accompanies it, which makes it still a technique of choice for the analysis of paintings. Indeed, as detailed in section 1.4 of the introduction, thanks to these advantages, SIMS has enabled the discovery of unsuspected elements (thanks to the molecular information) within the pictorial layers of paintings and their precise localisation (thanks to the good spatial resolution). And this for elements present even in very small quantities (thanks to the great sensitivity of the technique of the order of few ppm). The example of starch having been presented in section 1.4 but also the

detection of animal proteins which made it possible to establish that the paint came from dyed wool, or from their manufacturing waste.

These assets also allow a precise analysis of the oil and its evolution, which in several studies has made it possible to determine precisely the nature of the binder and to discover certain details. It is in this sense that within the framework of our research it was observed throughout the analyses that free fatty acids were present at the surface in low molecular weight and disappeared exponentially with depth.

Finally, another aspect that would also be worth investigating is the comparison of results obtained with SIMS with results obtained using the other methods mentioned in this thesis.

Starting with the results obtained with infrared at IRPA for the same samples as those analysed in this work. This would address a key difference between the two methods which is the depth of information, SIMS analyses the extreme surface and infrared gives deep information, it is therefore difficult to know where the compound is located. For example, with infrared, it is possible to observe the presence of oxalates, but without much more precision since it is difficult to know the precise depth of penetration of infrared. The SIMS therefore allow a much better localisation. It is obviously more complex than that but these comparison studies would also help to answer the question of the validity of the SIMS technique in the project.

A final, more personal point that I would like to address, which was mentioned in the introduction, concerns the validity of the metox project which, through the study of the formation of oxalates and soaps, seeks to limit the formation of crusts on the surface that degrades the visual rendering of the work of art, and which perhaps attempts to limit a natural phenomenon of protection of the painting.

"A work of art is made to be seen" answers this question as simply as perfectly, in my opinion. Indeed, for a work of art to be a witness to our history and all that it has gone through, it must still be possible to decipher it. Restoring and preserving it is not to deny the past but rather first to understand what the brilliant artists of the time did in order to determine what has happened to it since then and finally to try to predict what will happen in the future.

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6 Annexes

6.1 Historical Context

An historical context is very interesting given that this project was born of the conviction that paintings are a privileged witness of our history and bear the traces of the plastic expression of their creators, who are very often, among those who are found at the base of the collections of the partners of this project, immense artists who have marked their time. Indeed, it is interesting to note that, even if only throughout the three centuries on which this project focuses, we can observe how, depending on the artist and the period, they appropriated the material differently. And this with a raw material (pigments, oils) that will remain more or less the same. The artist therefore handles this material to express what he wants, the way he perceives the world. We can therefore observe, for example, strong differences between the way of playing with light between a Rubens [25] [26] and a van Eyck [27].]

Van Eyck's reputation for patience is indisputable, he was known to superimpose up to 10 layers of paint, to allow them to dry optimally, taking care at each stage to smooth them out. It is this regularity that brings all the purity and brilliance to the colours of his works thanks to the particular interaction of light through these different layers. Of course, at that time, they did not master the physics that governed these phenomena, but that did not prevent them from understanding the effects that this could have on the visual rendering of the final work. This approach is easily understandable through the context of the time and its conception of reality, considering colours and lights as divine.

After that, artists would begin to lose this patience and work differently with light, seeking to develop other aspects in their works.]

It is interesting to note that if the differences between the painting styles of a van Eyck and a Rubens have been highlighted, this is largely due to the importance of the political, religious and theological context on the pictorial process of the period under consideration. Indeed, two important events of the 16th century deserve to be highlighted to show the split that can exist between the world of van Eyck (beginning of XVth) and that of Rubens (end of the XVIth/ beginning of the XVIIth).

The first is the Council of Trent, which issued its decree on painting in 1563. The second was the great iconoclastic wave that marked the effective start of the Netherlands revolt against Spain in August 1566. This was accompanied by the destruction of thousands of works of art, including paintings, sculptures and stained glass.

The period that followed was complicated for the art world, with the departure from the country of many artists of reformed or even new faith, the fall in the economy and therefore in the budgets dedicated to the commissioning of works of art, but above all due to a sort of tacit and general consensus considering the production of new paintings as futile. Indeed, it seemed coherent to ask why create new works that could be destroyed the following day by iconoclasts (particularly notable events in November 1576 called Spanish fury).

In parallel to this, there was a religious instability between the doubt about Catholicism and the polemic about Protestantism, raising questions about the validity and status of painting itself. Indeed, how could the fundamentally unlimited character of the divine be captured by purely and intrinsically material objects like paintings? Can they really mediate between man and God? These were the questions raised during this period by great reformers who wanted to put the people back at the centre, as the true image of God, to the detriment of the paintings to which too much money had been spent. It should be noted that if it is true that these ideas were those of the Protestants, they continued to resonate for many years and therefore throughout Rubens' life.

It is therefore understandable how the idea of colours and lights as divine were rethought in relation to an era in which van Eyck, for example, lived, since the paintings themselves no longer had to represent a mediation between the divine and the earthly world. Art could henceforth have a different vocation and scope and therefore the way in which art was produced was undeniably rethought.

This contextualisation also makes it possible to realise even more clearly the precious character of the works that precede this period of instability.

6.2 Results of the analysis of pure oxalates and soaps powders

This section contains a summary of all the results obtained for the analysis of the pure powders carried out within the framework of this thesis, but also of the results obtained by C. Poleunis in order to allow a reproducibility study to confirm the results obtained.

Résumé des résultats de l'analyse des poudres par Hadelin																
Negatif																
N_Statute_Ca	C_18H_35O_2-	Total Counts	I/Hot													
Mean	4182	9199436	0.05%													
Standard_Deviation				0.003%												
N_Statute_Cu	C_18H_35O_2-	C_36H_71O_4-	C_36H_71O_4-	C_36H_71O_4-	Total Counts	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot
Mean	70618	21756	23170	4957	16691024	0.44%	0.14%	0.003%	0.14%	0.006%	0.001%					
Standard_Deviation							0.006%									
N_Statute_Cu	C_18H_35O_2-	C_36H_71O_4-	C_36H_71O_4-	C_36H_71O_4-	Total Counts	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot
Mean	369941	139559	137995	160914	53062	1523428	2.44%	2.37%	0.91%	0.16%	0.35%					
Standard_Deviation								0.093%	0.080%	0.030%	0.030%	0.011%				
N_Statute_K	C_18H_35O_2-	Total Counts	I/Hot													
Mean	154216	15176218	3.39%													
Standard_Deviation			0.291%													
N_Statute_Pb	C_18H_35O_2-	C_36H_69O_4Pb-	C_36H_69O_4Pb-	C_36H_69O_4Pb-	C_36H_69O_4Pb-	C_36H_69O_4Pb-	C_36H_69O_4Pb-	C_36H_69O_4Pb-	C_36H_69O_4Pb-	C_36H_69O_4Pb-	C_36H_69O_4Pb-	C_36H_69O_4Pb-	C_36H_69O_4Pb-	C_36H_69O_4Pb-	C_36H_69O_4Pb-	C_36H_69O_4Pb-
Mean	95455	42674	131364	25616	29772	13486	2241247	4.26%	0.19%	0.007%	0.18%	0.11%	0.04%	0.005%	0.06%	0.003%
Standard_Deviation									0.217%							
N_Statute_Zn	C_18H_35O_2-	C_36H_69O_4Zn-	C_36H_69O_4Zn-	C_36H_69O_4Zn-	Total Counts	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot	I/Hot
Mean	428100	82915	41818	3438	1385993	3.20%	0.62%	0.29%	0.23%	0.03%	0.001%	0.000%				
Standard_Deviation								0.063%	0.014%	0.002%	0.001%	0.000%				
N_Azotate_Ca	C_9H_14O_4C-	Total Counts	I/Hot													
Mean	5131	6570978	0.08%													
Standard_Deviation			0.002%													
N_Azotate_Cu	C_9H_14O_4C-	C_9H_14O_4C-	Total Counts	I/Hot												
Mean	32093	16682	9352646	0.35%												
Standard_Deviation				0.042%												
N_Azotate_K	C_9H_14O_4C-	C_9H_14O_4C-	Total Counts	I/Hot												
Mean	735072	2703	933354	2.41%												
Standard_Deviation				0.005%												
N_Azotate_Pb	C_9H_14O_4C-	C_9H_14O_4C-	C_9H_14O_4C-	C_9H_14O_4C-	C_9H_14O_4C-	C_9H_14O_4C-	C_9H_14O_4C-	C_9H_14O_4C-	C_9H_14O_4C-	C_9H_14O_4C-	C_9H_14O_4C-	C_9H_14O_4C-	C_9H_14O_4C-	C_9H_14O_4C-	C_9H_14O_4C-	C_9H_14O_4C-
Mean	118813	39615	14988	21804	82240	36774	33324	11856145								

83

Résumé des résultats de l'analyse des oxalates par Claude																								
Négatif																								
N_PbOx	Pb	*207Pb	*206Pb																					
Moyenne	80768.5625	34621.7725	36347.8	36347.8	36347.8	36347.8	36347.8	36347.8	36347.8	36347.8	36347.8	36347.8	36347.8	36347.8	36347.8	36347.8	36347.8	36347.8	36347.8	36347.8	36347.8	36347.8	36347.8	36347.8
Standard_Deviation																								
N_ZnOx	C_20_4H	ZnO	ZnOH																					
Moyenne	29228.25	84148.215	66195.72	66195.72	66195.72	66195.72	66195.72	66195.72	66195.72	66195.72	66195.72	66195.72	66195.72	66195.72	66195.72	66195.72	66195.72	66195.72	66195.72	66195.72	66195.72	66195.72	66195.72	66195.72
Standard_Deviation																								
N_CuOx	CuO_2	HSCuO_2	C_2HO_4																					
Moyenne	34746.3625	14540.115	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875	81851.8875
Standard_Deviation																								
N_Kox	K	HC_2O_4	HC_2O_4																					
Moyenne	294678.2425	656262.5375	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325	973855.7325
Standard_Deviation																								
Les résultats de la 2ème analyse sont très divergents du reste (directement problème de calibration)																								
N_CuOx	Cu	CuO_2	CuO_2																					
Moyenne	12058.8225	2365.635	13695.055	13695.055	13695.055	13695.055	13695.055	13695.055	13695.055	13695.055	13695.055	13695.055	13695.055	13695.055	13695.055	13695.055	13695.055	13695.055	13695.055	13695.055	13695.055	13695.055	13695.055	13695.055
Standard_Deviation																								
N_CuOx	HC_2O_4	HC_2O_4																						
Moyenne	6177.8475	7049.845	568895.25	568895.25	568895.25	568895.25	568895.25	568895.25	568895.25	568895.25	568895.25	568895.25	568895.25	568895.25	568895.25	568895.25	568895.25	568895.25	568895.25	568895.25	568895.25	568895.25	568895.25	568895.25
Standard_Deviation																								
Donc globalement les mêmes valeurs, seul différence pour le K où elles sont bien plus importantes et très légèrement pour le Cu qui sont aussi plus élevés pour Claude																								
Positif																								
P_CuOx	Cu+	CuO+	Cu_2O+																					
Moyenne	818377.6275	298080.83	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725	260107.8725
Standard_Deviation																								
P_PbOx	PbO_2	PbO																						
Moyenne	317.8325	426915.6875	158000.8	158000.8	158000.8	158000.8	158000.8	158000.8	158000.8	158000.8	158000.8	158000.8	158000.8	158000.8	158000.8	158000.8	158000.8	158000.8	158000.8	158000.8	158000.8	158000.8	158000.8	158000.8
Standard_Deviation																								
P_CuOx	Cu+	HSCu+	HSCu_2O_3																					
Moyenne	860232.785	263456.885	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675	3824.0675
Standard_Deviation																								
P_Kox	K+	HC_2O_4																						
Moyenne	2781396.313	2919.7525	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5	35499780.5
Standard_Deviation																								

Figure 6.1: Summary of all the results obtained for the analysis of the pure powders

6.3 Results of the analysis of the mock-ups

6.3.1 Slides

Slide of oil mixed with Lead Stearates

Other analyses than those already presented in the results, confirming these.

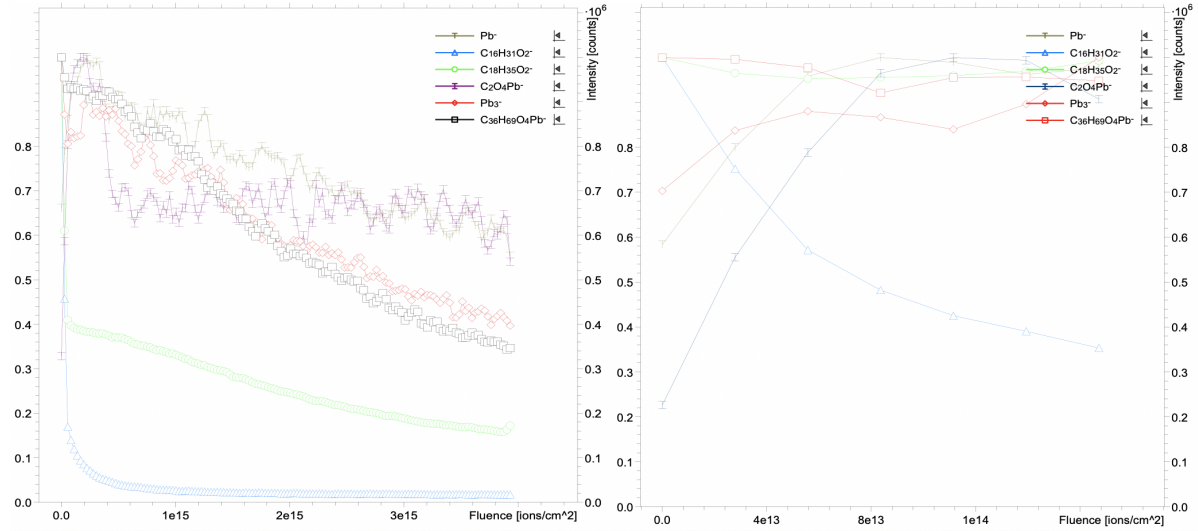


Figure 6.2: Profile (on the left) and limited profile (on the right)of Slide of oil mixed with Lead Stearates in Negative

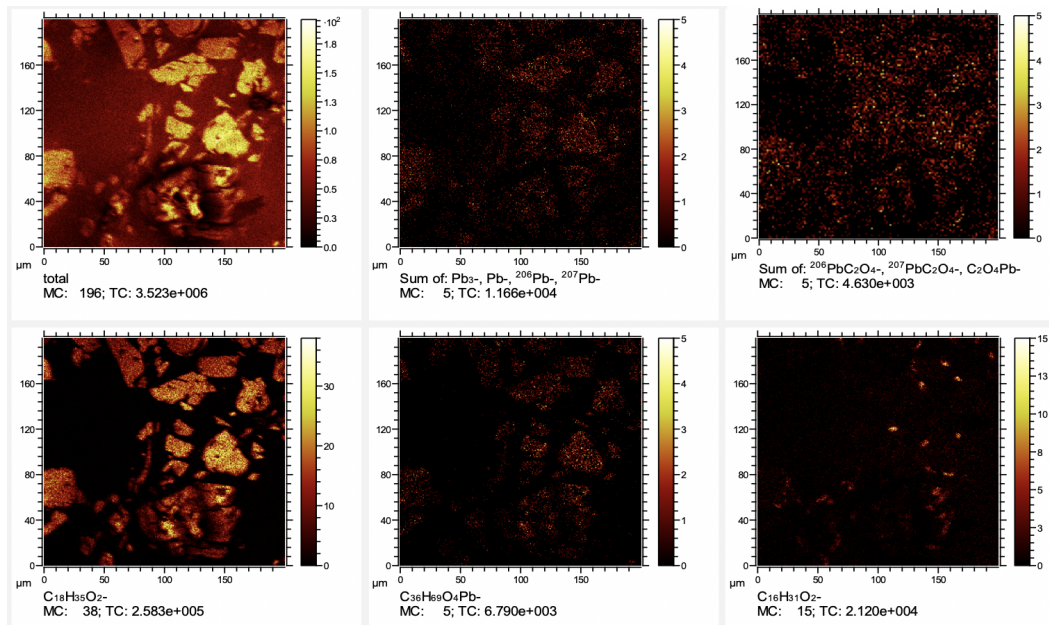


Figure 6.3: Images at optimal depth of slide of oil mixed with Lead Stearates in negative mode

Slide of oil mixed with Copper Stearates

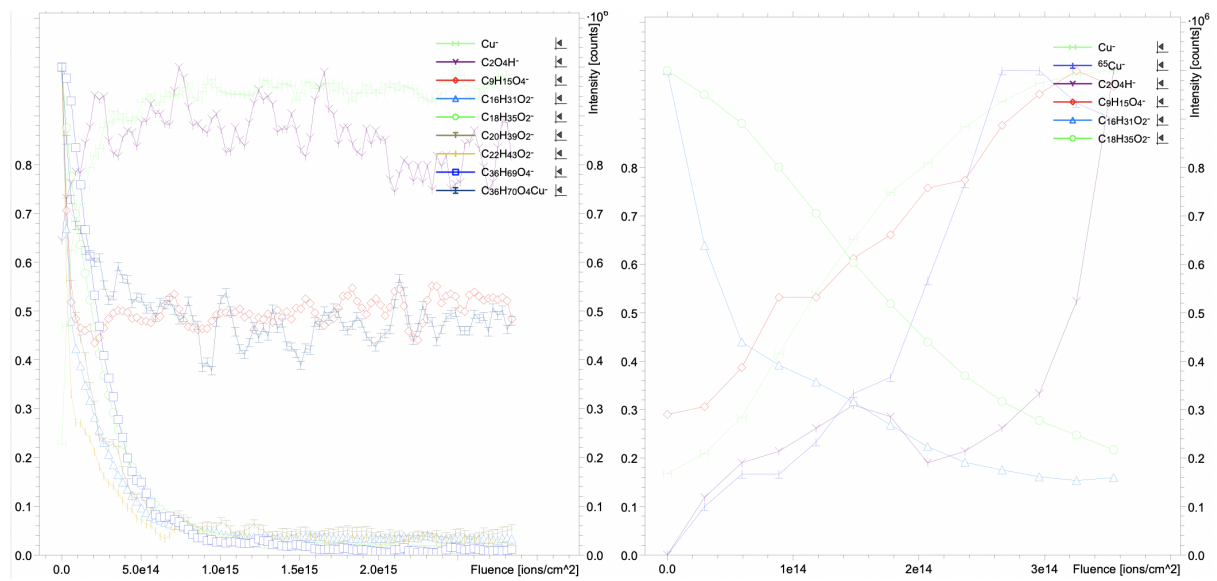


Figure 6.4: Profile (on the left) and limited profile (on the right) of Slide of oil mixed with Copper Stearates in negative mode

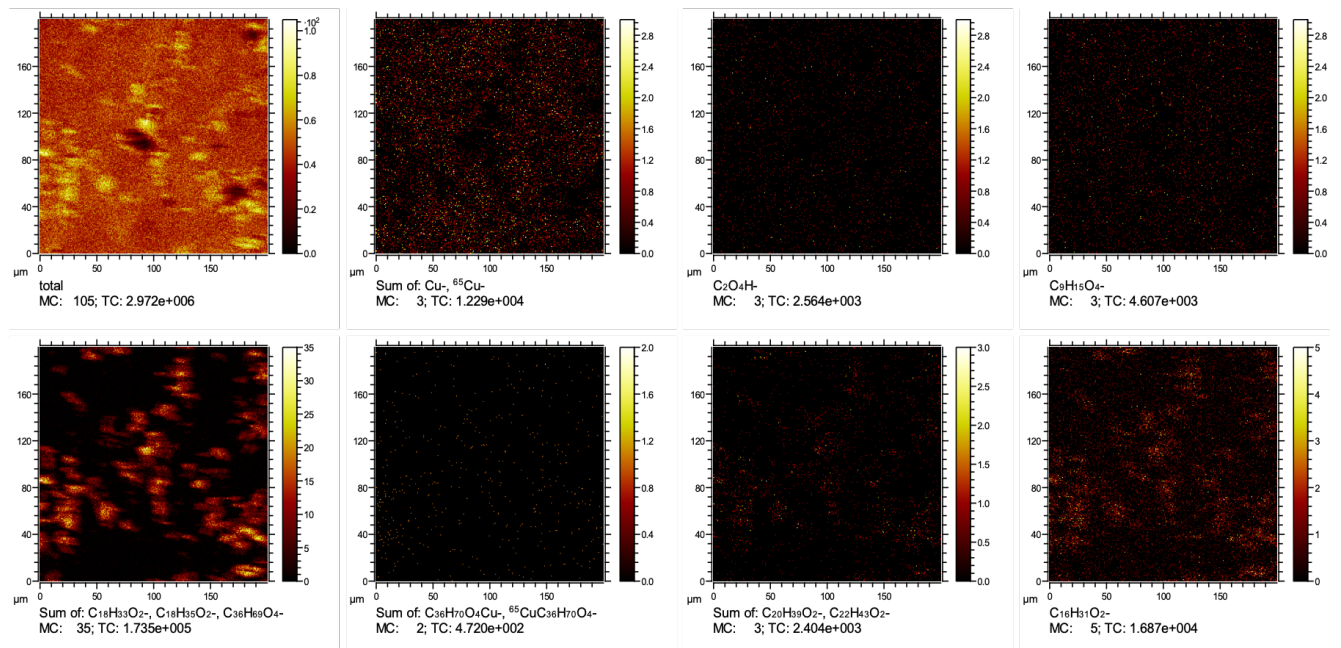


Figure 6.5: Images at optimal depth of slide of oil mixed with Copper Stearates in Negative mode

Slide of oil mixed with Calcium Stearates

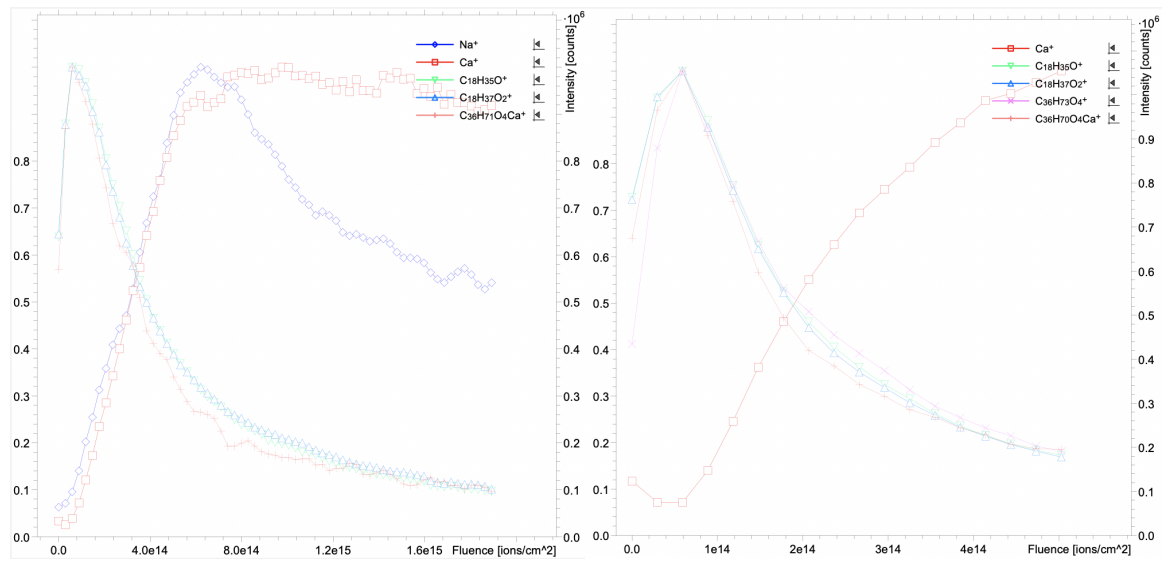


Figure 6.6: Profile (on the left) and limited profile (on the right) of Slide of oil mixed with calcium stearates in negative mode

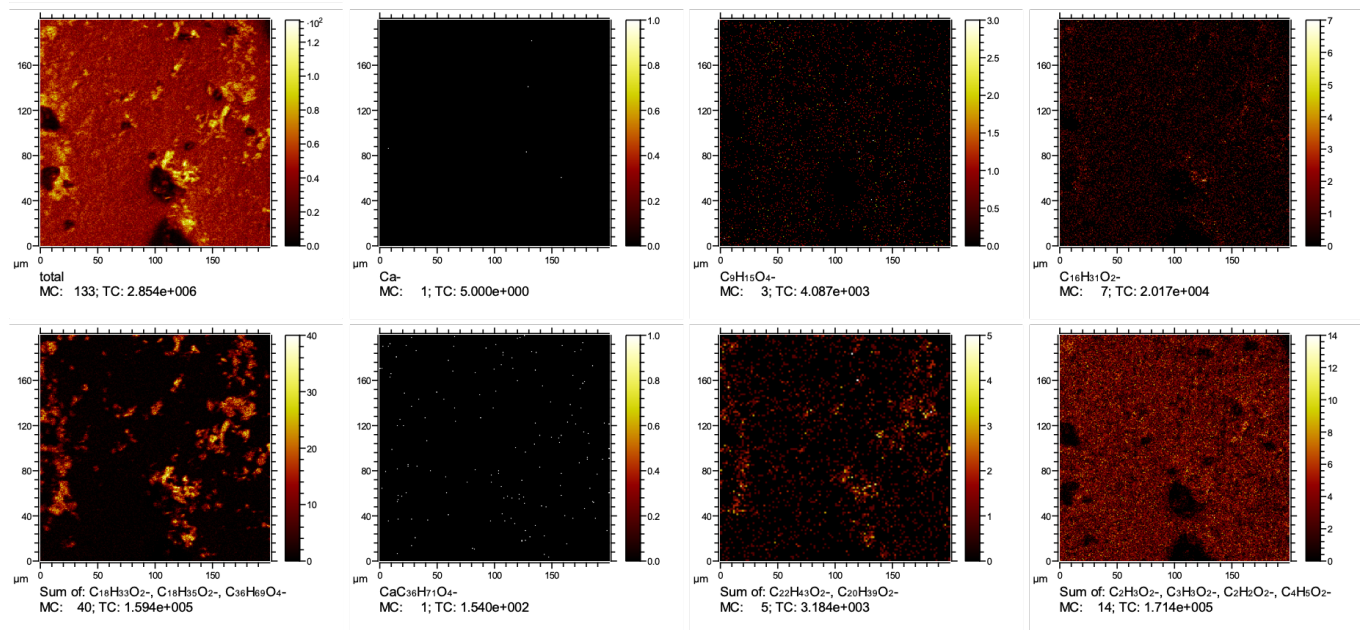


Figure 6.7: Images at optimal depth of slide of oil mixed with calcium stearates in Negative mode

Slide of oil mixed with Zinc Stearates

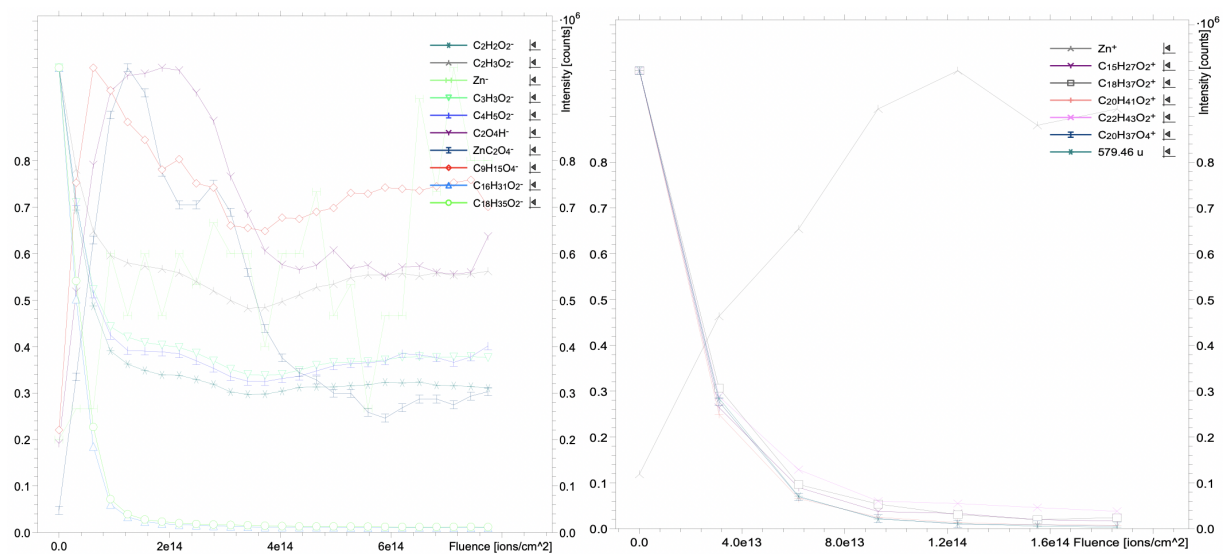


Figure 6.8: Profile (on the left) and limited profile (on the right) of Slide of oil mixed with Zinc stearates in negative mode

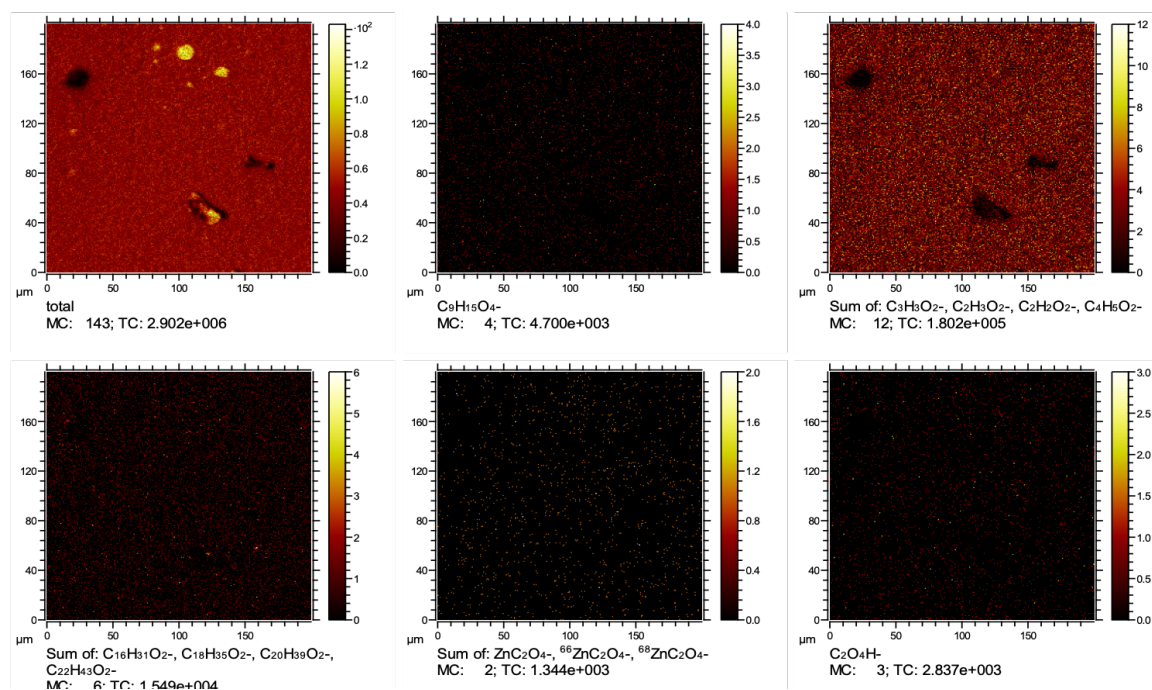


Figure 6.9: Images at optimal depth of slide of oil mixed with Zinc stearates in negative mode

Slide of oil mixed with Lead Oxalates

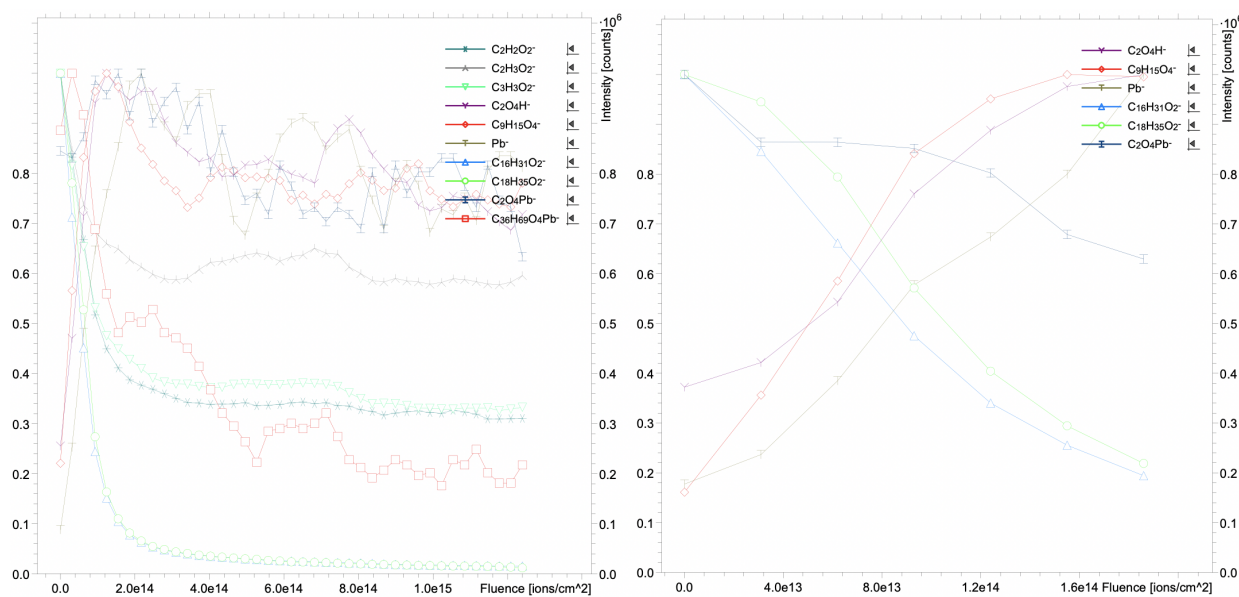


Figure 6.10: Profile (on the left) and limited profile (on the right) of Slide of oil mixed with Lead Oxalates in negative mode

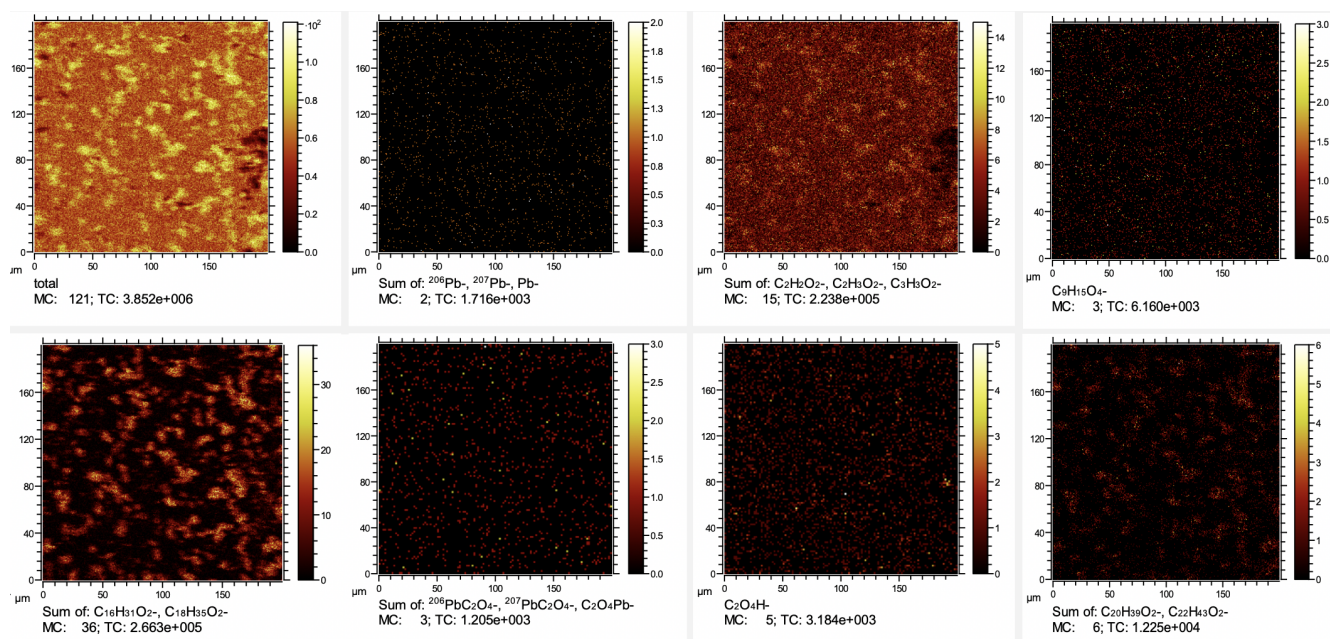


Figure 6.11: Images at optimal depth of slide of oil mixed with Lead oxalates in negative mode

Slide of oil mixed with Copper Oxalates

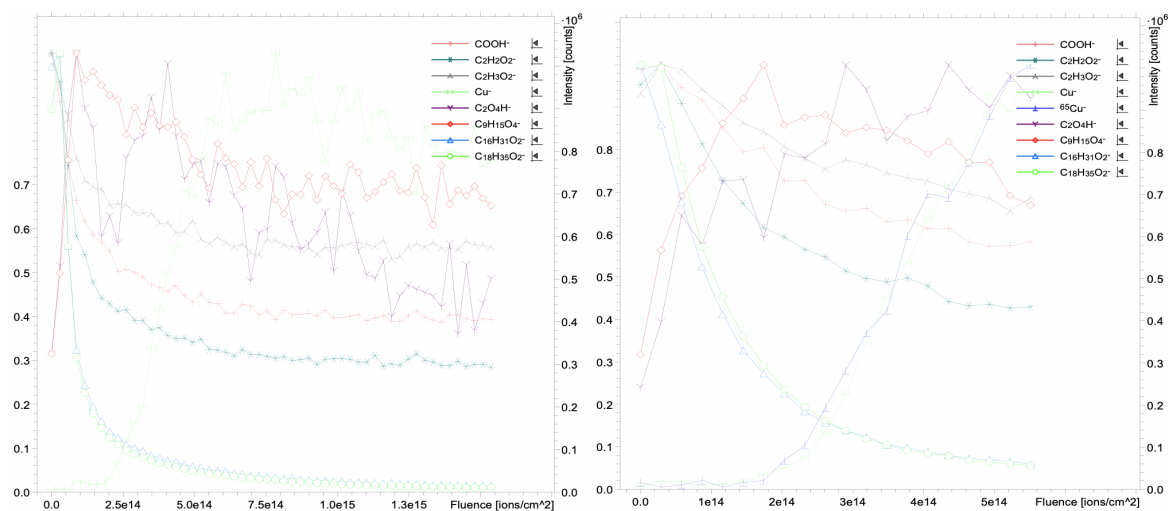


Figure 6.12: Profile (on the left) and limited profile (on the right) of Slide of oil mixed with Copper oxalates in negative mode

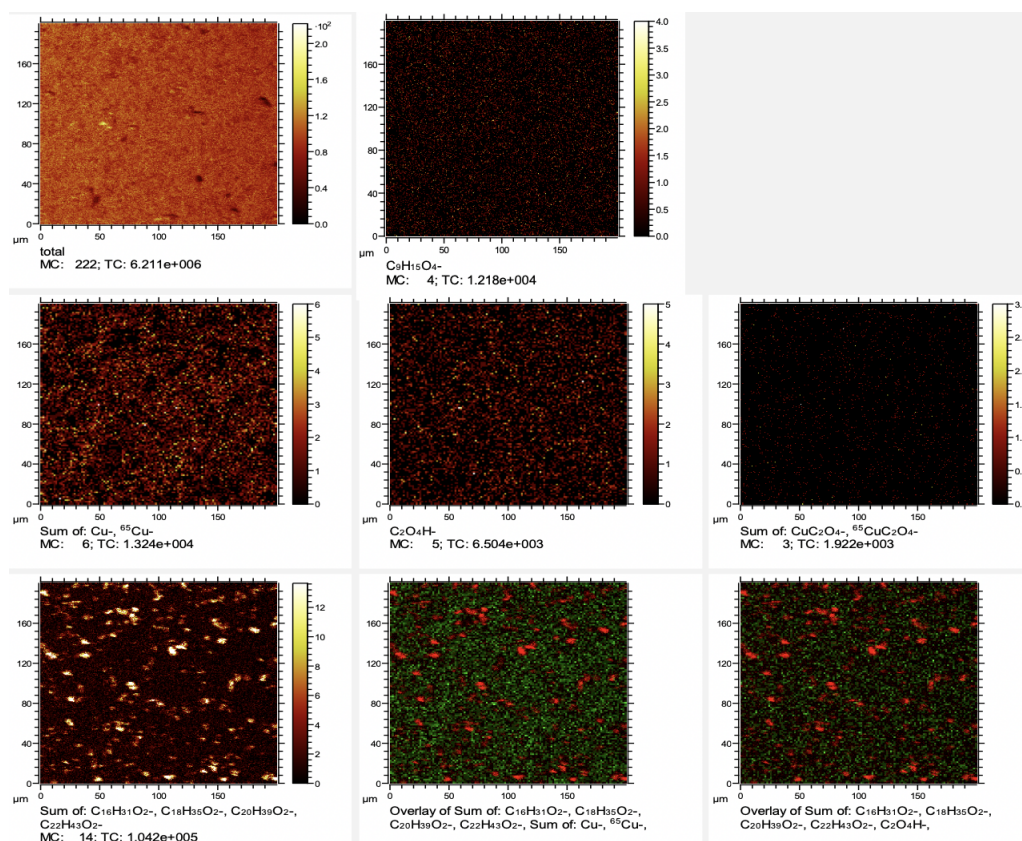


Figure 6.13: Images at optimal depth of slide of oil mixed with with Copper oxalates in negative mode

Slide of oil mixed with Calcium Oxalates

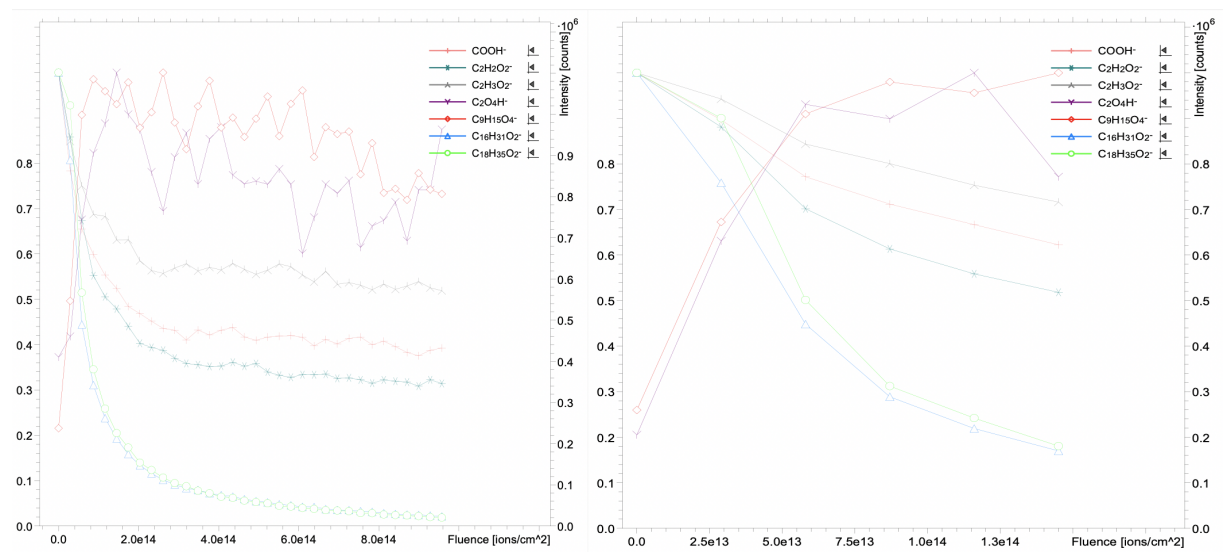


Figure 6.14: Profile (on the left) and limited profile (on the right) of Slide of oil mixed with Calcium Oxalates in negative mode

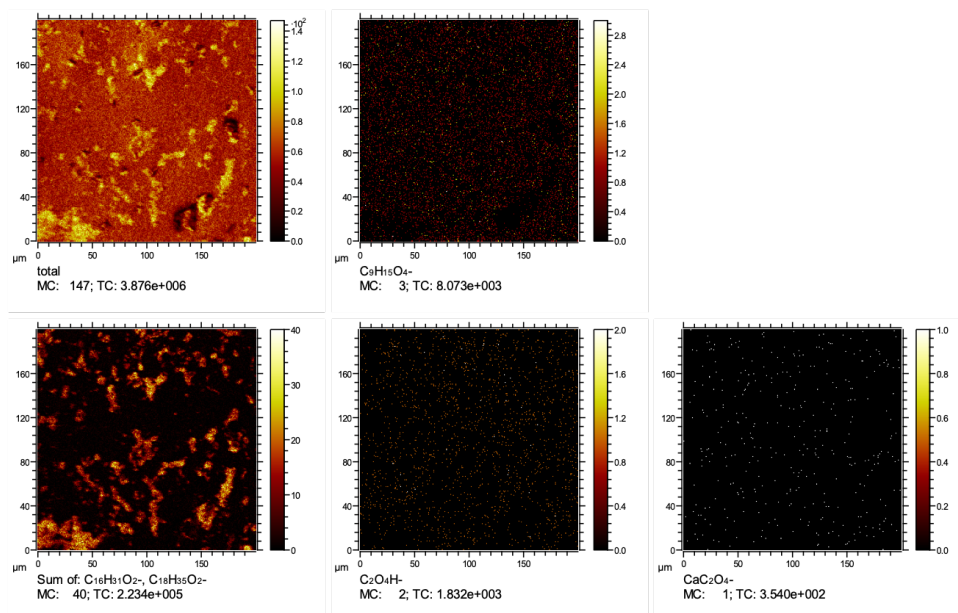


Figure 6.15: Images at optimal depth of slide of oil mixed with Calcium Oxalates in negative mode

6.3.2 Cross-sections

Cross-sections of oil mixed with Copper Stearates

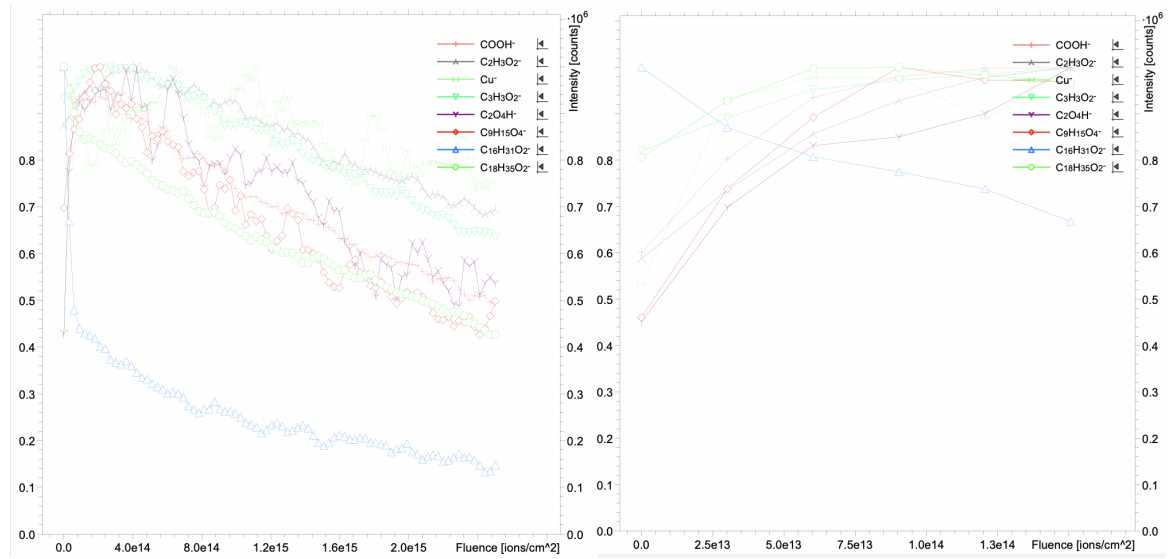


Figure 6.16: Profile (on the left) and limited profile (on the right) of Cross-sections of oil mixed with Copper Stearates in negative mode

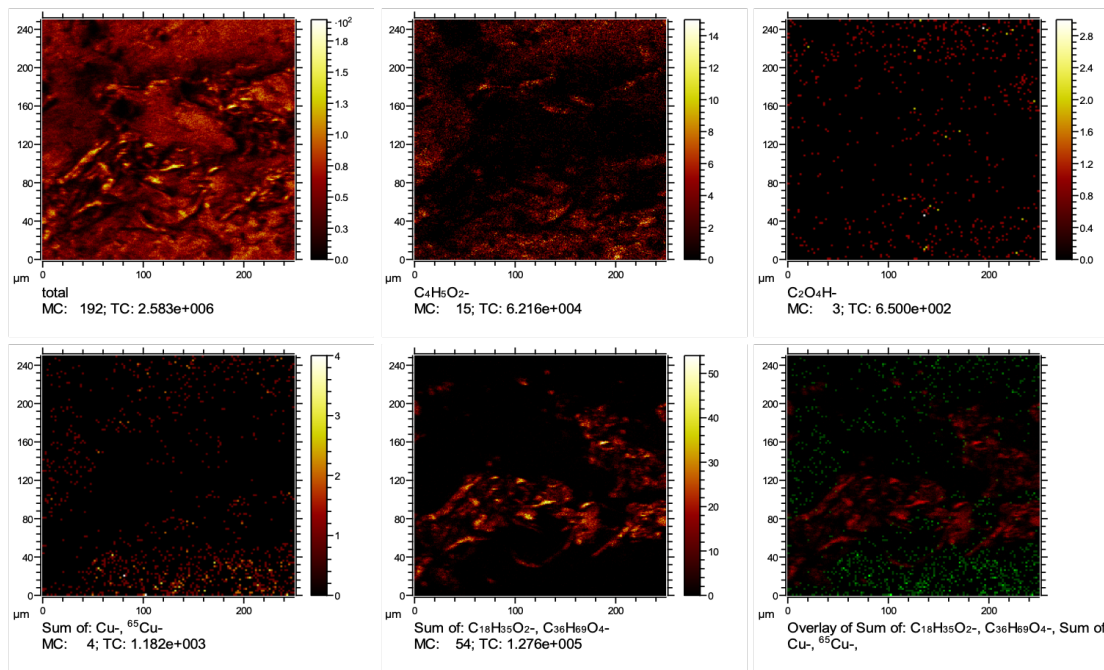


Figure 6.17: Images at optimal depth of cross-sections of oil mixed with Copper Stearates in negative mode

Cross-sections of oil mixed with Calcium Stearates

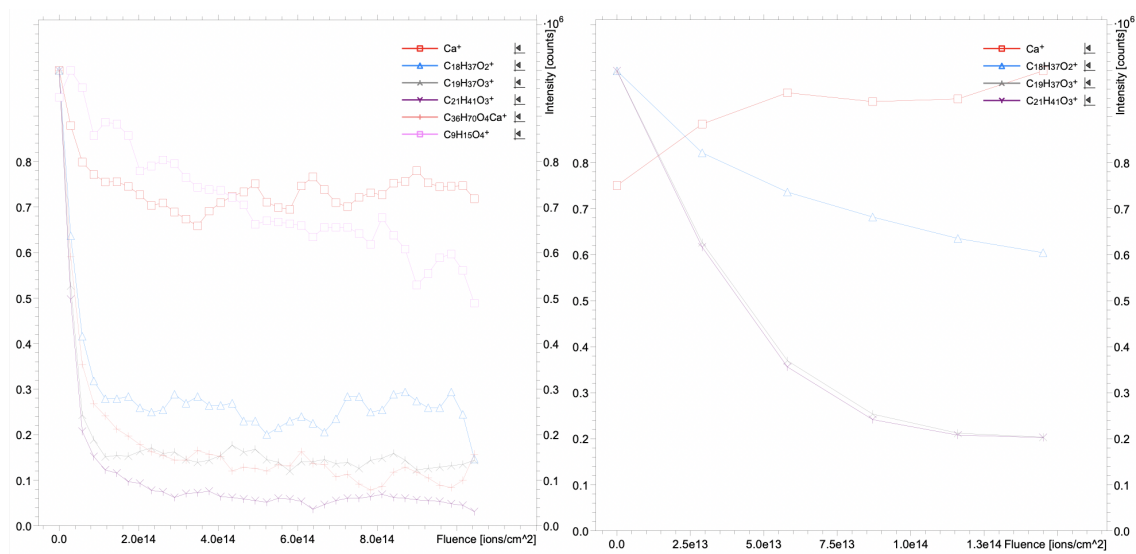


Figure 6.18: Profile (on the left) and limited profile (on the right) of Cross-sections of oil mixed with Calcium Stearates in positive mode

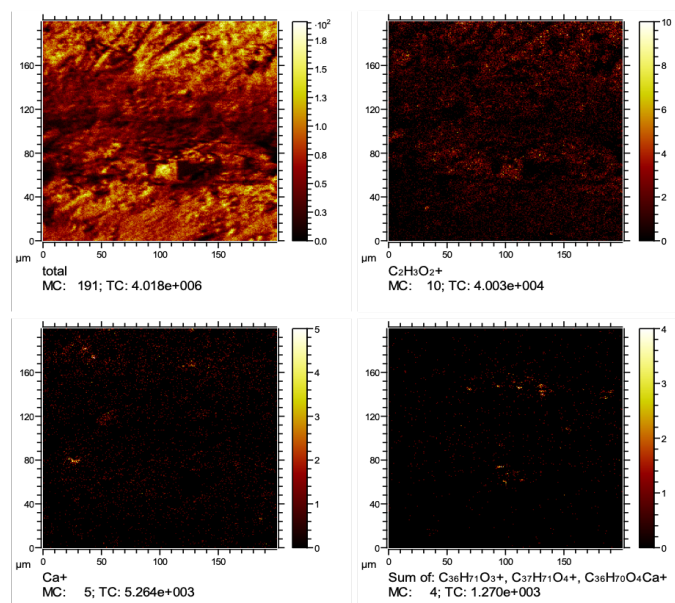


Figure 6.19: Images at optimal depth of cross-sections of oil mixed with Calcium Stearates in positive mode

Cross-sections of oil mixed with Zinc Stearates

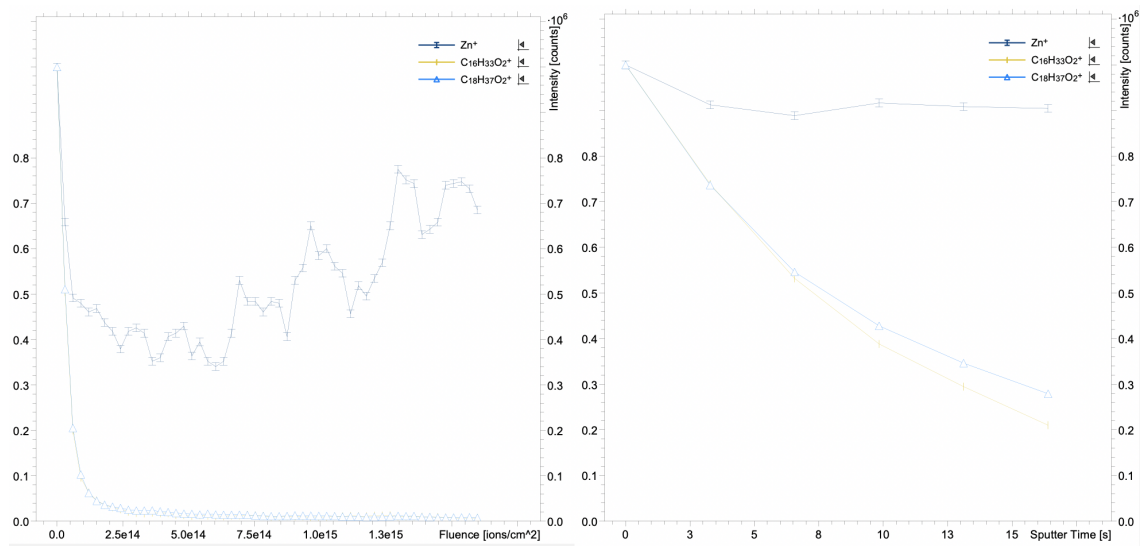


Figure 6.20: Profile (on the left) and limited profile (on the right) of Cross-sections of oil mixed with Zinc Stearates in positive mode

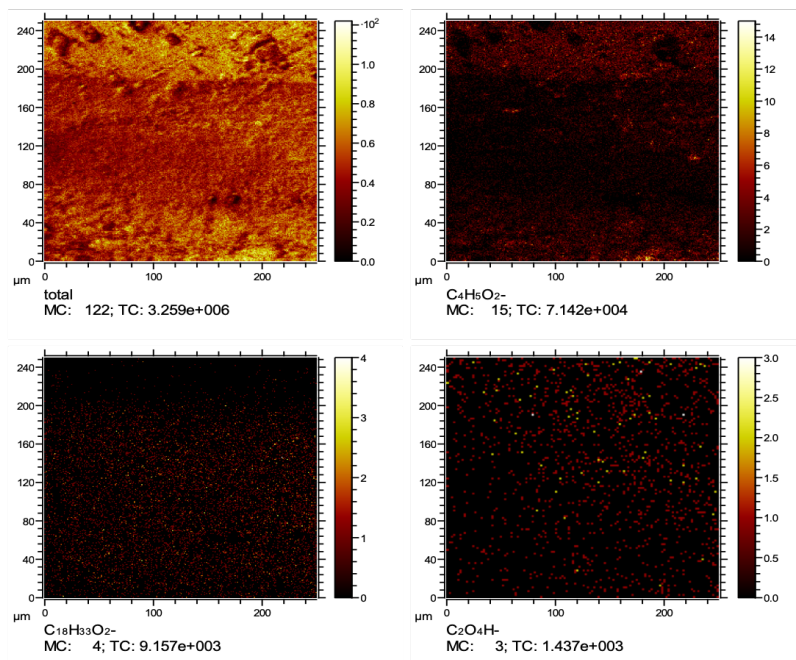


Figure 6.21: Images at optimal depth of cross-sections of oil mixed with Zinc Stearates in negative mode

Cross-sections of oil mixed with Lead Oxalates

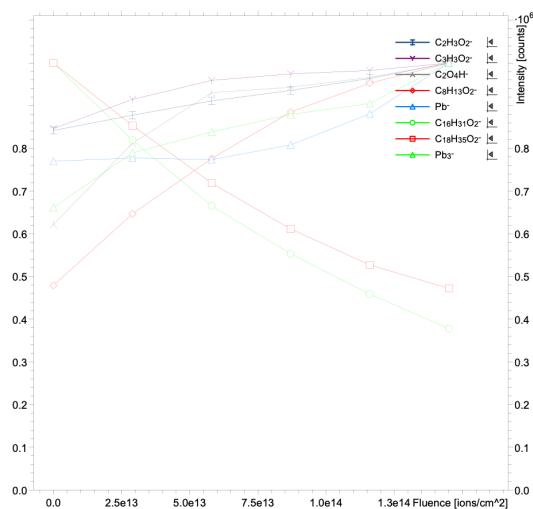


Figure 6.22: Profile (on the left) and limited profile (on the right) of Cross-sections of oil mixed with Lead Oxalates in positive mode

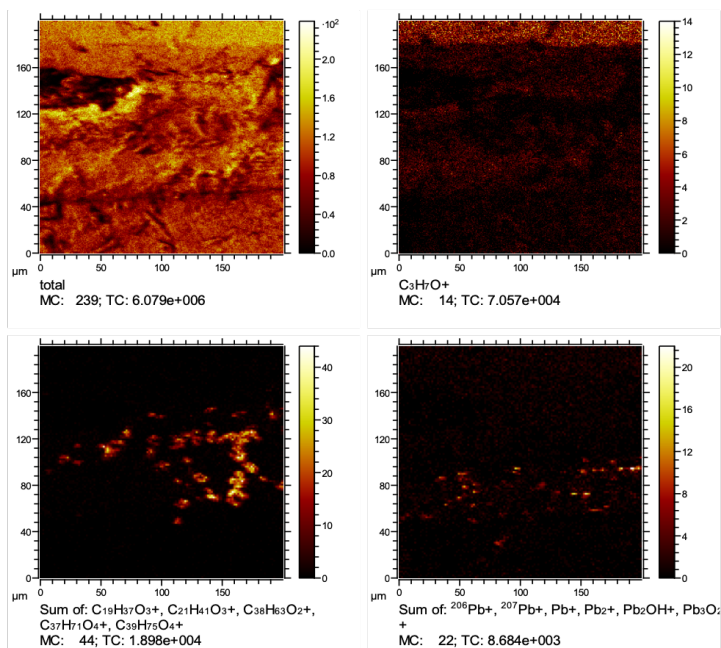


Figure 6.23: Images at optimal depth of cross-sections of oil mixed with Lead Oxalates in negative mode

6.4 Results of the analysis of the real samples

6.4.1 Red Sample from the Mystic Lamb of van Eyck

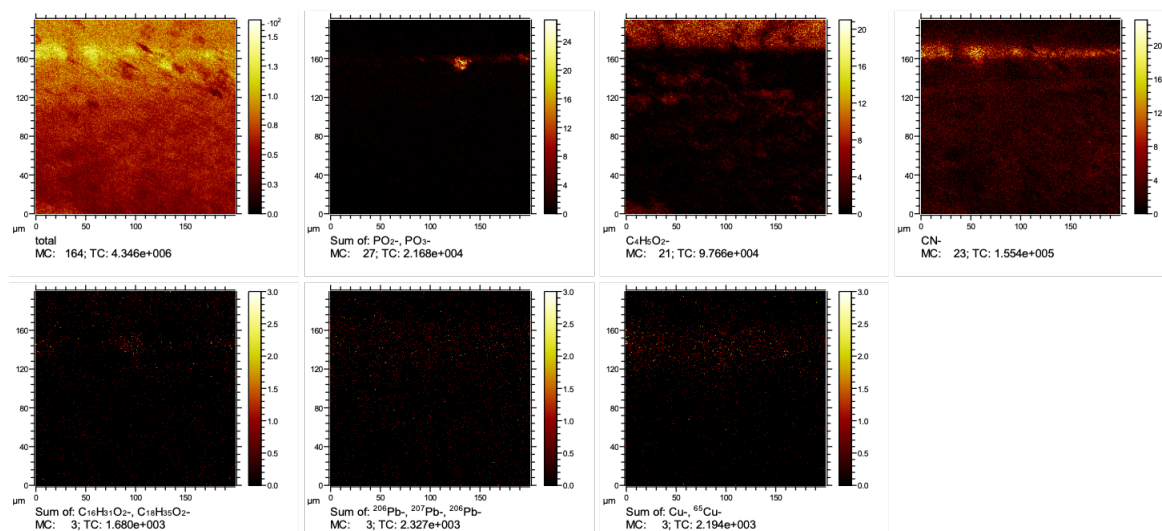


Figure 6.24: Images of the red sample from the mystic lamb in negative mode

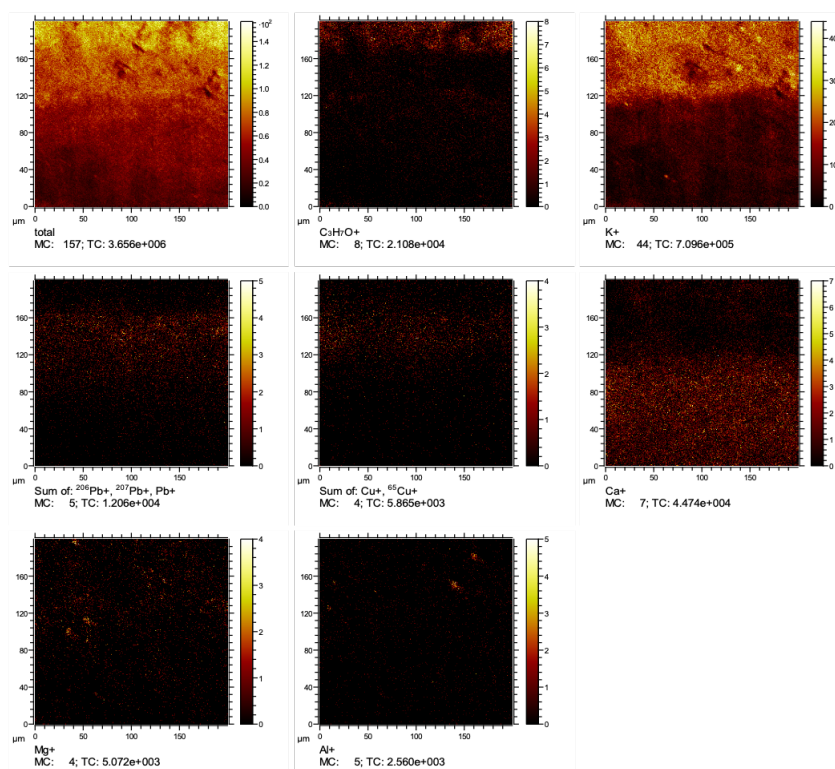


Figure 6.25: Images of the red sample from the mystic lamb in positive mode

6.4.2 Sample from the "Adam et Eve" painting of the master of the Mansi Magdalene

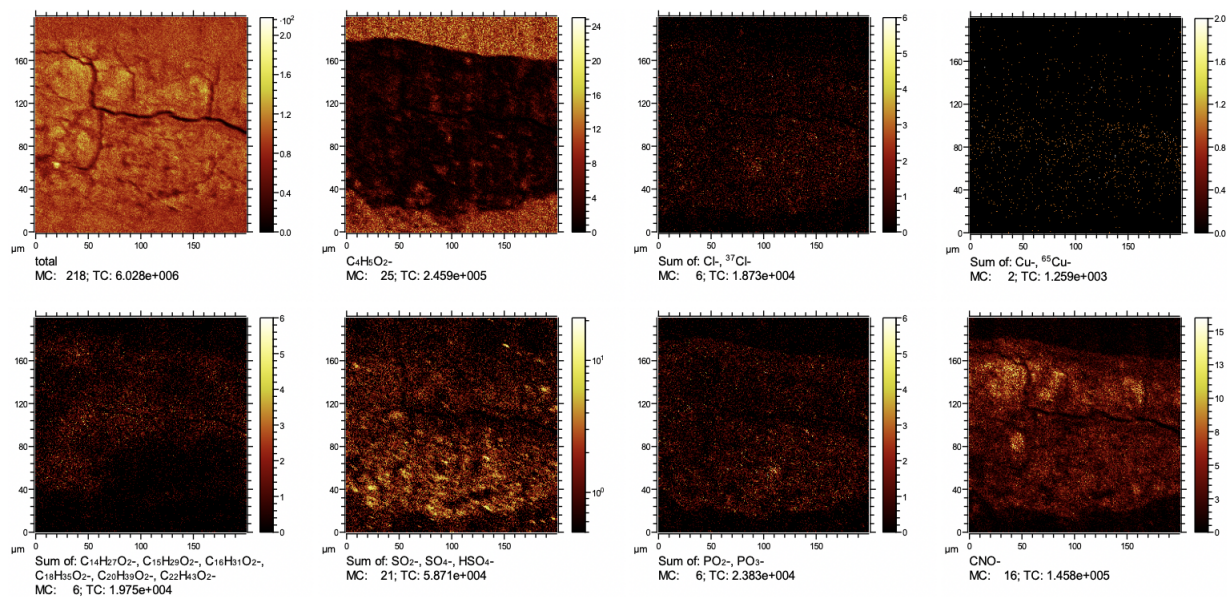


Figure 6.26: Images of the sample from the "Adam et Eve" in negative mode

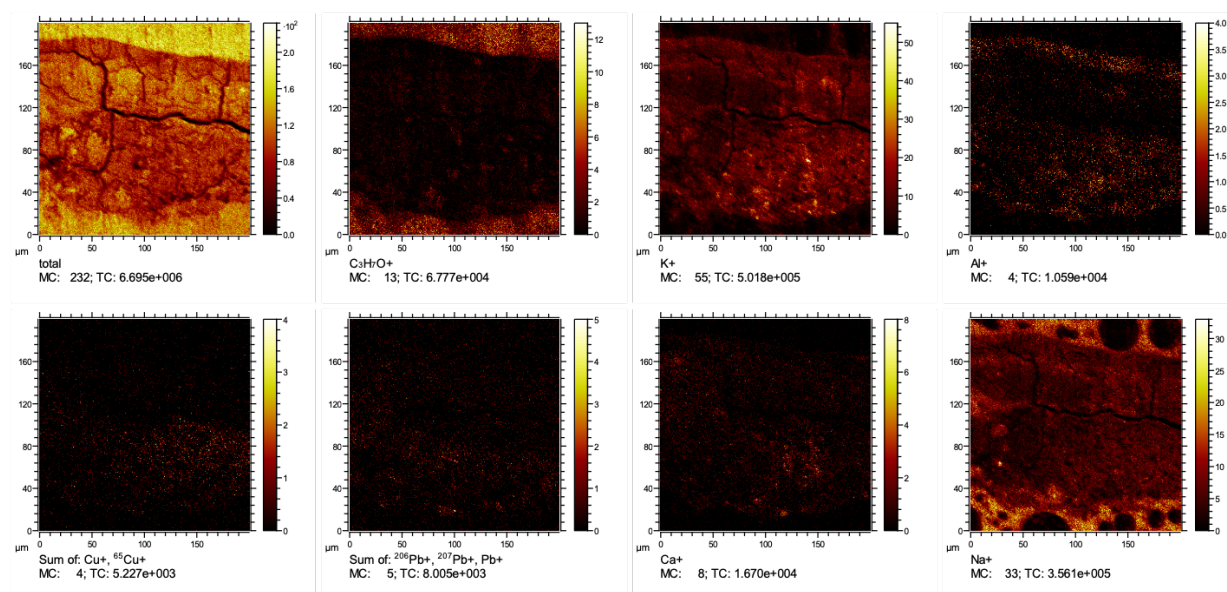


Figure 6.27: Images of the sample from the "Adam et Eve" in positive mode

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