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BSc in Physics Engineering

ANALYSIS OF MICRO AND NANOPLASTICS WITH X-RAY PHOTOELECTRON SPECTROSCOPY

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*“If I quit now, I will soon be back where I started.
And when I started I was desperately wishing to
be where I am now.” (Anonymous)*

ABSTRACT

Microplastic pollution has become an increasingly relevant issue in recent years and thus there have been many studies on the analysis of these microparticles regarding their identification. The most used techniques for this purpose are Fourier-Transform Infrared Spectroscopy (FT-IR) and Raman Microspectroscopy (RM). X-ray Photoelectron Spectroscopy (XPS) is also utilised, although a lot less frequently because of its limitations when working with polymers, such as accumulation of charge on the sample, limited spectral resolution to identify specific functional groups and the difficulties associated with analysing a non-uniform sample, which is inevitable when working with microparticles. However, XPS is a highly surface sensitive technique and can be very useful in MP analysis. Namely, the application of XPS in this area is the study subject of this thesis.

In this work, three industrial plastics were analysed with XPS: PVC, PA6 and PET. Reference samples of the indium substrate and the three plastics were prepared and analysed. The resulting spectra were fitted in accordance with literature. Afterwards, the relationship between the coverage of plastic in a sample and the signal intensities was studied by performing a calibration for each of the plastics, for which several samples were prepared with different percentages of coverage. As an additional necessary step, the thicknesses of the indium oxide-hydroxide and hydrocarbon contamination layers covering the metallic bulk indium were measured in order to properly account for the line intensity of indium, which was then used for the calibration. This way, a procedure is established for the quantification of different plastic particles deposited atop the indium surface.

Keywords: X-ray Photoelectron Spectroscopy, Microplastics, Oxide-hydroxide layer, Hydrocarbon contamination, Coverage, Surface analysis

RESUMO

A poluição de microplásticos tem-se tornado um problema cada vez mais relevante nos últimos anos e, por isso, tem havido muitos estudos sobre a análise de micropartículas no que toca à sua identificação. As técnicas mais utilizadas para este propósito são a Espetroscopia de Infravermelho por Transformada de Fourier (FT-IR) e Microespectroscopia de Raman (RM). A Espetroscopia de Fotoeletrões com Raios-X (XPS) também é usada, embora muito menos frequentemente devido às suas limitações a trabalhar com polímeros, tais como acumulação de carga na amostra, resolução espectral limitada para identificação de grupos funcionais específicos e as dificuldades associadas com a análise de uma amostra não-uniforme, o que é inevitável quando se trabalha com micropartículas. Contudo, XPS é uma técnica altamente sensível à superfície e pode ser muito útil na análise de microplásticos. Nomeadamente, a aplicação de XPS nesta área é o objeto de estudo desta tese.

Neste trabalho, foram analisados três plásticos industriais: PVC, PA6 e PET. Foram preparadas e analisadas amostras de referência do substrato de índio e dos três plásticos. Os espectros resultantes foram ajustados de acordo com a literatura. De seguida, foi estudada a relação entre a cobertura de superfície pelo plástico numa amostra e a intensidade do sinal ao realizar uma calibração para cada um dos plásticos, para a qual foram preparadas várias amostras com diferentes percentagens de cobertura. Adicionalmente, foram medidas as espessuras das camadas de óxido-hidróxido de índio e de contaminação por hidrocarbonetos que cobrem o volume metálico de índio com o objetivo de considerar apropriadamente a intensidade da linha de índio, que foi depois utilizada na calibração. Deste modo, é estabelecido um procedimento para a quantificação de diferentes partículas de plástico depositadas sobre a superfície de índio.

Palavras-chave: Espetroscopia de Fotoeletrões com Raios-X, Microplásticos, Camada de óxido-hidróxido, Contaminação por hidrocarbonetos, Cobertura de superfície, Análise de superfícies

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ACRONYMS

AC	acrylic
AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscopy
FT-IR	Fourier-Transform Infrared
GC-MS	Gas Chromatography-Mass Spectrometry
MP	microplastic
NP	nanoplastic
PA	polyamide
PE	polyethylene
PES	polyester
PET	polyethylene terephthalate
PP	polypropylene
PS	polystyrene
PVC	polyvinyl chloride
RM	Raman Microspectroscopy
UHV	ultra-high vacuum
XPS	X-ray Photoelectron Spectroscopy

CHEMICAL SYMBOLS

$In(OH)_3$ Indium(III) hydroxide

In_2O_3 Indium(III) oxide

INTRODUCTION

Microplastic (MP) and nanoplastic (NP) are synthetic polymers that are becoming the most persistent contaminants in marine and freshwater environments. They can be categorised as primary MP, comprising particles that were produced intentionally for a specific purpose (e.g. microbeads in cosmetic products or preproduction plastics that are raw material for producing larger plastic items), and secondary MP, which is the result of fragmentation of larger pieces of plastic [2, 3]. According to the National Oceanic and Atmospheric Administration (NOAA) [4], MPs are defined as particles smaller than 5 mm while NPs are defined by the European Commission as particles ranging from 1 nm to 100 nm [5]. This would place MP in the particle size range of 100 nm to 5 mm. However, the particles with sizes between 100 nm and 1 μ m have also been referred to as sub μ -plastic [2].

The technique used in this study is X-ray Photoelectron Spectroscopy (XPS), which represents an innovation regarding the application of the method to MP. XPS is a highly surface sensitive technique, with great capability for qualitative and quantitative analysis. However, due to the complexity of the experiment and the data analysis, as well as some difficulties faced when working with polymers, it is not frequently used in MP analysis. The most popular techniques in this field of analysis are Fourier-Transform Infrared Spectroscopy and Raman Microspectroscopy, as well as Gas Chromatography-Mass Spectrometry methods. This dissertation aims to demonstrate how XPS application can be useful in MP analysis, despite its limitations. The project will consist of the following steps:

- Getting samples of a few industrial plastics to analyse with XPS.
- Turning the plastics into powder.
- Development of the data analysis procedures for the quantification of the laterally non-uniform samples by XPS.
- Analysing surface coverage to study the quantification abilities of XPS in such samples.

- Determining the minimum quantity of microplastics that can be detected with the available XPS instrument.

STATE OF THE ART

In recent years, there have been more and more studies done on the impact of the current pollution problem in our oceans and rivers. A large part of it is plastic pollution and the micro and nanoparticles of plastic are particularly problematic, since these can't be easily collected. Therefore, in the scientific community, there have been studies on the analysis of these micro and nanoplastics regarding their identification and localisation with the application of a few different techniques which will be stated and described in this chapter.

The analysis of microplastics is usually done with vibrational spectroscopy methods integrated with optical microscopy to provide imaging, which enables the analysis of individual particles. This provides information on particle size and its distribution, particle geometry and spectroscopic identification. However, it becomes increasingly difficult to get good results with this methodology as the particle size decreases ($<10\text{ }\mu\text{m}$) because of an increase in the number of small particles and due to the limits of detection of the methods. In the analysis of sub μ - and nanoplastic, it's necessary to apply a combination of different techniques in order to get all the information that might be needed, like particle size, distribution and geometry and spectroscopic identification. This eliminates the need for single particle analysis with spectroscopic methods and only demands measurements of a whole sample [2].

Fourier-Transform Infrared (FT-IR) Spectroscopy is a form of vibrational spectroscopy that relies on the absorbance, transmittance or reflectance of infrared light and it is the most used spectroscopic technique in MP analysis [6, 7]. When the sample is irradiated, some wavelengths may be absorbed while others can merely pass through the sample unaffected. The molecular bonds in the sample have distinct vibrational frequencies and absorb different amounts of energy. These losses of energy correspond to the peaks returned in a 'fingerprint' spectrum that can provide identification of the sample (Fig. 2.1).

There are several sampling techniques for FT-IR analysis but when analysing polymers the ATR mode is usually employed, in which the FT-IR spectrometer is coupled with an Attenuated Total Reflectance (ATR) accessory, which allows the IR spectrum of a material to be obtained simply by pressing the sample against a transparent crystal. The IR light passes through the crystal into the sample, where the energy is absorbed and then the light is reflected back into the crystal to generate the spectrum.

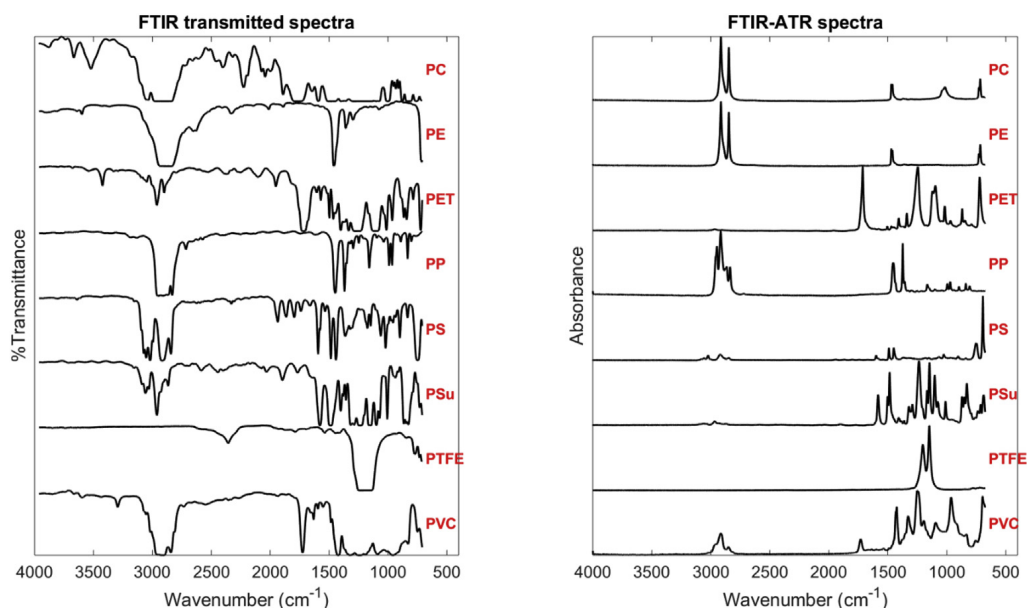


Figure 2.1: Examples of FT-IR spectra of plastics obtained in transmission and ATR modes [8].

FT-IR can only be applied for the bulk analysis of sub μ - and nanoplastic, since the size limit for FT-IR single particle analysis is in the range of 10 μ m [2].

There is a commercial set-up that combines FT-IR with Atomic Force Microscopy (AFM), in order to record chemical images with a spatial resolution below the diffraction limit. In this setup, IR absorption at the location of the tip causes thermal expansion, which induces an oscillation of the AFM cantilever tip. With that, spectral and spatial information in the range of 50 nm can be obtained [9].

Another technique that is very usual in the analysis of MP is Raman Microspectroscopy (RM) [10–12]. A monochromatic laser (which can be in the visible range, near infrared or near ultraviolet) is focused on a sample and the radiation interacts with the molecular vibrations of the bonds, resulting in a shift in energy of the scattered photons. This shift is called 'Raman shift' and it is the difference between the incident light and the scattered light. If the scattered light has a higher wavelength than the laser, it is called Stokes scattering; if it is lower, it is called Anti-Stokes scattering. These kinds of scattering are inelastic and they're the ones that are most relevant in RM. There is also

Rayleigh scattering, which is elastic, and it happens when the scattered light is exactly at the same wavelength of the incident light. The Raman shifts are unique to each molecular bond, and thus give a vibrational 'fingerprint' spectrum (example in Fig. 2.2).

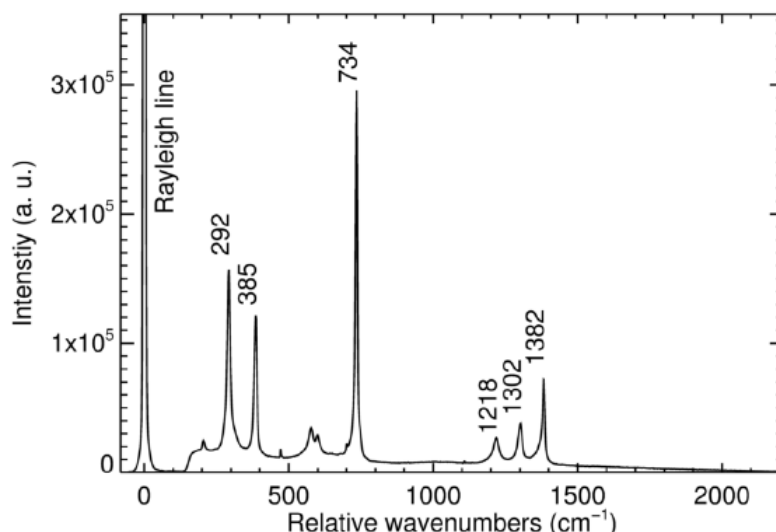


Figure 2.2: Raman spectrum of a Teflon sample [13].

This spectrum is complementary to the FT-IR spectrum because FT-IR only activates vibrational modes that alter the dipole moment (asymmetrical stretch) and RM activates vibrational modes that alter the polarizability (symmetrical stretch) [14]. FT-IR spectroscopy is sensitive to hetero-nuclear functional group vibrations and polar bonds, such as O-H or N-H. RM, on the other hand, is sensitive to homo-nuclear molecular bonds. For example, it can distinguish between C-C, C=C and C≡C bonds. Therefore, using both techniques provides complete information about the molecular vibrations and allows for an increased probability of accurately identifying the plastic particles.

Since the light source does not need to be infrared light, shorter wavelength lasers (e.g. 532 nm) can be utilised, which results in higher spatial resolution. Therefore, RM can be applied for the analysis of MP particles down to 1 μm [12]. RM has the potential for single particle analysis of sub μ -plastic because Raman microscopes are confocal, giving them submicrometer resolution. However, it would take several days to identify a representative number of particles.

Besides spectroscopy, Gas Chromatography-Mass Spectrometry (GC-MS) methods are other quite common approaches in MP analysis [2, 12]. GC-MS combines two powerful techniques to provide the identification of compounds and potentially a quantitative analysis. Gas chromatography (GC) is a separation science technique that is used to separate the chemical components of a sample mixture and then detect them to determine their presence and/or how much is present. A sample is volatilised and carried by an inert gas through a coated glass capillary column. The time it takes a specific compound

to pass through the column to a detector is called its “retention time”, which can be used for identification when compared to a reference. However, GC alone cannot be used for the identification of unknown materials, which is why pairing it with mass spectrometry (MS) can be useful.

MS is an analytical technique that measures the mass-to-charge ratio (m/z) of charged particles and therefore can be used to determine molecular weight and elemental composition. In the usual MS step of GC-MS, compounds leaving the GC column are fragmented by electron impact and the charged fragments are detected, subsequently producing a spectrum that can be used to identify the molecules in the sample. The general instrumentation setup is schematised in Fig. 2.3.

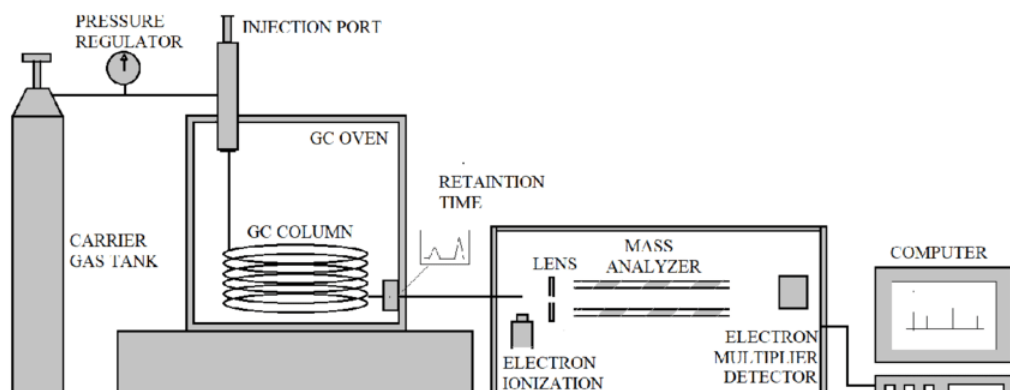


Figure 2.3: Schematic representation of a typical GC-MS setup [15].

There are two methods of GC-MS. One of them is Py-GC-MS (Pyrolysis Gas Chromatography Mass Spectrometry). Pyrolysis is a thermal decomposition process of organic material at elevated temperatures in an anaerobic environment. By applying heat to a sample that is comparable to the energy of specific bonds, the molecule will fragment in a reproducible way. The fragments are then separated by the analytical column to produce the chromatogram (pyrogram) which contains both qualitative and quantitative information. The number of peaks, the resolution by capillary GC, and the relative intensities of the peaks permit discrimination among many similar formulations, making pyrolysis a powerful tool in the identification of unknown samples. The other one is TED-GC-MS (Thermoextraction Desorption Gas Chromatography Mass Spectrometry), which uses heat (instead of solvent extraction) to release organic compounds from the adsorbent and transfer the entire collected sample to a gas chromatograph for analysis [2].

However, these two techniques have limits of detection that are too high for sub μ - and nanoplastic detection without preconcentration, which is the process in which the concentration of a sample is increased to be suitable for analytical determination. Since the mass of these particles in environmental samples can be expected to be very low, the step of preconcentration would be essential. Yet, there is no available data on sub μ - and

nanoplastic content in the environment, so it's quite difficult to project the requirements for limits of detection and preconcentration factors. Py-GC-MS and TED-GC-MS are faster than spectroscopic single particle analysis but can't provide information on particle size and distribution, as well as morphology or aggregation, which will have to be obtained through other particle characterisation techniques [2].

The application of XPS in MP analysis represents an innovation and a challenge. It has been applied in some studies as a complementary method of identification of bulk polymers [16, 17], but it is not used in this field nearly as frequently as FT-IR and RM because of the challenges that are faced when working with polymers in XPS [18] and also because it is an expensive technique that requires ultra-high vacuum (UHV) conditions due to its high sensitivity to surface contamination and data analysis with XPS can be fairly time consuming.

The analysis of polymers with XPS requires removal of low molecular weight material, solvents, salts, and buffers to enable the collection of useful data and to avoid issues with cross contamination. Control samples are often necessary, as the evaluation of XPS data works best when comparing samples. However, this is the case for all the previously mentioned techniques as well.

The identification and quantification of specific functional groups on the surface can also be challenging. XPS is not the best technique for identifying functional groups with necessary specificity due to limitations in spectral resolution and peak overlap. Because of this, complementary techniques can sometimes be necessary to unambiguously identify the polymers. Alternatively, examination of the valence band spectra can help to fingerprint polymers. In instances where there is adequate prior knowledge of the sample, it's acceptable to assign spectral features to species that are known to be associated with the sample but cannot be clearly resolved in the spectra. However, a significant amount of knowledge and confidence in the quality of the sample is necessary to justify this approach, criteria that may only be satisfied with well-defined reference materials.

Another important consideration in the analysis of electrically non-conductive materials is the potential for differential sample charging to affect data quality. The emission of electrons from the sample surface leaves a positively charged surface which, in the case of a conductive material in contact with earth, will be quickly neutralised by the flow of delocalised or free electrons from the bulk to the surface. In the case of non-conductive materials, such as polymers, a residual surface charge remains and will affect the kinetic energy of emitted electrons. Often this leads to peaks becoming distorted, spectra from different regions or depths of the sample being at different potentials, and worse, those potentials changing over time, for instance, during data collection. There are ways to

combat this accumulation of charge, through either an electron flood gun or a combination of electron and ion beams directed at the sample being analysed. Although it is practically impossible to achieve 100% charge neutralisation within the whole specimen, it is possible to obtain an equilibrium state at the sample surface where all spectral peaks are shifted by a constant, stable value and the peak shapes themselves remain unaffected.

The ideal sample geometry for XPS analysis is an atomically flat surface, which is not the case when working with microparticles. Thus, the analysis of powders or small particles like micro and nanoplastics can be problematic because:

1. They tend to outgas significantly due to a large surface area, which means longer pump-down times (possibly overnight) are required.
2. They do not present a large continuous surface area to the x-ray beam and since everything that is in the line-of-sight of the detector can potentially generate a signal, if it can “see” the support underneath the powder particles, either around one particle or through gaps between particles, a corresponding signal will be acquired, which is not always desired.
3. There can be shadowing effects due to the irregularly shaped surface, which affects the signal intensity.
4. In the case of non-conductive (polymer) materials, they are more prone to differential charging.

However, despite the difficulties, the XPS technique has potential advantages in polymer analysis when compared to other methods. It is superior to vibrational spectroscopic techniques, like RM and FT-IR, in bond identification, it provides direct identification of a particular element, and it is the best tool for quantification purposes.

X-RAY PHOTOELECTRON SPECTROSCOPY

3.1 Principles

X-ray Photoelectron Spectroscopy (XPS) is a particular case of photoelectron spectroscopies (PES), in which X-ray photons are used to excite and ionise the atoms of the sample under analysis. XPS is used as an analytical technique to determine surface chemical composition and identify the bonds between the atoms in a sample by probing the electronic structure of occupied states at the surface and near-surface region of the sample. Its base is the photoelectric effect, in which the electron, initially in a state with binding energy E_b , absorbs a photon of energy $h\nu$ and leaves the solid with kinetic energy

$$E_k = h\nu - E_b - \phi$$

where $\phi = E_{vacuum} - E_{Fermi}$ is the work function of the material. However, on their way towards the spectrometer, the photoelectrons additionally change their energy due to the contact potential between the sample and the spectrometer. Therefore, the measured kinetic energy of the detected photoelectrons is

$$E_k = h\nu - E_b - \phi_s \quad (3.1)$$

where ϕ_s is in fact the work function of the spectrometer.

The ejected electron can come from a core level or from the occupied portion of the valence band, but XPS focuses mainly on electrons in deep core levels. XPS can be used to analyse all elements in the periodic table, except for hydrogen and helium because these elements have no core electrons, they have only the valence shell.

Although XPS predominantly focuses on photoelectrons and their kinetic energy, ejection of electrons through other processes also occurs. An ejected photoelectron leaves a core hole in the atom, and following the departure of said photoelectron, an electron from a higher energy orbital will drop down to fill the hole. This releases energy, equal to the difference in energy between the two orbitals, that can be emitted as a characteristic

X-ray photon or transferred to an electron in an outer shell, which is ejected then as an Auger electron.

The Auger electron is labelled after the orbital shells involved in the transitions and its kinetic energy is, to a first approximation, a function of the orbital energies themselves and not of the radiation responsible for the production of the core hole. For example, the Auger electron from a transition in which the initial ionisation occurs in level X, followed by the filling of the hole in level X by an electron from level Y and ejection of an electron from level Z, would be labelled XYZ, and its kinetic energy would be

$$E_{XYZ} = E_X - E_Y - E_Z - \phi_s \quad (3.2)$$

Since the excitation energy has no influence on the kinetic energy of the Auger electron, Auger peaks therefore occupy fixed positions on a kinetic energy scale, whereas photoelectron peaks sit at fixed positions on a binding energy scale. By changing the photon energy, the two types of peak can be made to move along different energy axes, which can be useful for purposes of identification.

It is worth mentioning that the type of notation shown in eq. (3.2), called X-ray notation, is more typically used in Auger Electron Spectroscopy (AES) which is a technique used for analysis of surface chemical composition in which the Auger emission process is the main focus. While X-ray notation can be and is used in XPS, spectroscopic notation is more usual [19]. The equivalence of the two types of notation is set out in Table 3.1.

Table 3.1: Equivalence of spectroscopic and X-ray notations.

Quantum numbers			Spectroscopic state	X-ray state
n	l	j		
1	0	1/2	1 s	K
2	0	1/2	2 s	L ₁
2	1	1/2	2 p _{1/2}	L ₂
2	1	3/2	2 p _{3/2}	L ₃
3	0	1/2	3 s	M ₁
3	1	1/2	3 p _{1/2}	M ₂
3	1	3/2	3 p _{3/2}	M ₃
3	2	3/2	3 d _{3/2}	M ₄
3	2	5/2	3 d _{5/2}	M ₅
etc.	etc.	etc.	etc.	etc.

Although there are rare cases in which photoelectron lines can overlap, no two elements share all the same binding energies, meaning that measuring the photoelectron kinetic energies enables elemental analysis. As is shown in eq. (3.1), any changes in the binding energy are reflected in the kinetic energy, which means that chemical information can be obtained since alterations in the chemical environment of an atom can be followed by monitoring changes in the photoelectron energies. These changes are denominated chemical shifts.

Chemical shifts are the result of the formation of chemical bonds between atoms. This process involves electron transfer, thus the charge density on the atoms is changed, which results in changing the electron binding energy. The binding energy of an electron at a given level is defined by the interaction between the Coulomb attraction to the nucleus and the shielding of this attraction by other electrons in the atom. Electron charge transfer to a given atom enhances the electron shielding and, consequently, weakens the electron binding energy (the corresponding peak shifts to lower binding energies, relative to the Fermi level). Conversely, electron charge transfer from a given atom weakens the electron shielding and enhances the electron binding to the nucleus (the peak shifts to the higher binding energies) [20]. The analysis of these chemical shifts is the main strategy for identifying chemical bonds in XPS.

All but s-type atomic orbitals appear in the spectrum as two peaks, designated as doublets, due to spin-orbital splitting. The doublets arise through spin-orbit $j - j$ coupling, which describes the orbital motion of an electron around an atomic nucleus. The total angular momentum j of an electron is the sum of the orbital momentum l and the spin s : $j = l + s$. For each j there are $2j + 1$ degenerate states and the ratio between the numbers of states equals the ratio of the areas of the two peaks. As the distance from the nucleus increases, the spin-orbit splitting also increases, as can be understood in Table 3.2.

Table 3.2: Spin-orbit splitting parameters.

Orbital	l	s	$j = l + s$	Area ratio
s	0	$\pm 1/2$	$1/2$	-
p	1	$\pm 1/2$	$1/2, 3/2$	1:2
d	2	$\pm 1/2$	$3/2, 5/2$	2:3
f	3	$\pm 1/2$	$5/2, 7/2$	3:4

Besides photoelectron and Auger lines, there are other peaks that can be present in a spectrum:

Satellites

X-ray sources produce a series of lines consisting of a main one with some minor lines that can cause small satellite peaks for each major photoelectron peak. These are designated X-ray line satellites and their intensities and spacings are characteristic of the particular X-ray anode material.

'Shake-up' lines are another type of satellites that occur after photoionisation when the resultant ion remains in an excited state, just a few eV above ground state. When this happens, the kinetic energy of the emitted photoelectron is reduced by a loss corresponding to the energy difference between the ground and excited states and this appears in the spectrum as a satellite with binding energy slightly higher than the main peak's.

Ghost peaks

Ghost lines are small peaks that result from X-radiation coming from a foreign material. They most commonly occur when a dual anode source is being utilised and there is Al purity in the Mg source, or vice-versa. The positions of these ghost peaks can be easily calculated.

Plasmon loss lines

A plasmon loss stems from interaction between photoelectrons and surface electrons in a solid. Electrons passing through a solid can excite a collective oscillation of bulk electrons. This is called a bulk plasmon energy loss, and if the frequency of oscillation is ω_b , then the plasmon energy loss is $\hbar\omega_b$. Subsequent plasmon losses can occur, resulting in the presence of a series of peaks in the spectrum, all equally spaced by $\hbar\omega_b$ but decreasing in intensity.

A more localised oscillation can happen at the surface, which is called a surface plasmon, with frequency ω_s and energy loss $\hbar\omega_s$ [21].

3.2 Instrumentation

A typical equipment for performing XPS consists of an X-ray source, an electron energy analyser, an electron detector/multiplier, all maintained under UHV, and a suitable electronic system to convert the detected signal into a readable spectrum (Fig. 3.1). This section will focus on the instrumentation used in this project, which was an upgraded XSAM 800 system manufactured by Kratos [22].

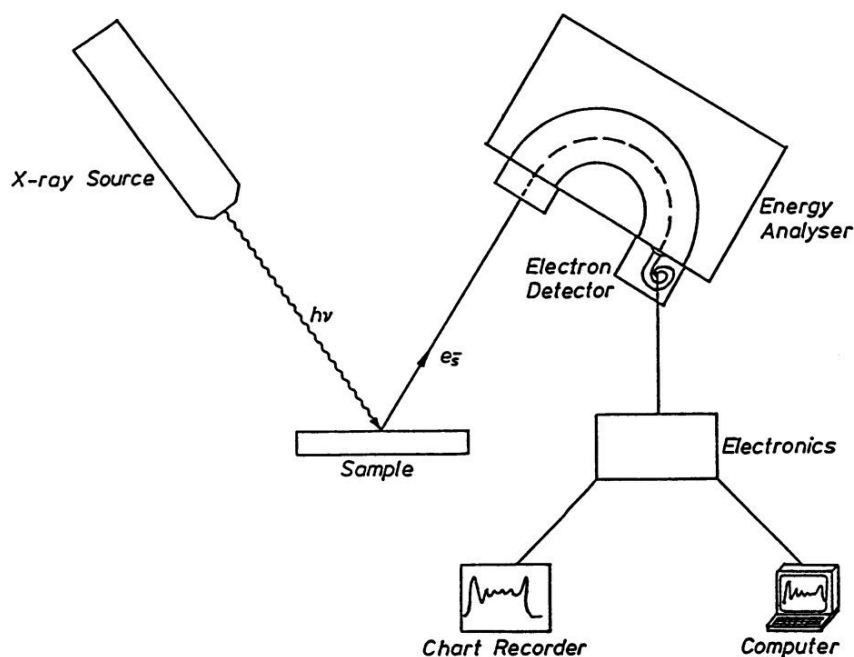


Figure 3.1: Schematic representation of a typical XPS equipment [21].

Vacuum

XPS requires conditions of UHV (pressures between 10^{-7} and 10^{-12} mbar) for two reasons. One of them is that the emitted electrons must not scatter off air molecules while travelling to the analyser, and this requires vacuum levels on the order of 10^{-5} - 10^{-6} mbar. The other reason is the high sensitivity to surface contamination, which is minimised when measurements are conducted under pressure conditions of 10^{-9} mbar and below [23].

X-ray source

A very important parameter to have in consideration when choosing an X-ray source for XPS is the photon energy of the source. Since XPS typically aims at binding energies within 1 keV, it's important to use a source with photon energy higher than that in order to keep high photoionisation cross-section.

Another important parameter is energy resolution. Due to the energy spread, or line-width, of an electron in a core level being very small, the line-width of the photoelectron energy depends on the line-width of the source. To extract detailed chemical information from the spectra and to be able to detect subtle chemical effects, an energy resolution better than 1.0 eV is necessary.

Other important factors are the conductivity of the source material — it should be a good conductor to enable fast removal of heat — and its compatibility with UHV.

Magnesium (Mg) and aluminium (Al) are often used as source materials because their exciting electron energies are high enough for efficient production of X-rays with electron bombardment, and also because they offer a good energy resolution, having line-widths of 0.70 and 0.85 eV, respectively.

Many sources are designed with dual anodes, one anode face coated with magnesium and the other with aluminium, and with two filaments, one for each face, thus providing a very quick change of the type of irradiation in use, if desired.

The X-radiation from Mg and Al sources is rather complex. The main $K\alpha$ lines are unresolved doublets and, therefore, should be labelled $K\alpha_{1,2}$. Other less intense lines also exist, named satellite lines, of which $K\alpha_{3,4}$ are the most relevant ones [19]. The separation energies of the satellite lines of Mg and Al and their intensities related to $K\alpha_{1,2}$ are presented in Table 3.3.

Table 3.3: Satellite lines of magnesium and aluminium [24].

X-ray line	Mg		Al	
	Separation from $K\alpha_{1,2}$ (eV)	Relative intensity (%) ($K\alpha_{1,2} = 100\%$)	Separation from $K\alpha_{1,2}$ (eV)	Relative intensity (%) ($K\alpha_{1,2} = 100\%$)
$K\alpha'$	4.5	1.0	5.6	1.0
$K\alpha_3$	8.4	9.2	9.6	7.8
$K\alpha_4$	10.0	5.1	11.5	3.3
$K\alpha_5$	17.3	0.8	19.8	0.4
$K\alpha_6$	20.5	0.5	23.4	0.3
$K\beta$	48.0	2.0	70.0	2.0

The separation of the $K\alpha_{1,2}$ doublet and elimination of satellites can be achieved by using a monochromator. This would also eliminate the bremsstrahlung background and reduce the line-width of the photon energy [19].

The X-ray source in the equipment used for this study is a non-monochromatic dual anode X-ray source with an Al/Mg anode with energies of 1486.6 eV and 1253.6 eV for the Al $K\alpha$ and Mg $K\alpha$ lines, respectively.

Energy analyser

After the photoelectrons have been produced, they must be separated according to their energy and then converted into a spectrum. The device responsible for this separation is the energy analyser, which works by only allowing the electrons within a defined energy interval to pass through.

The electrons emitted from the sample travel through the electron-optical column to the analyser, which is a hemispherical energy analyser (Fig. 3.2), consisting of two concentric hemispherical electrodes with a difference of potential between them that generates a radial electric field that bends the trajectory of charged particles. The pass energy, i.e., the energy the electrons need to have to pass through, is defined by the potential difference between the hemispheres.

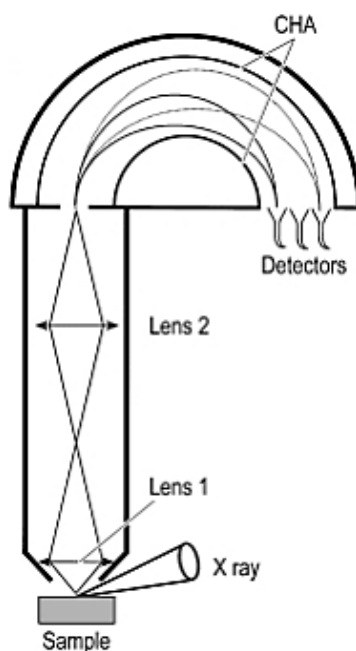


Figure 3.2: Generalised schematic representation of the concentric hemispherical analyser with the electron-optical column [19].

The instrument that was used has an unconventional geometry, in which the measured value of the angle between the incident directions of the X-ray beam and the direction of the emitted photoelectrons reaching the energy analyser is $\psi = 69^\circ$. However, in a typical XPS spectrometer, this angle is 54° .

XPS measurements are performed in Fixed Analyser Transmission (FAT) mode, which keeps constant the energy of the detected electrons inside the analyser (pass energy). The energy scan is performed in the electron-optical column by decelerating the electrons from the measured kinetic energy to the pass energy. This mode is to maintain a high and constant energy resolution throughout the spectrum.

On this particular instrument, there are two magnification modes, low and high, which determine the size of the acceptance area of the energy analyser. Each mode has different voltages applied on the electrodes of the column.

Detector

The device used for the detection of the electrons was a channel electron multiplier (CEM), commonly referred to as channeltron.

Channeltrons are hollow tubes made of a dielectric material and they usually have a spiral shape. Distinct potentials are applied at the entrance and at the exit in a way that creates a high potential difference that accelerates the electrons through out the length of the tube. Every time an electron collides with a wall of the channeltron, it emits secondary electrons. That is why this type of detector is designated as an electron multiplier. It has an attainable gain of about 10^8 , which means that for each electron that entered the channeltron, 10^8 others can be created.

The detection system consists of three channeltrons, each provided with its pre-amp channel. Working with three detectors significantly increases the signal to noise ratio, and therefore reduces the data acquisition time.

The three detectors are positioned to produce trajectories with slightly different radii, and consequently different energies. Therefore, the three acquired spectra need to be shifted with respect to each other for an energy value that is proportional to the pass energy. There is a range of pass energies to choose from, 10 to 80 eV, and that choice determines the analyser transmission and resolution [22].

3.3 Quantification

A composition quantification analysis can be made from the intensities of the peaks of each element. The intensity I of a photoelectron peak of element i and kinetic energy E_i in a homogeneous solid can be simplified as

$$I(E_i) = J_x n_i \frac{d\sigma_i}{d\Omega} T(E_i) \lambda_i \quad (3.3)$$

where J_x is the photon flux, n_i is the concentration of the element in the solid, $\frac{d\sigma_i}{d\Omega}$ is the differential photoionisation cross-section for the orbital concerned, $T(E_i)$ is the transmission function of the spectrometer and λ_i is the inelastic mean free path (IMFP), corresponding to a straight line approximation in which elastic scattering of photoelectrons is neglected

[25, 26]. Differential photoionisation cross-section can be expressed as

$$\frac{d\sigma_i}{d\Omega} = \frac{\sigma_i}{4\pi} \left[1 - \frac{\beta_i}{4} (3\cos^2\psi - 1) \right], \quad (3.4)$$

where σ_i is the total photoionisation cross-section, β_i is the asymmetry parameter and ψ is the angle between the X-ray beam and the outgoing direction of detected electrons. In the case of the conventional geometry (characterised by $\psi = 54^\circ$, as already mentioned), the differential cross-section depends only on the total photoionisation cross-section: $\frac{d\sigma_i}{d\Omega} = \frac{\sigma_i}{4\pi}$. If this is not the case, knowledge of the asymmetry parameter is also necessary to properly quantify the XPS signal.

$T(E_i)$ is the product of the acceptance solid angle of the spectrometer ($\Delta\Omega$), the acceptance area of the spectrometer (A) and the detection efficiency (D):

$$T(E_i) = \Delta\Omega AD \quad (3.5)$$

Since the spectrometer works in fixed analyser transmission mode, the transmission function can be written as

$$T(E_i) = \frac{k}{E_i^n} \quad (3.6)$$

where k is a constant, E_i is the kinetic energy of photoelectrons corresponding to an orbital i and $0.5 < n < 1$ [27]. In the XPS setup utilised $n = 1$ [22], so the expression can be simplified to $T(E_i) = \frac{k}{E_i}$.

The IMFP is the average path that an electron with a given energy travels between successive inelastic collisions. It depends on the kinetic energy and is also material dependent (Fig. 3.3).

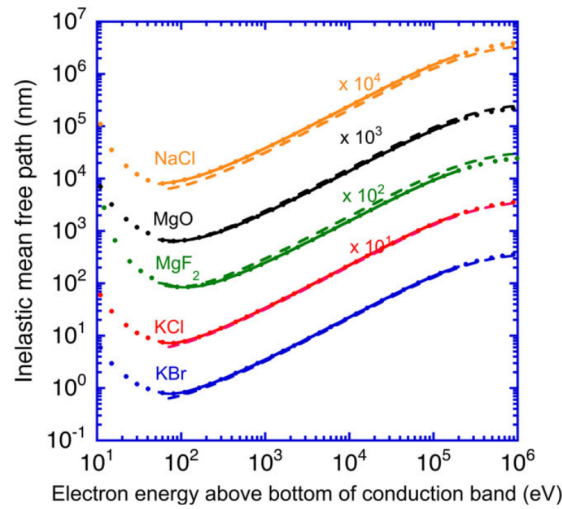


Figure 3.3: Plots of calculated IMFPs as a function of electron kinetic energy for KBr, KCl, MgF_2 , MgO , and NaCl . The different types of lines (circles, dashed and solid) represent distinct methods of calculation [28].

When the sample is non-uniform in depth, the expression for the line intensity depends on the depth distribution of a particular element. The fraction of the line intensity $dI(E_i, z)$ coming from a layer of thickness dz at depth z can be written as

$$dI(E_i, z) = J_x n_i(z) \frac{d\sigma_i}{d\Omega} T(E_i) \varphi_i(z) dz \quad (3.7)$$

where $\varphi_i(z)$ is the emission depth distribution function (EDDF) of the electrons leaving the sample without energy loss [26]. This parameter takes into account the effect of the elastic scattering of photoelectrons.

When elastic scattering of photoelectrons is neglected, the following approximation can be made:

$$\varphi_i(z) \approx \exp\left(-\frac{z}{\lambda_i}\right) \quad (3.8)$$

But in quantitative analysis of in-depth non-uniform samples, the IMFP is usually replaced with the effective attenuation length (EAL), L_i . The EAL is a useful parameter in XPS that substitutes the IMFP in expressions for the signal attenuation due to an overlayer to correct for elastic scattering of the photoelectrons [29]. It shows exactly the same trends as the IMFP concerning their energy and material dependences and can be calculated for any photoelectron line and material using NIST Standard Reference Database 82 [30].

The signal corresponding to an element i can be calculated by integrating the expression 3.7 along the sample depth:

$$I(E_i) = J_x \frac{d\sigma_i}{d\Omega} \frac{k}{E_i} \int_0^\infty n_i(z) \varphi_i(z) dz \quad (3.9)$$

Assuming that the concentration $n_i(z)$ is the same throughout the depth z :

$$I(E_i) = J_x \frac{d\sigma_i}{d\Omega} \frac{k}{E_i} n_i L_{Q_i} \quad (3.10)$$

Quantities L_{Q_i} result from numerical integration of EDDF in the range $(0, \infty)$ and represent quantitative attenuation lengths.

Now, assuming a multi-phase system in which there is a phase 'b' covered with layer 'o' and the same element 'i' is present in both phases, the photoelectron line will have two contributions [26]:

$$I_i^b = J_x n_i^b \frac{d\sigma_i}{d\Omega} \frac{k}{E_i} L_{Q_i}^b e^{-\frac{d_o}{L_i^o}} \quad (3.11)$$

$$I_i^o = J_x n_i^o \frac{d\sigma_i}{d\Omega} \frac{k}{E_i} L_{Q_i}^o \left(1 - e^{-\frac{d_o}{L_i^o}}\right) \quad (3.12)$$

From the ratio of the two intensities

$$\frac{I_i^o}{I_i^b} = \frac{n_i^o L_{Q_i^o}}{n_i^b L_{Q_i^b}} \left(e^{\frac{d_o}{L_i^o}} - 1 \right) \quad (3.13)$$

one can express the thickness of layer 'o':

$$d_o = L_i^o \ln \left(\frac{n_i^b L_{Q_i^b} I_i^o}{n_i^o L_{Q_i^o} I_i^b} + 1 \right) \quad (3.14)$$

This approach is frequently applied in analysis of single-layer structures, such as a bulk metal covered with a thin oxide layer.

In many cases, though, the surface of the sample is also covered with a layer of hydrocarbon contamination. To determine the thickness of this third layer, an equivalent approach that accounts for the attenuation caused by both overlayers is necessary. This derivation is made in chapter 4 for the specific data of this thesis.

The usual strategy to perform a quantitative evaluation of surface composition is by carrying out calculations based on experimentally determined sensitivity factors. Determination of surface composition by this method assumes that the sample is homogeneous, which is rarely the case. But even so, this method provides a valuable way of comparing similar specimens.

The sensitivity factor (SF_i) for element i is defined as the quotient of I_i and n_i [21]:

$$SF_i = \frac{I_i}{n_i} = J_x \frac{d\sigma_i}{d\Omega} \frac{k}{E_i} L_{Q_i} \quad (3.15)$$

This means the sensitivity factor is not only J_x dependent but also material dependent because of L_{Q_i} . However, the value of J_x can not be measured with standard XPS setups. Therefore, relative sensitivity factors (RSF) are used, which are sensitivity factors relative to one element. Carbon 1s is often used for this purpose because of its assigned SF value of 1.00. Because J_x is the same for both elements, its value is not necessary to calculate the RSF_i :

$$RSF_i = \frac{SF_i}{SF_C} \quad (3.16)$$

That way, not only the J_x dependence ceases to exist, but also the material dependence, as long as the two elements belong to the same chemical compound. This is often denominated atomic sensitivity factor (ASF) because it depends only on information about the atom.

The relative concentration of element i is given by:

$$c_i = \frac{\frac{I_i}{RSF_i}}{\sum_j \frac{I_j}{RSF_j}} \quad (3.17)$$

where j corresponds to all the elements present in the sample. In multi-phase systems, the existence of in-depth or lateral non-uniformity can lead to a large error, thus this expression for concentration should only be applied as a relative semi-quantitative method for direct comparison between a set of similar samples.

PROCEDURES

To assess the quantitative ability of XPS, three industrial plastics were chosen as reference, PVC, PA6 and PET, and indium was picked to be used as the substrate in which the plastic microparticles are to be pressed on for analysis. Samples of the substrate and the plastics were prepared with 100% coverage and analysed to be used as reference for the several samples that were prepared with different levels of coverage afterwards, to perform calibrations for the purpose of studying the influence of coverage on the XPS results. Additionally, the in-depth non-uniformity of the indium substrate was considered as a part of the surface coverage analysis.

4.1 Choice of the substrate

The plastic powder samples need to be pressed onto a soft metallic substrate in order to secure mechanical support and electrical contact. It was determined that indium was the best choice because it is soft enough to grip the microparticles and its binding energy peaks are somewhat far from the ones expected to be observed in the plastics' spectra, therefore not interfering with them. It was also taken into consideration the colour of the substrate, due to the necessity for contrast with the particles during image analysis.

4.2 Reference plastics

As the impact of plastic in the environment becomes more prevalent, the number of research studies about the topic increase. Many of these studies focus on the types of polymers that are typically found as pollutants.

A study about microplastics in marine and estuarine species from the coast of Portugal [31] showed that microparticles of plastic of various lengths, sizes and colours are contaminating organisms via ingestion, absorption and others, and the polymer analysis revealed the presence of polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET) and polyamide (PA).

In another study [32], research was done on how microplastics act as vectors of major ocean pollutants and a series of studies were gathered about polymers found in water bodies in different parts of the world, which showed that PE, PP, PS, PVC, PET and PA were the most commonly found.

One study about the accumulation of microplastic on shorelines worldwide [33] found present in eighteen shores across six continents microparticles of polyester (PES), which is PET in fibre form, acrylic (AC), PP, PE and PA.

A group of researchers did a meta-analysis about the distribution of plastic polymer types in the marine environment [34] and concluded that the most abundant plastic types polluting aquatic environments are PE, PES, PA, AC, PE and PP.

Based on this data, three polymers were chosen as objects of study for this project: PVC, PET and PA, specifically PA6 (polyamide 6 or nylon 6). Unlike some of the other plastics such as PE or PP that have in their composition the same elements found in hydrocarbon contamination, which would hinder the identification process, these three polymers have something that makes them more easily identifiable in XPS spectra. PVC and PA6 have characteristic elements in their composition not encountered as typical contaminants, which are chlorine and nitrogen, respectively. In the case of PET, its characteristic element is oxygen. While oxygen can be found in surface contamination, COO groups are not standard and with the assistance of literature the peaks related to PET can be identified.

For the purpose of this thesis, the plastics studied were not in their pure form but were industrial samples, since that is how they are most usually found in the environment. The plastics were kindly provided by Ensinger GmbH and Simona AG, through the Portuguese distributor company SOVE.

4.3 Preparation of the samples

The plastics were turned into powder using a Dremel rotary tool with a sanding disc attachment. This method provides particles in the millimetre range and below.

For each sample the indium substrate was scraped with a scalpel to remove as much of the oxide layer as possible. Four reference samples were prepared and analysed: one of the indium substrate and one of each of the three plastics. The plastic samples were prepared by pressing a layer of microplastics onto the substrate, in a way that no indium was left exposed. The indium sample was prepared with a layer of isopropanol over it, which dried before being put in the chamber for analysis. The indium sample was prepared this way because the various samples used later on for the coverage calibration process were prepared by making a suspension of isopropanol with the microparticles of each plastic and these were put on the substrate with a dropper.

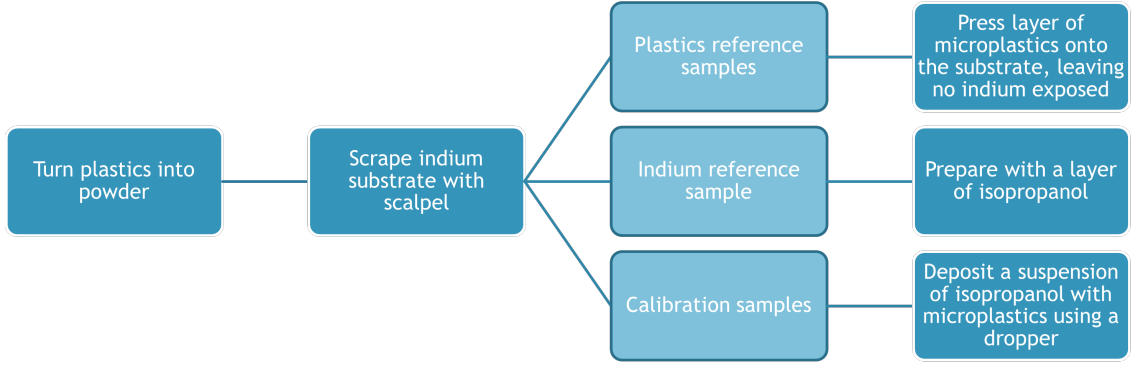


Figure 4.1: Representative schematic of the preparation of the samples.

4.4 Acquiring of spectra

The XPS data were acquired under pressures in the range of 10^{-8} to 10^{-9} mbar, because vapour pressure of the samples was affecting the vacuum conditions. The source used was a dual anode X-ray source using non-monochromatic Mg $K\alpha$ irradiation with energy of 1253.6 eV and FAT mode with pass energy of 40 eV and low magnification mode were employed. The survey spectra were recorded with binding energy starting at 0 eV and ending at 600 eV. Detailed spectra were taken with the same pass energy, but with longer dwell time and the reduced energy step of 0.2 eV.

4.5 Determining the thickness of the overlayers

The indium samples in this study are multi-phase systems with three layers: a bulk substrate of indium, an oxide-hydroxide layer with thickness d_{ox} and a hydrocarbon contamination layer of thickness d_c (Fig. 4.2).

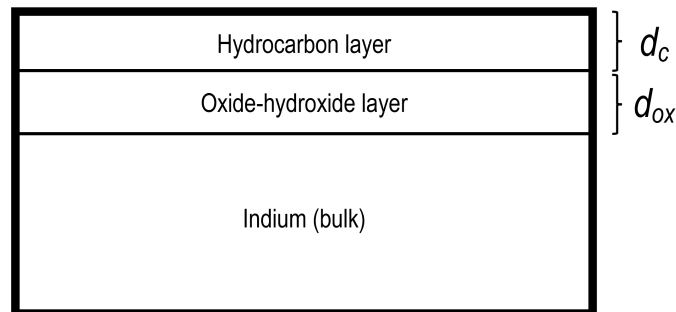


Figure 4.2: Schematic representation of the layers in a sample.

The expressions that allow for the calculation of d_{ox} and d_c thickness are derived in this section.

4.5.1 Indium oxide-hydroxide layer

Indium is a metal and, when exposed to air, it inevitably gets oxidised on its surface. In this case, a layer comprised of two different chemical compounds developed on the indium substrate's surface: Indium(III) oxide (In_2O_3) and Indium(III) hydroxide ($In(OH)_3$).

It is possible to find the fraction of In_2O_3 in the oxide-hydroxide layer, X , and thus the corresponding fraction of $In(OH)_3$, $1 - X$, by fitting the O 1s line because the two species O^{2-} and OH^- have different binding energies [35, 36]. The result of the fitting will be the fraction of oxygen signal that corresponds to In_2O_3 , which can also be expressed as

$$a = \frac{X \cdot n_O^{In_2O_3}}{X \cdot n_O^{In_2O_3} + (1 - X) \cdot n_O^{In(OH)_3}} \quad (4.1)$$

where $n_O^{In_2O_3}$ and $n_O^{In(OH)_3}$ are the concentrations of oxygen in In_2O_3 and $In(OH)_3$, respectively. The concentrations n can be calculated as

$$n = \frac{N_{Av} \rho}{M} \cdot \text{Number of atoms}, \quad (4.2)$$

where N_{Av} is the Avogadro number, ρ is the density, M is the molar mass and the expression is multiplied by the number of atoms of the element present in the chemical formula, which in this particular case would be the number of oxygen atoms in the oxide.

By rearranging the eq. (4.1) to isolate X , we get the expression that represents the fraction of In_2O_3 in the layer:

$$X = \frac{a \cdot n_O^{In(OH)_3}}{n_O^{In_2O_3} + a \cdot \left(n_O^{In(OH)_3} - n_O^{In_2O_3} \right)} \quad (4.3)$$

The value of X obtained this way will be used in further calculations.

The signal intensity of indium from the metallic bulk can be expressed as

$$I_{In} = J_x n_{In} \frac{d\sigma_{In}}{d\Omega} L_{Q_{In}} T_{In} \exp\left(-\frac{d_{ox}}{L_{In,ox}}\right) \quad (4.4)$$

where J_x is the x-ray flux, n_{In} is the concentration of indium, $\frac{d\sigma_{In}}{d\Omega}$ is its differential photoionisation cross-section of the corresponding In orbital, $L_{Q_{In}}$ is the effective attenuation length for quantitative analysis in In metal, T_{In} is its transmission function. The exponential function expresses the attenuation of photoelectrons as they make their way to the surface, in which d_{ox} is the thickness of the oxide overlayer and $L_{In,ox}$ is the effective attenuation length of indium through the oxide-hydroxide layer.

It's possible to express the signal intensity of indium in the oxide using the expression for the signal from the overlayer (eq. (3.12)):

$$I_{ox} = J_x n_{ox} \frac{d\sigma_{In}}{d\Omega} L_{Q_{ox}} T_{In} \left(1 - \exp\left(-\frac{d_{ox}}{L_{In,ox}}\right) \right) \quad (4.5)$$

where n_{ox} is the concentration of indium in the oxide and $L_{Q_{ox}}$ is the effective attenuation length for quantitative analysis of the In line in the oxide, while all the other terms remain the same as in eq. (4.4).

By dividing the expressions (4.4) and (4.5) and solving for d_{ox} , we get the expression that represents the thickness of the oxide-hydroxide overlayer:

$$d_{ox} = L_{In,ox} \ln \left(1 + \frac{I_{ox}}{I_{In}} \frac{n_{In}}{n_{ox}} \frac{L_{Q,In}}{L_{Q,ox}} \right) \quad (4.6)$$

The value of X comes into play in the calculations of n_{ox} , $L_{In,ox}$ and $L_{Q,ox}$, which are calculated as linear combinations of the contributions corresponding to the oxide and hydroxide compounds, respectively, as shown in the following expressions:

$$n_{ox} = X \cdot n_{In}^{In_2O_3} + (1 - X) \cdot n_{In}^{In(OH)_3} \quad (4.7)$$

$$L_{In,ox} = X \cdot L_{In,ox}^{In_2O_3} + (1 - X) \cdot L_{In,ox}^{In(OH)_3} \quad (4.8)$$

$$L_{Q,ox} = X \cdot L_{Q,ox}^{In_2O_3} + (1 - X) \cdot L_{Q,ox}^{In(OH)_3} \quad (4.9)$$

The signal intensities are the areas of the peaks of the measured spectra. Since contributions of the bulk and oxide-hydroxide layer can be resolved in the In 3d_{5/2} line, all the terms on the right side of eq. (4.6) are known or can be calculated and measured, which enables us to determine the thickness of the oxide-hydroxide layer d_{ox} .

4.5.2 Hydrocarbon layer

Adsorption of atmospheric hydrocarbons onto the surface of a sample, during or after preparation, before introduction into UHV not only results in the presence (or increase of intensity) of C 1s signal in the spectrum due to the hydrocarbon overlayer, commonly referred to as adventitious carbon, but also in the attenuation of the signals from other elements present in the sample [37]. Adventitious carbon is generally comprised of a variety of hydrocarbon species (mainly saturated aliphatic hydrocarbons) with small amounts of oxygen. In this work, the hydrocarbon layer is modelled as paraffin (C₂₆H₅₄) in which some of the carbon atoms are substituted with oxygen.

A typical spectrum of adventitious carbon shows a C 1s line with C-C, C-H bonds and some single or double bonds with oxygen, such as C-O, C=O, C-OH, C-O-C and O-C=O [38–40].

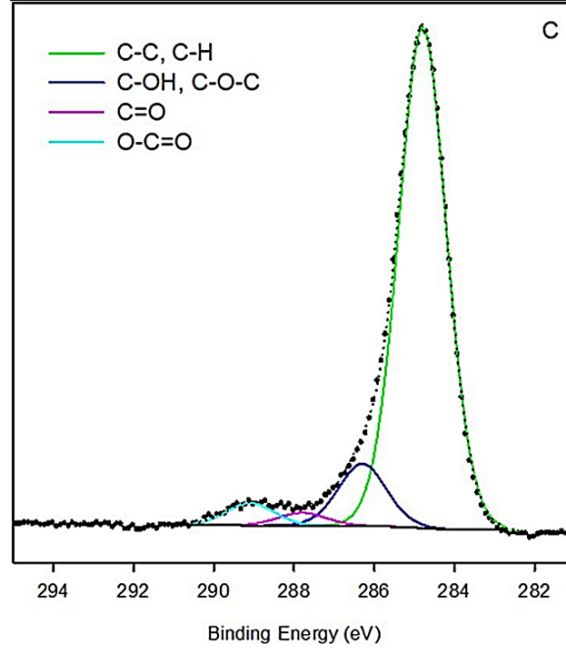


Figure 4.3: Example of a spectrum of C 1s line attributed to adventitious carbon [41].

In the case of our samples, the signal from the indium substrate is attenuated by both the oxide-hydroxide and hydrocarbon layers, whilst the signal coming from the indium in the oxide-hydroxide layer is attenuated by the hydrocarbon layer. The indium 3d and 4d lines have different signal intensity attenuations by the hydrocarbon overlayer due to different kinetic energies of the corresponding photoelectrons. By rewriting the corresponding expressions, it is possible to estimate the thickness of the hydrocarbon layer.

The signal intensity of In 3d can be written as

$$I_{3d} = J_x \frac{d\sigma_{3d}}{d\Omega} T_{3d} e^{-\frac{d_c}{L_{3d,c}}} \left[\underbrace{L_{Q_{b,3d}} n_{In,b} e^{-\frac{d_{ox}}{L_{3d,ox}}}}_{(a)} + \underbrace{L_{Q_{ox,3d}} n_{In,ox} (1 - e^{-\frac{d_{ox}}{L_{3d,ox}}})}_{(b)} \right] \quad (4.10)$$

(c)

where (a) represents the contribution of the In 3d intensity from the bulk, which is attenuated by the oxide-hydroxide layer, (b) represents the contribution of the In 3d signal coming from the oxide-hydroxide layer, and (c) includes the attenuation of the In 3d intensities from the bulk and from the oxide-hydroxide layer, caused by the hydrocarbon contamination overlayer.

By analogy, the signal intensity of In 4d can be written as follows:

$$I_{4d} = J_x \frac{d\sigma_{4d}}{d\Omega} T_{4d} e^{-\frac{d_c}{L_{4d,c}}} \left[L_{Q_{b,4d}} n_{In,b} e^{-\frac{d_{ox}}{L_{4d,ox}}} + L_{Q_{ox,4d}} n_{In,ox} (1 - e^{-\frac{d_{ox}}{L_{4d,ox}}}) \right] \quad (4.11)$$

From the ratio of both intensities is given the thickness of the hydrocarbon overlayer:

$$d_c = \frac{\ln \left(\frac{I_{3d}}{I_{4d}} \frac{d\sigma_{4d}/d\Omega}{d\sigma_{3d}/d\Omega} \frac{T_{4d}}{T_{3d}} \frac{\left[L_{Qb,4d} n_{In,b} e^{-\frac{d_{ox}}{L_{4d,ox}}} + L_{Qox,4d} n_{In,ox} (1 - e^{-\frac{d_{ox}}{L_{4d,ox}}}) \right]}{\left[L_{Qb,3d} n_{In,b} e^{-\frac{d_{ox}}{L_{3d,ox}}} + L_{Qox,3d} n_{In,ox} (1 - e^{-\frac{d_{ox}}{L_{3d,ox}}}) \right]} \right)}{\frac{1}{L_{4d,c}} - \frac{1}{L_{3d,c}}} \quad (4.12)$$

where I_{3d} and I_{4d} are the experimental line intensities.

RESULTS AND DISCUSSION

5.1 Reference samples

In this section are the XPS spectra that resulted from the analysis of the reference samples of indium, PVC, PA6 and PET with the estimated fittings.

Some general information about the fittings should be mentioned:

- The software used is CasaXPS. The measurements are represented by the bright red points and the fittings are the lines inside the fitting region.
- All satellites were removed since these can affect the intensities of the peaks if there is an overlap.
- All lines in all samples have the Shirley background, except the few where the overall slope is downwards which have the Linear background. However, with the Shirley background, the In 3d line gets cut between the two peaks ($3d_{5/2}$ and $3d_{3/2}$). For this reason, only the $3d_{5/2}$ peak was fitted.
- All peaks are fitted to GL(30) line shape.

5.1.1 Indium substrate

The indium sample was prepared with a layer of isopropanol, which dried before being introduced into the instrument. This is because it is meant to be used as reference for the fittings of the spectra from the samples used for the calibration, which were prepared by depositing a suspension of isopropanol with the microparticles of each plastic on the indium substrate.

In the indium substrate spectra, there should be present the peaks corresponding to In 3d and 4d, an O 1s line due to the oxidation and a C 1s line because of the hydrocarbon contamination.

According to the literature data [35, 42], the separation of In(0) and In(+3) in the In $3d_{5/2}$ line is 1.1 eV and In(0) contribution is narrower. The relative peak position between

In_2O_3 and $In(OH)_3$ in the O 1s line is 1.8 eV while the relative position between the O 1s and the In 3d_{5/2} lines in In_2O_3 is 85.2-85.6 eV. O 1s in In_2O_3 is at about 530.0 eV.

The results of the experimental spectra are in the figures below: In 3d and 4d (Figures 5.1 and 5.2, respectively), O 1s (Fig. 5.3) and C 1s (Fig. 5.4).

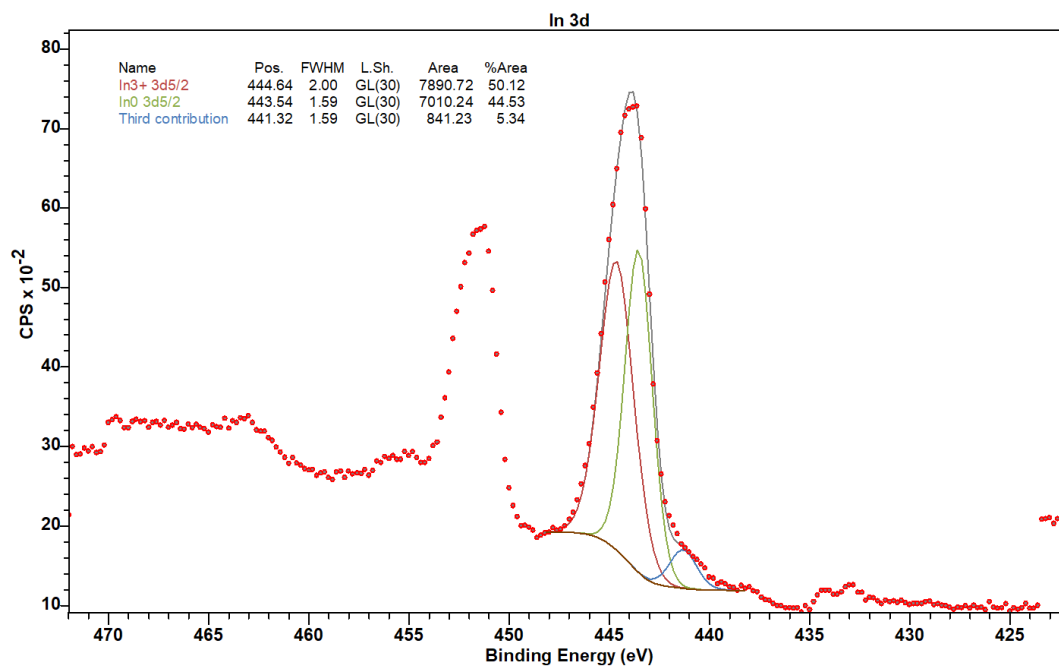


Figure 5.1: Reference spectrum of the In 3d line for the indium substrate.

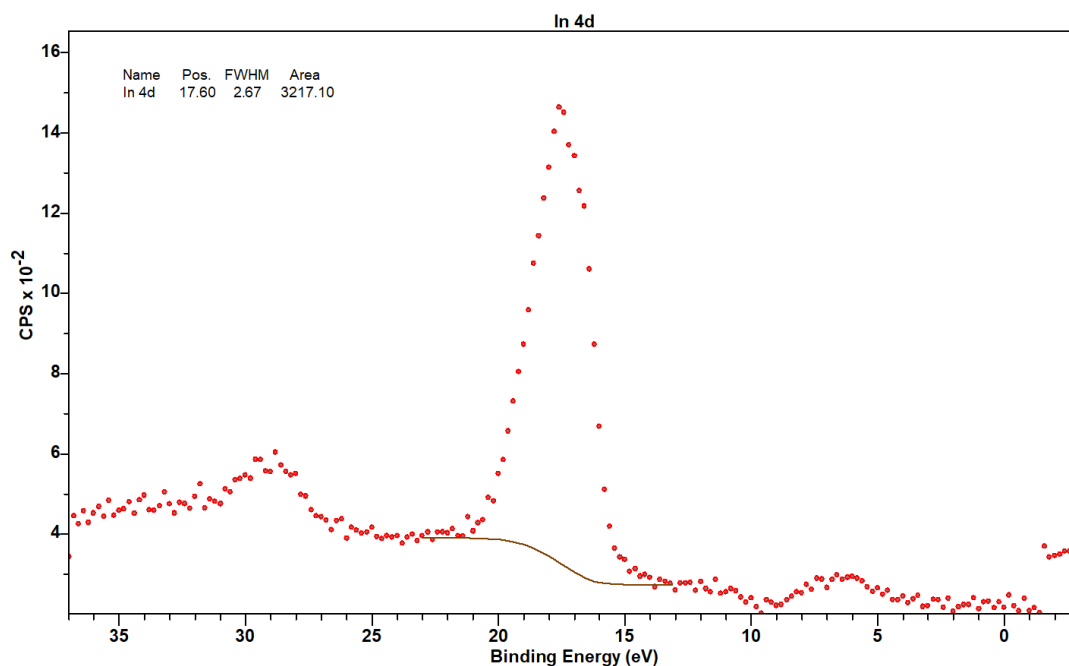


Figure 5.2: Reference spectrum of the In 4d line for the indium substrate.

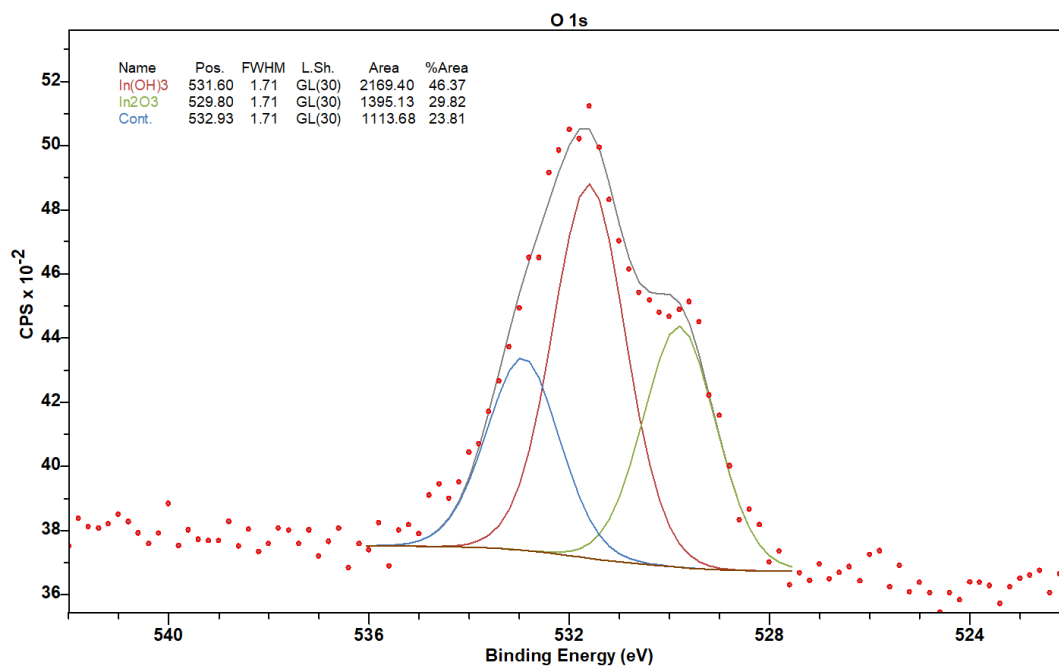


Figure 5.3: Reference spectrum of the O 1s line for the indium substrate.

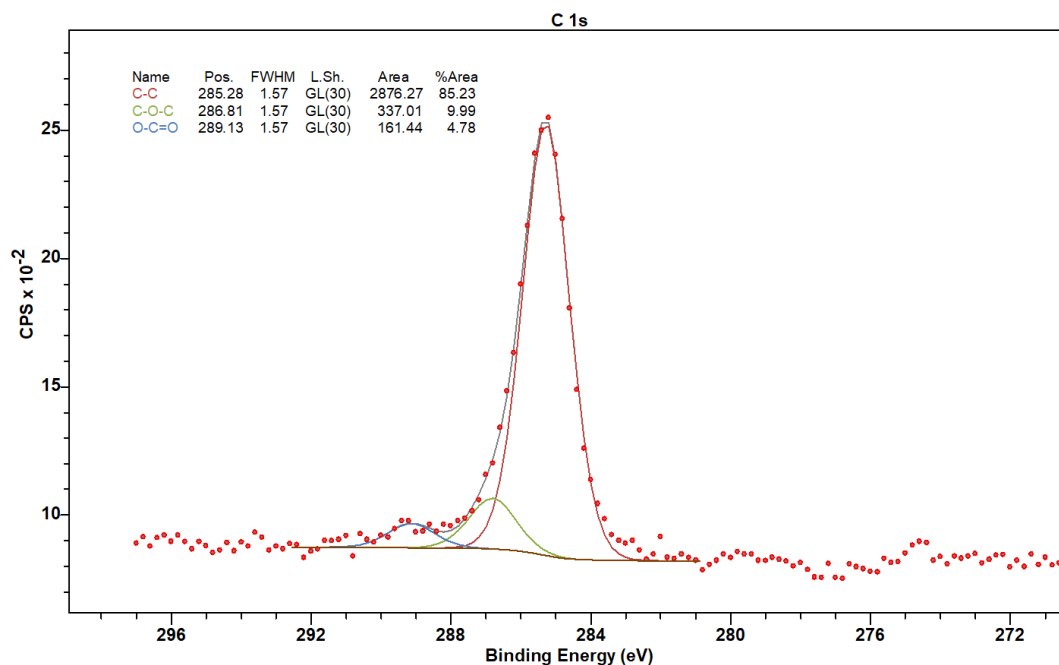


Figure 5.4: Reference spectrum of the C 1s line for the indium substrate.

The In $3d_{5/2}$ line is fitted to two contributions: In(3+) and In(0). In(0) is typically narrower and their distance is fixed to 1.1 eV. There is a very small third peak of lower binding energy which is often observed in In 3d spectra but its physical interpretation

is unknown [35]. The In 4d line was not fitted because it was not necessary for further calculations (Fig. 5.2).

The O 1s line (Fig. 5.3) is fitted to three contributions with equal width and the distance between In_2O_3 and $In(OH)_3$ contributions was fixed to 1.8 eV after an initial fitting. The third contribution corresponds to the organic contamination.

The C 1s line is fitted to three contributions, a large peak corresponding to C-C, C-H bonds and two smaller peaks of higher binding energy that correspond to C-O and COO bonds (Fig. 5.4). This spectrum is typical for adventitious carbon.

The calculated thickness of the oxide-hydroxide layer, d_{ox} , is 1.41 nm, and the fraction of In_2O_3 in the layer is 39.64%. The calculated thickness of the contamination layer, d_c , is 2.81 nm.

5.1.2 Polyvinyl chloride (PVC)

PVC's composition is C_2H_3Cl , so C 1s and Cl 2p lines are expected to be present in the experimental spectra.

According to the literature [38], C 1s has two contributions of equal intensity and width, situated at 285.90 and 287.00 eV. Cl 2p has one contribution with Cl 2p_{3/2} at 200.64 eV.

The resulting spectrum for C 1s is in Fig. 5.5 and the one for Cl 2p is in Fig. 5.6. In addition to the main carbon and chlorine photoelectron lines, the major oxygen contribution (line O 1s) was also observed in the survey spectra (Fig. 5.7).

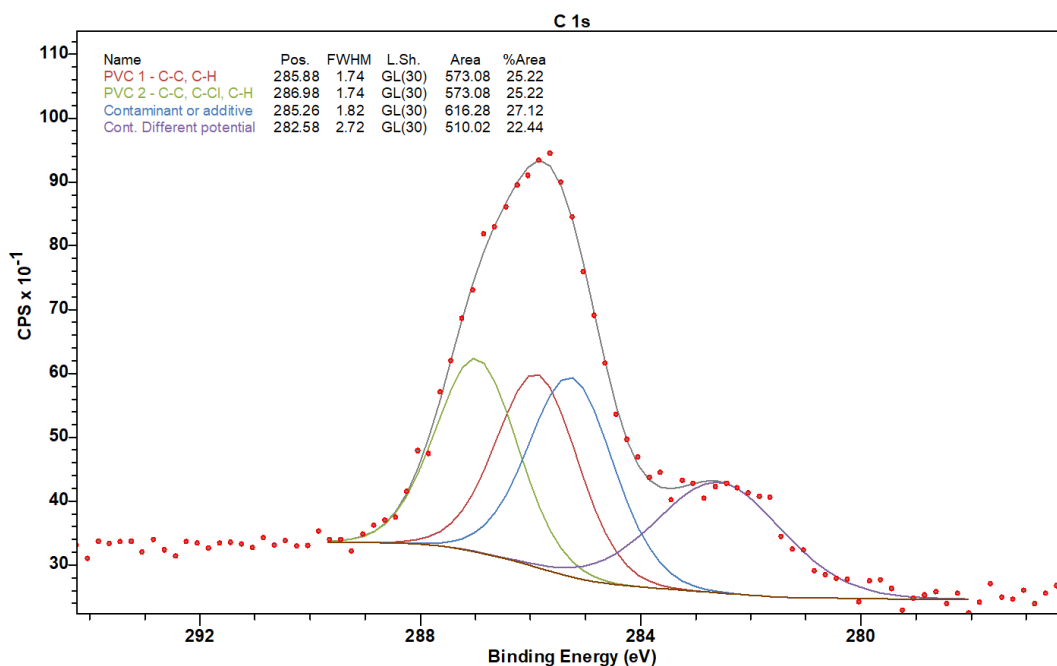


Figure 5.5: Reference spectrum of the C 1s line for PVC.

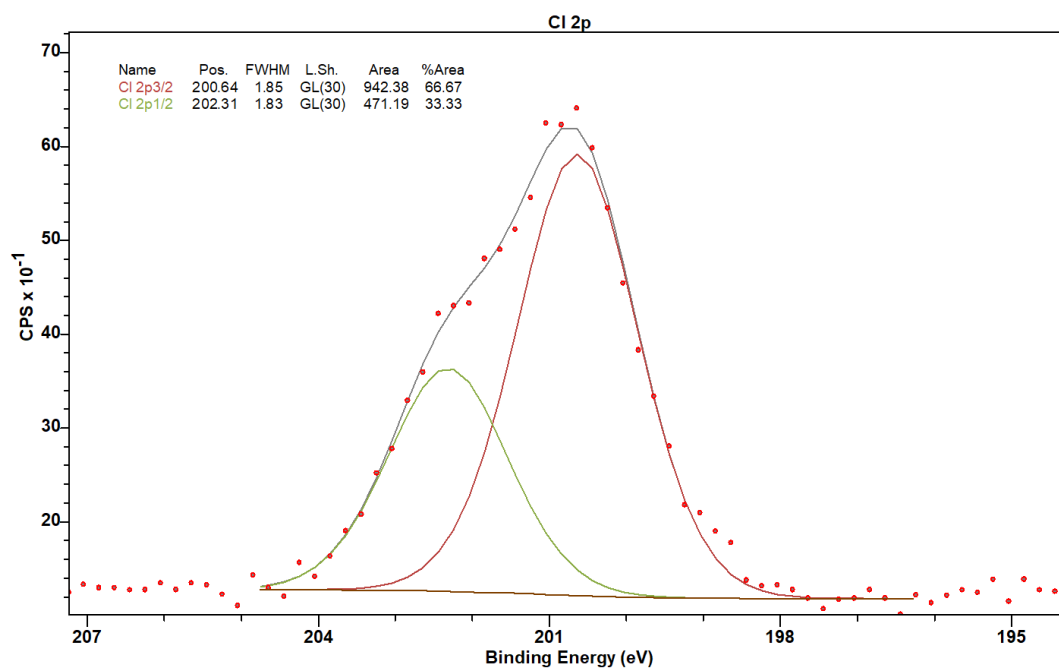


Figure 5.6: Reference spectrum of the Cl 2p line for PVC.

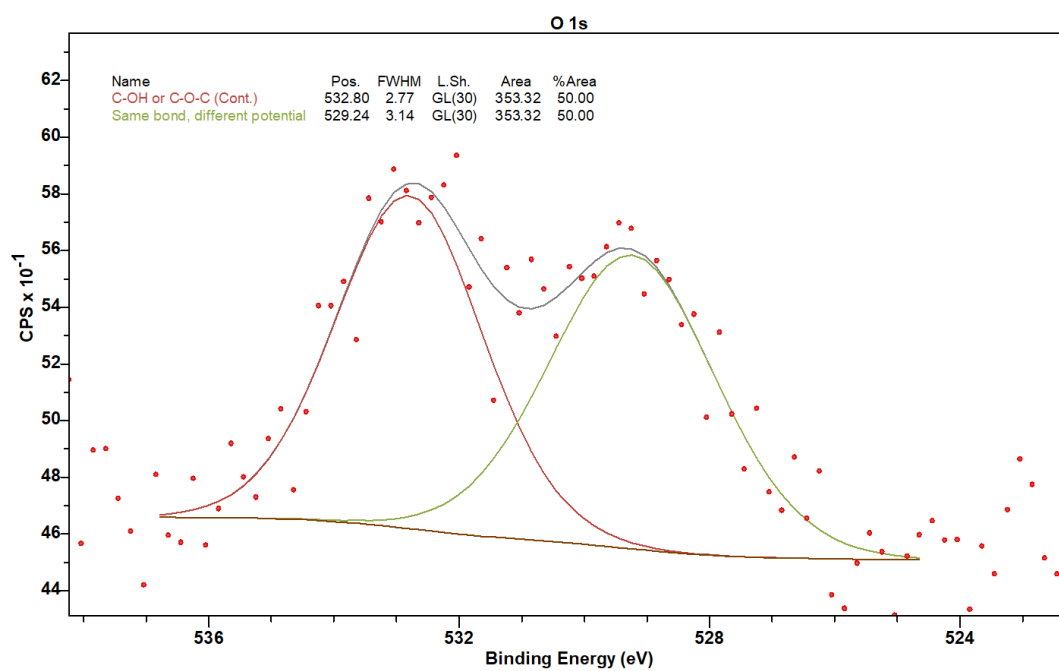


Figure 5.7: Reference spectrum of the O 1s line for PVC.

All the PVC spectra were calibrated in accordance with the Cl 2p_{3/2} peak, which is positioned at 200.64 eV in literature.

In the C line (Fig. 5.5) there are two contributions that belong to PVC and two others: a hydrocarbon contamination peak at 285.3 eV and one peak at 282.6 eV that implies differential charging between the hydrocarbons and the PVC, for it is likely the same hydrocarbon bond but at a different potential.

The Cl (Fig. 5.6) line looks as expected, showing both of spin orbit peaks clearly.

There is also a O 1s line (Fig. 5.7) with two peaks. One corresponds to either contamination or additives since oxygen is not in PVC's composition, and the one with lower binding energy is probably the same bond but at a different potential. These two peaks sit at 531.80 and 529.24 eV, with equal intensities and a shift of around 2.56 eV, being very close to the relative peak shift of the two additional contributions of the C 1s line.

The quantification is determined using sensitivity factors obtained by multiplying the known transmission functions with the cross-sections and the calculated quantitative attenuation lengths for each element in each plastic, similarly to what is described in eq. (3.15). Taking the case of PVC as an example, the sensitivity factors for C and Cl in PVC are:

$$SF_C = L_{Q_C} \frac{d\sigma_C}{d\Omega} T_C \quad (5.1)$$

$$SF_{Cl} = L_{Q_{Cl}} \frac{d\sigma_{Cl}}{d\Omega} T_{Cl} \quad (5.2)$$

The concentrations are calculated with eq. (3.17), using the line intensities in the spectra.

Since only 54.44% of the total intensity of the C line belongs to PVC, then multiplying it with that fraction gives the intensity of C from PVC. That makes the concentration ratio of C:Cl equal to approximately 65:35, which is quite close to the wanted result of 66.7:33.3 (according to the composition formula).

This method of quantification was applied for the PA6 and PET reference samples as well.

5.1.3 Polyamide 6 (PA6)

The composition of PA6 is C₆H₁₁NO. Therefore, there should be a C 1s line, a N 1s line and a O 1s line present in the experimental spectra.

Following the literature [38], C 1s has four contributions: the major one is at 285.00 eV and the other three have the same intensity being a quarter of the intensity of the first contribution, with equal widths, and have binding energies of 285.31, 286.00 and 288.01 eV. O 1s and N 1s have one contribution each, at 531.35 eV and 399.77 eV, respectively.

The measured spectrum for C 1s is in Fig. 5.8, the one for O 1s is in Fig. 5.9 and the one for N 1s is in Fig. 5.10.

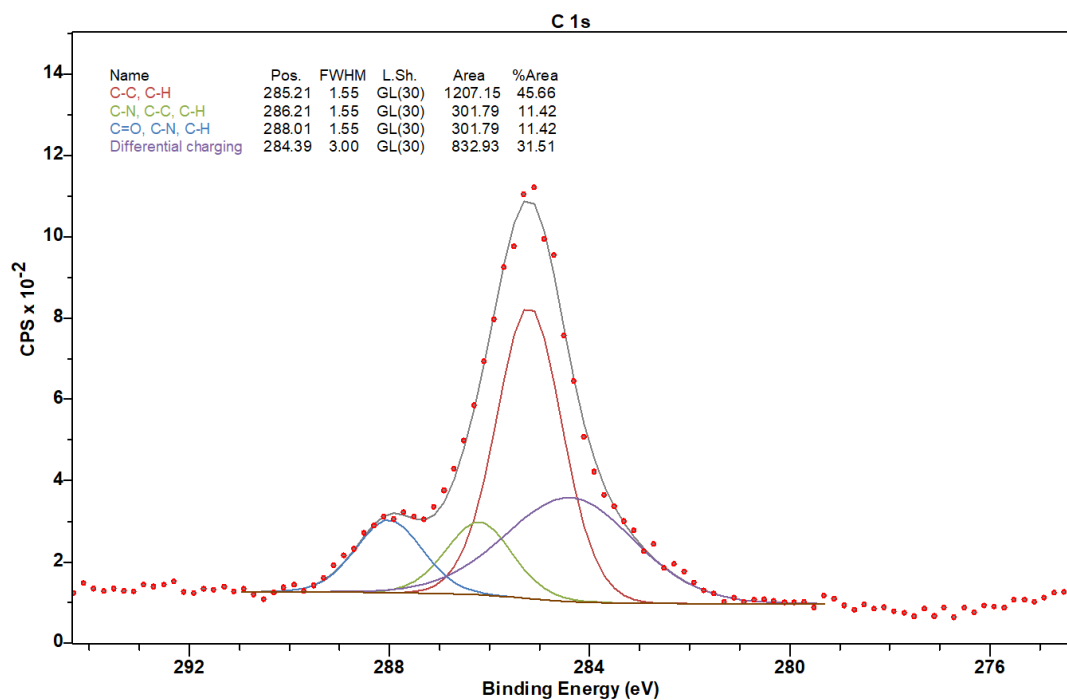


Figure 5.8: Reference spectrum of the C 1s line for PA6.

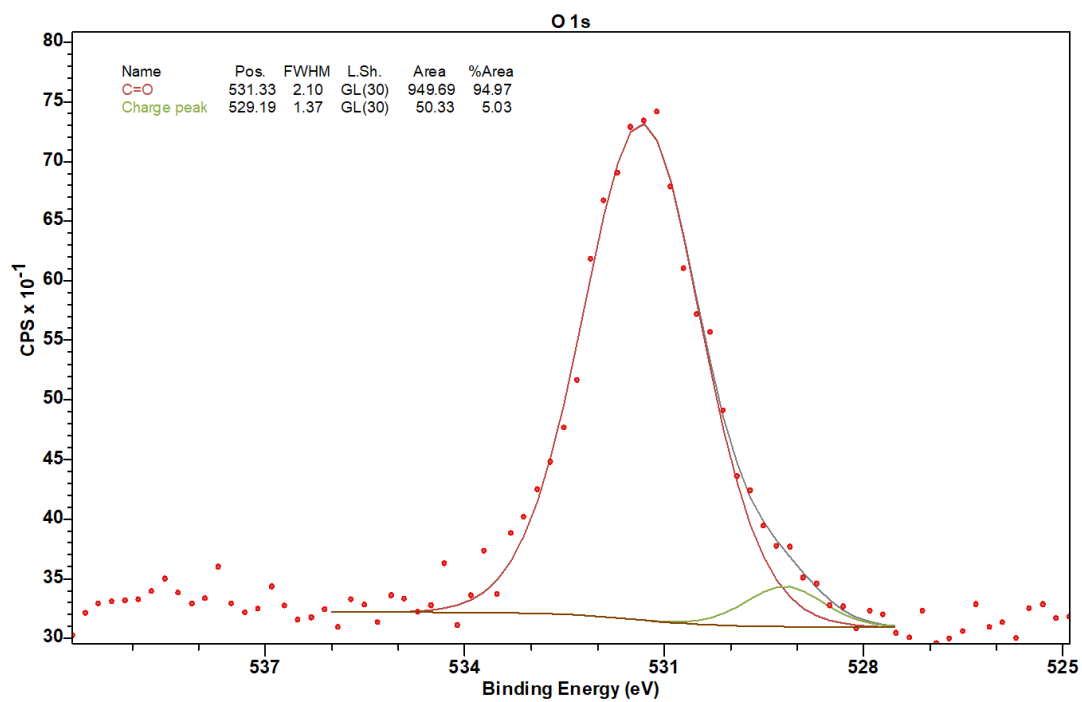


Figure 5.9: Reference spectrum of the O 1s line for PA6.

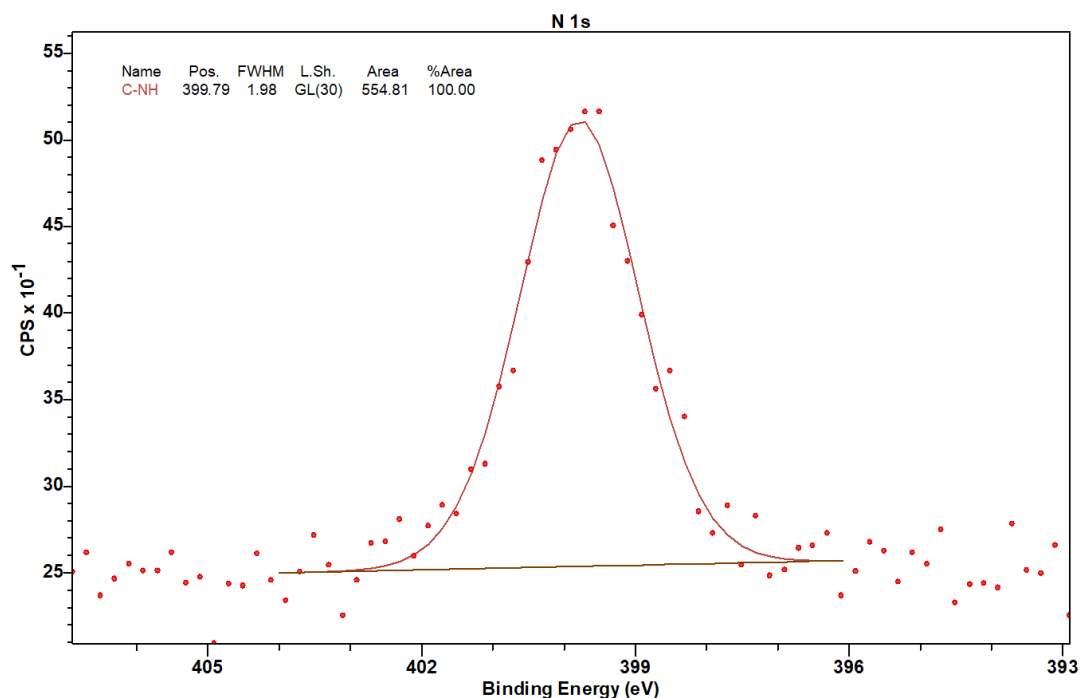


Figure 5.10: Reference spectrum of the N 1s line for PA6.

All the PA6 spectra were calibrated according to the N 1s peak, positioned at 399.77 eV.

Although four peaks are shown in the literature for the C line [38, 43], it was decided to make the fitting with only three of them, since the peak at 285.31 eV is so close to the major peak (at 285.00 eV). Thus, in the C line (Fig. 5.8) we see three contributions after introducing the appropriate constraints concerning the relative positions and intensities, which belong to PA6 and look as expected. However, there is an extra peak around 284.3 eV, which does not belong to PA6. This extra peak may be caused by differential charging of PA6 or it could be due to additives.

The same happens in the O line (Fig. 5.9), where we see the peak that belongs to Nylon and then a very small peak at 529.19 eV caused by differential charging. However, knowing that its intensity relative to the PA6 contribution of the O 1s line is much smaller than that of the C 1s contribution at 284.3 eV, it appears that the latter contribution is not PA6.

The N line (Fig. 5.10) looks just as expected, which confirms further that the contributions of the C 1s and O 1s lines at lowest binding energies cannot be attributed to PA6.

The expected concentration ratio is C:N:O = 75:12.5:12.5. In this case, to get a good fitting it was necessary to know before-hand the fraction of carbon that belongs to PA6 in the C line. Keeping in mind that the most reliable line is N 1s, since this one is 100% related to nylon and the other two can be partially related to different contamination/additives, it was found that a fraction close to 0.69 is the one that gives a ratio of concentration closest to the expected. With this information, we were able to fit the extra peak (the one

that does not belong to Nylon) as about 31% of the total carbon intensity, which made for a very good fitting overall, the concentration ratio being C:N:O = 74.7:12.5:12.8.

5.1.4 Polyethylene terephthalate (PET)

PET's composition is $C_{10}H_8O_4$, which means there should be present the lines for C 1s and O 1s.

As stated in literature [38], C 1s has three contributions: the major one is at 284.70 eV and the other two are each a third of its size and sit at 286.24 and 288.66 eV. O 1s has two contributions of similar width and intensity at 531.62 and 533.22 eV.

The measured spectra are below, C 1s is in Fig. 5.11 and O 1s in Fig. 5.12.

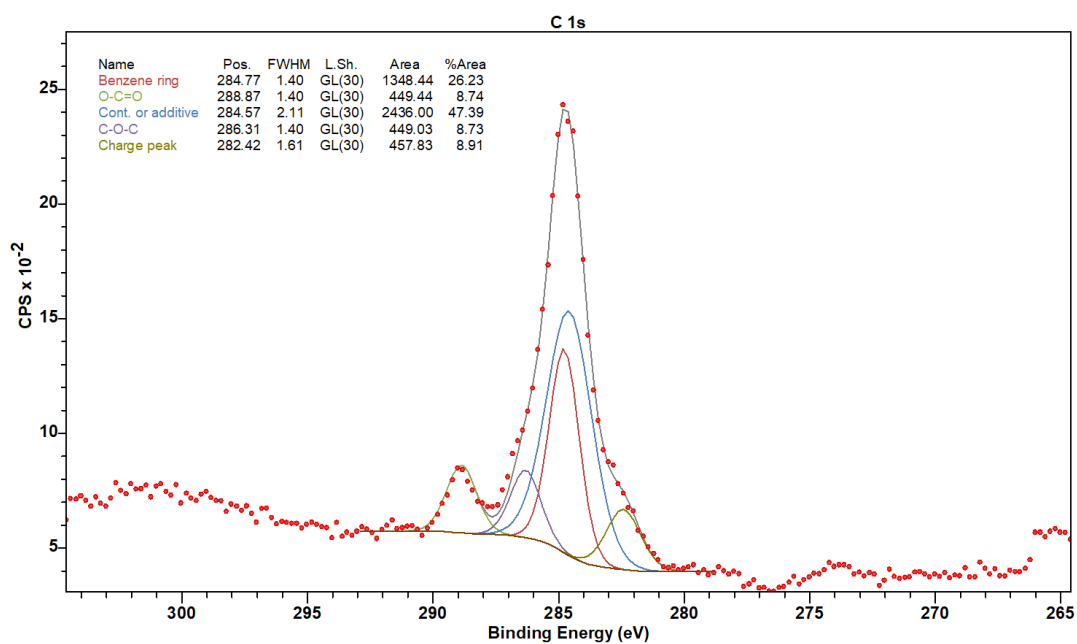


Figure 5.11: Reference spectrum of the C 1s line for PET.

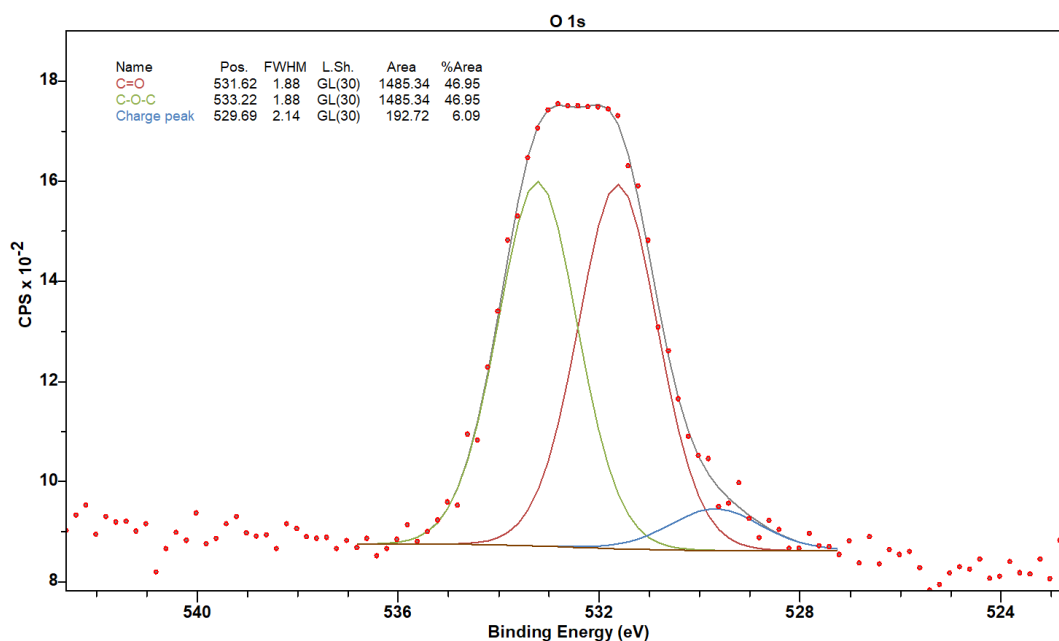


Figure 5.12: Reference spectrum of the O 1s line for PET.

All the PET spectra were calibrated in accordance with the O 1s peaks that belong to the polymer, positioned at 531.62 and 533.22 eV.

C 1s (Fig. 5.11) has a similar shape to what is expected, however, the major peak seems much more intense than anticipated. This means that at that same binding energy there is another peak that corresponds to either surface contamination or to an additive. Besides, there is also a small peak at 282.42 eV caused by differential charging. Therefore, we see a total of five contributions in the C line.

The O 1s (Fig. 5.12) line looks as expected, but also with a small peak at different potential at 529.69 eV.

The concentration ratio should be C:O = 71.4:28.6. The fraction of PET measured in the C line is 43.70%. That makes the concentration ratio of C:O equal to approximately 69.6:30.4, which is close to the expected result.

The quantification of the plastics was performed under the assumption of lateral non-uniformity of the samples, i.e., a sample consisting of additive and plastic regions. This assumption provided a very good accordance with the expected plastics composition, which implies that it is correct.

5.2 Coverage measurement using image analysis

One of the objectives of this dissertation was to study how the level of coverage of microparticles in a sample can influence the XPS data results and what would be the

minimum quantity that would be detected by the instrument. For this purpose, several samples of the three plastics were prepared with different levels of coverage, ranging from 2% to 80%, and analysed with XPS to observe how the line intensities of the indium substrate and the plastic behaved as the coverage changes.

The coverage, θ , was estimated by taking photographs of the samples with a phone's camera and analysing them with an image analysis software, *ImageJ*. The photographs were taken at angles that helped to reduce the reflections, since these greatly hamper the image analysis process. This means that the photos were not always taken from the top angle, which can affect the total area detected by the camera, potentially making it underestimated. It is worth mentioning that even with this method, it was impossible to get photographs totally free of reflections. For these reasons, the coverage results are not completely accurate.

The image analysis process started out by improving as much as possible the contrast between the particles and the substrate. After this step, the image is turned to binary, where the substrate is white and the particles are black. Subsequently, there was a fair amount of manual editing of the image in order to remove the remaining reflections to the greatest extent. The next step was measuring the percentage of surface area occupied by the black colour inside the total area of the substrate. Fig. 5.13 shows images of a PET sample prepared in the beginning of the experimental period to test the software and define the procedure for image analysis, and it exhibits the three main steps for the coverage measurement: taking the photo; improving contrast; making binary of the photo.

The images used for the calibration process of the plastics are in Appendix A.

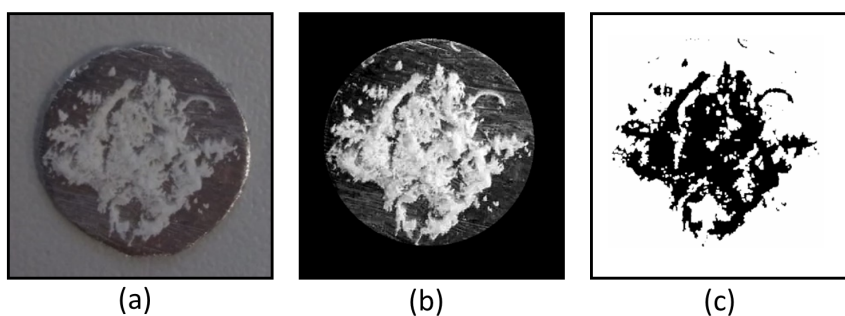


Figure 5.13: Images of a test sample of PET indicating the three main stages of coverage measurement: (a) photo; (b) contrasted photo; (c) binary of the photo.

Near the end of the experimental period, in the light of an opportunity to use a portable microscope camera, a comparison analysis was made between photos taken with

the phone and ones taken with a microscope in order to know if the phone's camera decreased the image quality to such a degree that it would significantly affect the estimated coverage.

Three samples of increasing coverage were prepared for each of the plastics, and for each sample a photo was taken with the phone as well as with the portable microscope (see Fig. 5.14 with photos of Sample 3 of PVC). Thereafter, the coverage was measured from the photos.

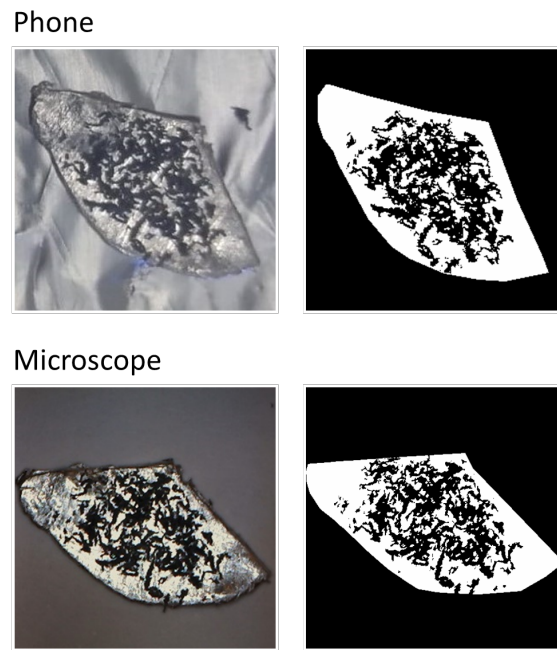


Figure 5.14: Photos and binaries of Sample 3 of PVC, photographed with phone *versus* microscope. For all the images used in the coverage comparison, see Appendix B.

Table 5.1: Absolute and relative discrepancies of coverage estimated with the photo from a phone *versus* a portable microscope.

Sample	Coverage (%)		Absolute discrepancy (%)	Relative discrepancy
	Microscope	Phone camera		
PVC 1	6.376	5.935	0.441	7%
PVC 2	11.789	12.136	-0.347	-3%
PVC 3	34.188	33.784	0.404	1%
PA6 1	5.401	5.899	-0.498	-8%
PA6 2	14.667	17.314	-2.647	-15%
PA6 3	39.938	39.541	0.397	1%
PET 1	12.770	13.571	-0.801	-6%
PET 2	19.622	25.110	-5.488	-22%
PET 3	49.436	48.622	0.814	2%

As can be seen in Table 5.1, there isn't a definite pattern in the difference between the coverage measured in a photo taken with a portable microscope and one taken with a phone. In most cases, the coverage is overestimated when the photo is taken with a

phone (in relation to the one taken with the microscope). This is because, even though the microscope detects more particles (the smaller ones), the lack of resolution of the phone makes the particles seem bigger than they actually are, increasing the coverage. However, since there isn't enough data to reach a conclusion about a pattern, it's fair to assume that, in average, the estimated coverage is not significantly affected by the poor image quality, although the uncertainty is considerable.

5.3 Relationship between the coverage and the line intensities

As the coverage increases, it's expected that the ratio of the intensities of plastic and indium also increases, since higher amounts of plastic should be detected. Based on this proposition and considering that $\theta \in [0, 1]$, the following expressions for both intensities were deduced:

$$I_{id} = J_x n_{id} \frac{d\sigma_{id}}{d\Omega} L_{Q_{id}} T_{id} \theta \quad (5.3)$$

$$I_{In} = J_x n_{In} \frac{d\sigma_{In}}{d\Omega} L_{Q_{In}} T_{In} (1 - \theta) \quad (5.4)$$

where the index 'id' corresponds to the line that is being compared with the indium line, thus depending on the plastic. For PVC, 'id' would be 'Cl', for PA6 it would be 'N' and for PET it would be a particular contribution of 'O'.

The ratio of these intensities is given by

$$\frac{I_{id}}{I_{In}} = \frac{d\sigma_{id}/d\Omega}{d\sigma_{In}/d\Omega} \frac{T_{id}}{T_{In}} \frac{n_{id}}{n_{In}} \frac{L_{Q_{id}}}{L_{Q_{In}}} \frac{\theta}{1 - \theta} \quad (5.5)$$

and from here, we find the theoretical relationship between the coverage and the intensities of plastic and indium:

$$\frac{1}{\theta} = \frac{I_{In}}{I_{id}} A + 1 \quad (5.6)$$

where A is a constant corresponding to the quotient of the parameters of each element.

$$A = \frac{d\sigma_{id}/d\Omega}{d\sigma_{In}/d\Omega} \frac{T_{id}}{T_{In}} \frac{n_{id}}{n_{In}} \frac{L_{Q_{id}}}{L_{Q_{In}}} \quad (5.7)$$

This derivation works only under the assumption that there is not surface contamination, which is unlikely, or that the attenuation is always the same (one constant value for indium and another for the plastic particles).

5.3.1 Calibrations of the plastics

As was previously mentioned, the three plastics (PVC, PA6 and PET) were calibrated for different levels of coverage with the purpose of finding its relationship with the ratio of intensities of the indium substrate and the plastic. Eq. (5.6) indicates that this relationship is expected to be linear. The results are demonstrated in Figures 5.15, 5.16 and 5.17, and the data values are presented in Tables 5.2, 5.3 and 5.4.

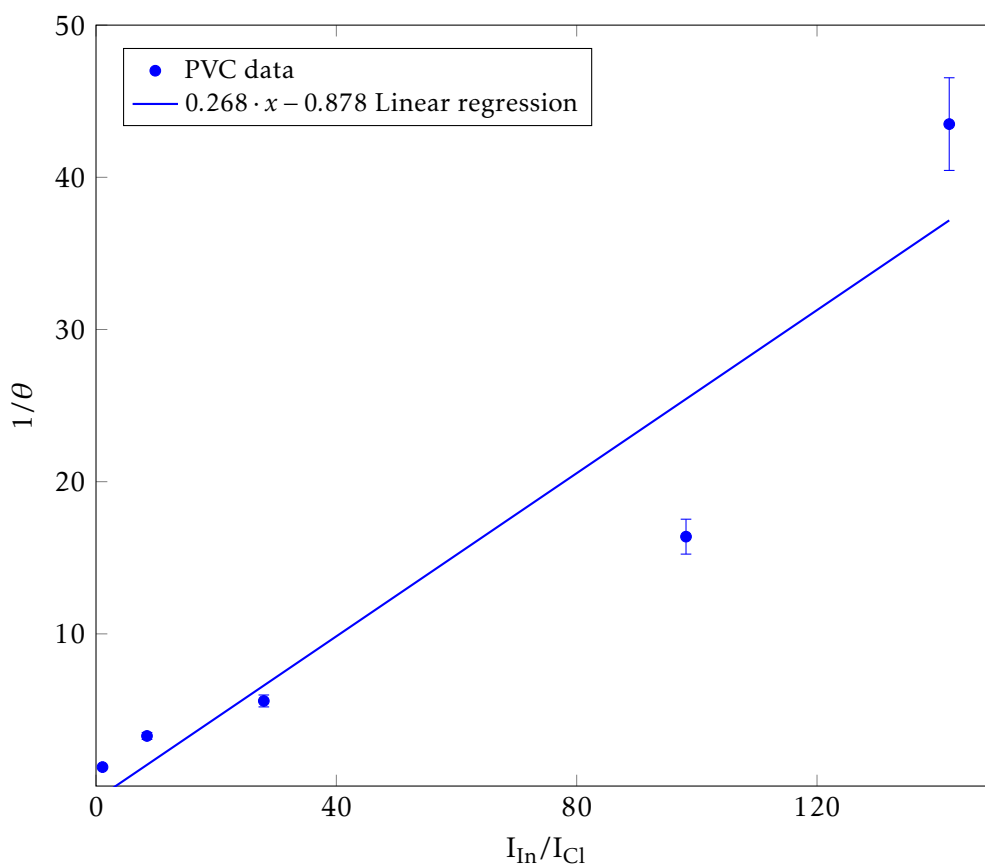


Figure 5.15: Calibration data of PVC.

Table 5.2: PVC data for the calibration.

Sample	θ	I_{In}/I_{Cl}	$1/\theta$
1	2.299%	142.004	43.497
2	6.102%	98.196	16.388
3	17.881%	27.930	5.593
4	30.377%	8.486	3.292
5	80.222%	1.083	1.247

The results for PVC look reasonably linear, as can be seen in Fig. 5.15. However, the experimental intercept is -0.878 when it should be 1, no other value has physical sense. So, it's clear that the point with the highest value of $\frac{1}{\theta}$ is not correct, because if it were removed, the slope would be reduced and the intercept would likely become positive.

The theoretical value of A is approximately 0.104, which is a bit lower than the experimental value, 0.268. This discrepancy can be due to an inaccurate coverage estimation, or due to contamination issues.

It is worth noting that the XPS instrument was able to detect a sample of PVC with around 2.3% coverage, which is very low, proving that this technique can be very competent in MP analysis.

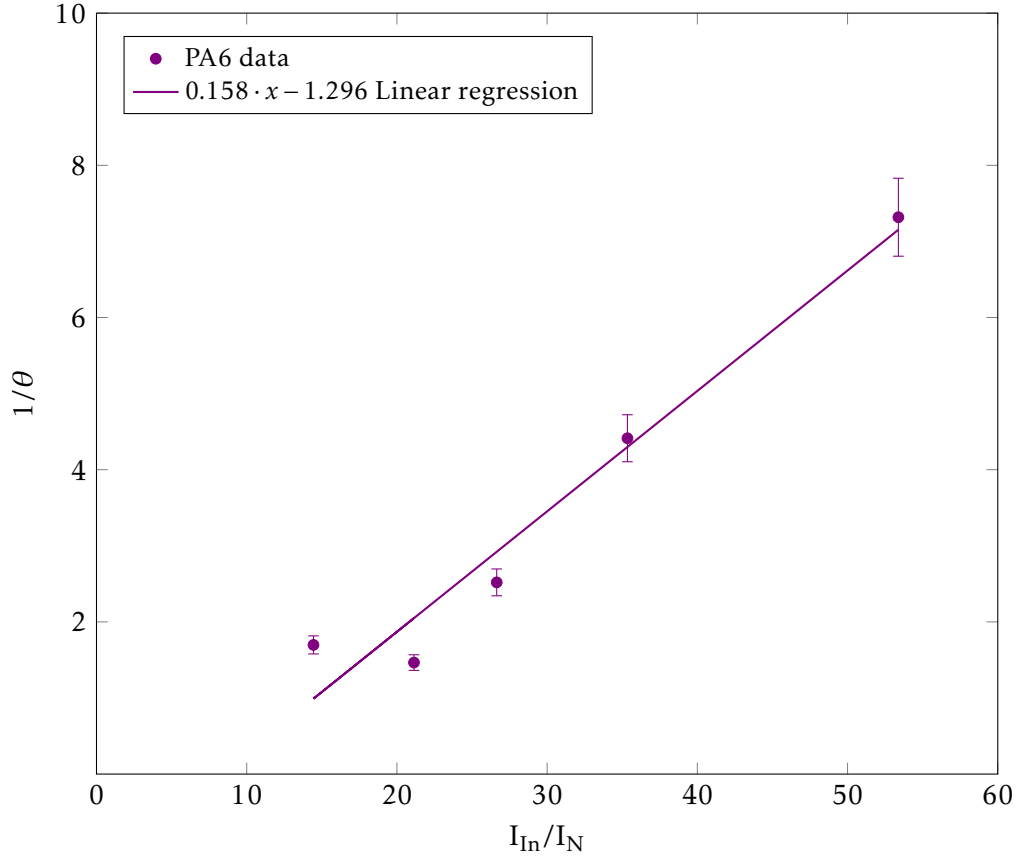


Figure 5.16: Calibration data of PA6.

Table 5.3: PA6 data for the calibration.

Sample	θ	I_{In}/I_N	$1/\theta$
1	13.665%	53.384	7.318
2	22.660%	35.346	4.413
3	39.694%	26.644	2.519
4	58.918%	14.446	1.697
5	68.244%	21.135	1.465

Although the results for PA6 appear to be fairly linear (Fig. 5.16), the negative intercept has no physical sense at all. There is non-linear behaviour at the highest values of coverage, where there is an apparent increase of $\frac{I_{In}}{I_N}$ with the coverage, which has no physical reason. Clearly, contamination needs to be considered to be affecting the signal intensities.

There is also a great discrepancy between the experimental value for A and the theoretical one, which is 0.044.

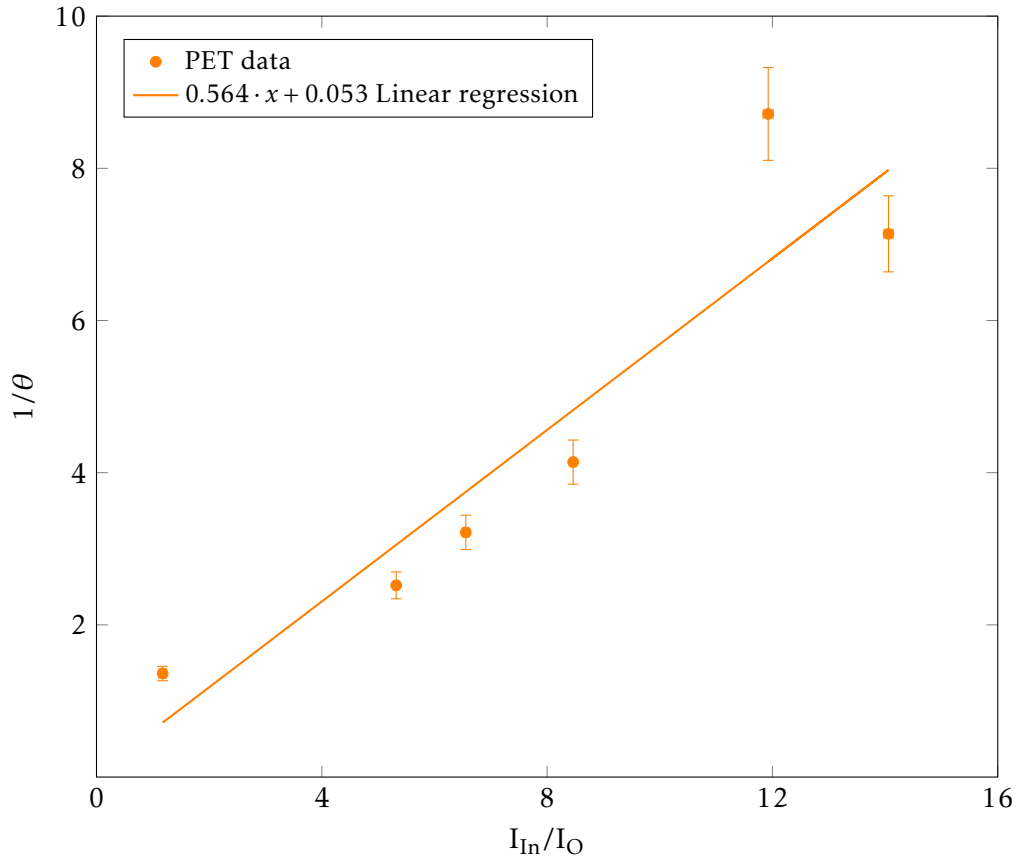


Figure 5.17: Calibration data of PET.

Table 5.4: PET data for the calibration.

Sample	θ	I_{In}/I_O	$1/\theta$
1	11.475%	11.924	8.715
2	14.008%	14.060	7.139
3	24.158%	8.462	4.139
4	31.097%	6.556	3.216
5	39.687%	5.321	2.520
6	73.471%	1.175	1.361

The results for PET appear quite linear as well, but just like for the other two plastics, the intercept value has no physical sense, although it is a better result compared with PVC and PA6.

The theoretical value for A is 0.189, which is much lower than the experimental value, at 0.564.

Sample 1 shows non-linear behaviour. If it were removed, the intercept would be a lot closer to 1 and the slope (corresponding to A) would improve as well by getting closer to the theoretical value.

5.3. RELATIONSHIP BETWEEN THE COVERAGE AND THE LINE INTENSITIES

5.3.1.1 Attenuation of indium

As was demonstrated in Chapter 4, the thickness of the overlayers can be calculated, and so the attenuation caused by each of them can too. Therefore, it's possible to estimate what the line intensity of indium would be if it were not attenuated by the overlayers.

The line intensity of indium without attenuation from the hydrocarbon layer, $I_{In}^{(b+ox)}$, can be written as

$$I_{In}^{(b+ox)} = I_{In}^{total} e^{\frac{d_c}{L_{3d,c}}} \quad (5.8)$$

where I_{In}^{total} is the total measured intensity of the In 3d_{5/2} line (both In(0) and In(+3) contributions), and by analogy, the line intensity of indium without attenuation from both the hydrocarbon layer and the oxide layer, $I_{In}^{(b)}$, is:

$$I_{In}^{(b)} = I_{In}^{total} \left(1 - \frac{I_{In}^{(+3)}}{I_{In}^{total}} \right) e^{\frac{d_c}{L_{3d,c}}} e^{\frac{d_{ox}}{L_{3d,ox}}} \quad (5.9)$$

where $I_{In}^{(+3)}$ is the intensity corresponding to the In(+3) contribution in the In 3d_{5/2} line.

In the interest of verifying if removing the attenuation of indium caused by the overlayers would make the results even more linear, the thickness of each top layer was calculated (Table 5.5) in order to get the values of the non-attenuated intensities of indium, and the same process of calibration was carried out. The results are shown in Figures 5.18, 5.19 and 5.20.

Table 5.5: Thickness values of the hydrocarbon contamination layer, d_c , and of the oxide-hydroxide layer, d_{ox} , calculated for all the samples used in the calibrations.

	Sample	θ	d_c (nm)	d_{ox} (nm)
PVC	1	2.299%	3.561	0.946
	2	6.102%	2.184	2.064
	3	17.881%	2.120	1.212
	4	30.377%	1.887	1.099
	5	80.222%	5.182	1.855
PA6	1	13.665%	2.730	2.048
	2	22.660%	3.051	1.332
	3	39.694%	4.893	1.320
	4	58.918%	1.117	1.585
	5	68.244%	3.104	1.697
PET	1	11.475%	1.150	1.888
	2	14.008%	1.271	2.114
	3	24.158%	1.595	1.875
	4	31.097%	2.260	1.758
	5	39.687%	1.277	1.698
	6	73.471%	3.213	2.047

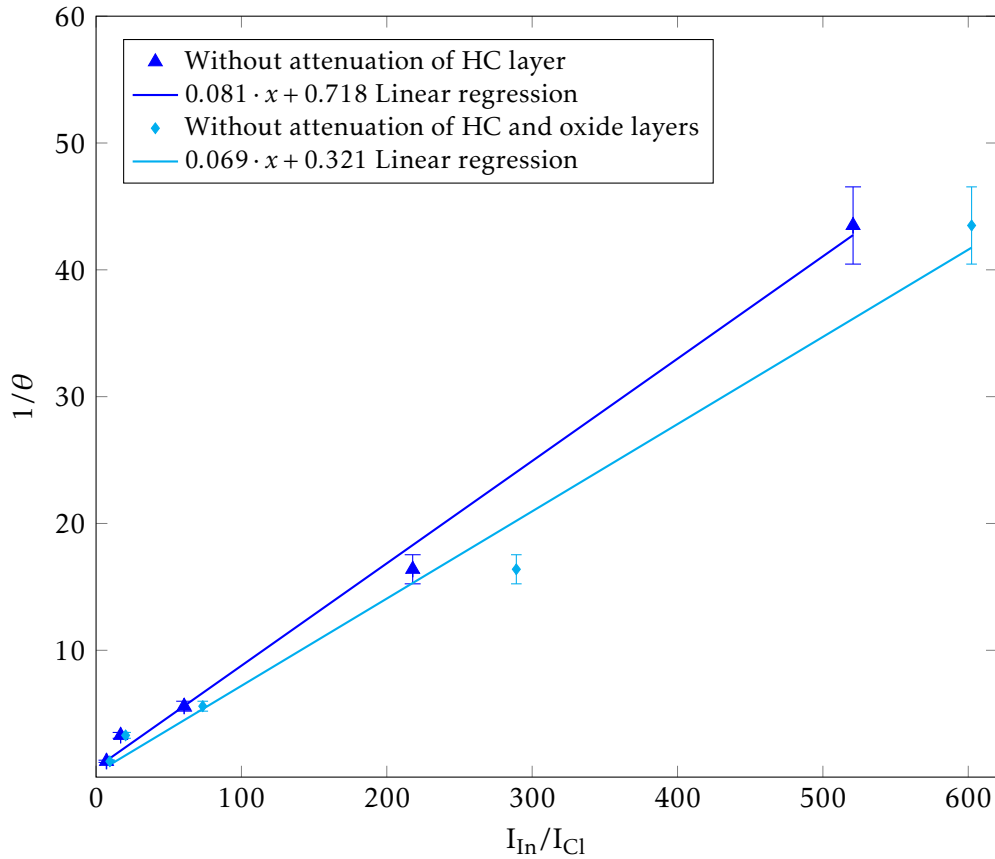


Figure 5.18: Calibration data of PVC using the line intensities of indium without attenuation of the hydrocarbon (HC) layer (dark blue triangular marks) and using the line intensities of indium without attenuation of both overlayers (light blue diamond marks).

The results show a significant increase in linearity for PVC (Fig. 5.18), particularly in the case where the attenuation of the hydrocarbon layer was removed from the In signal. The intercept is 0.718, which is a greatly improved result, and the experimental A value is 0.081, being quite close to the theoretical value of 0.104.

The fact that there was such an improvement when removing the attenuation caused by the hydrocarbon layer means that the problem was the contamination on the In substrate. Being that the result is still not completely ideal, it's very possible that there is also a contamination layer on top of the plastic causing attenuation of the Cl signal intensity.

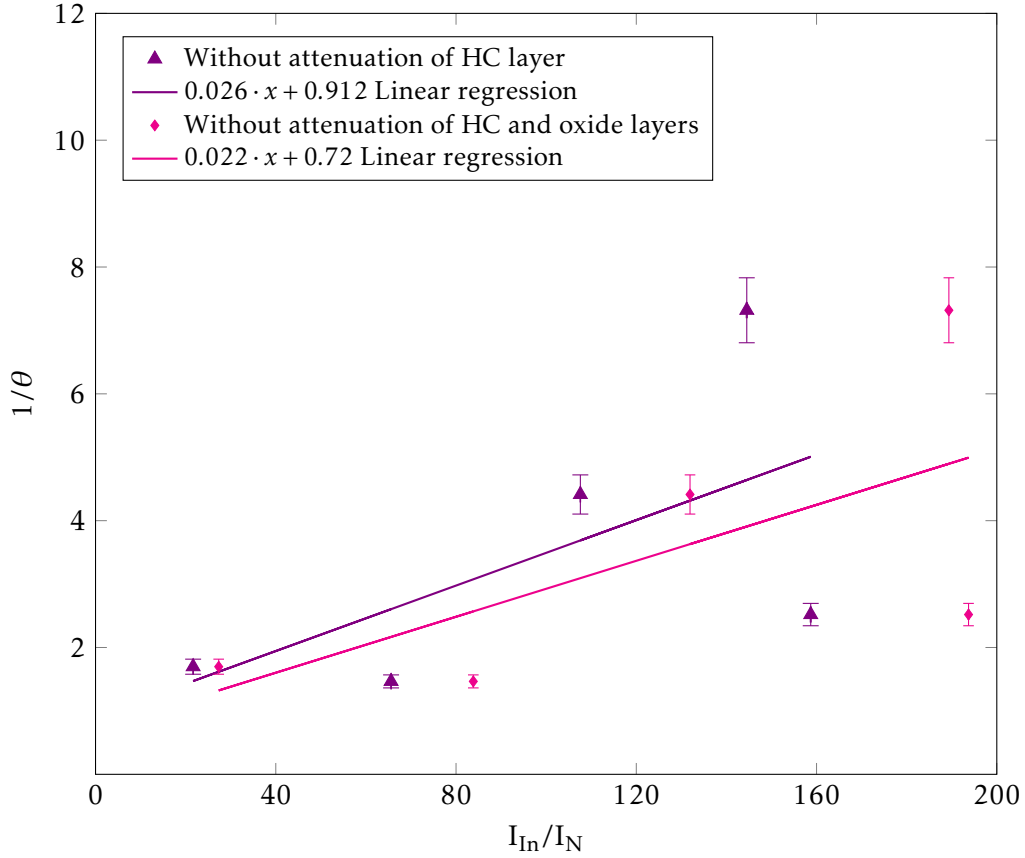


Figure 5.19: Calibration data of PA6 using the line intensities of indium without attenuation of the hydrocarbon (HC) layer (violet triangular marks) and using the line intensities of indium without attenuation of both overlayers (magenta diamond marks).

Looking at the linear regression equation on Fig. 5.19, we see that the slope appears to have improved, actually having been reduced to an even lower value than the theoretical value, and the intercept is exceptionally close to 1. However, looking at the actual plot, it becomes obvious that there is a huge loss of linearity, and the seemingly very linear result that the equation presents is not exact at all. The data points have become scattered, avoiding any linear tendency between them.

This implies that there may be some surface contamination of PA6, which was not considered. The fact that the calibration of PA6 shows generally worst results than the other two plastics, before and after the correction for the overlayers, and that there is non-linear behaviour even for the high coverage values (which are less likely to be poorly estimated), supports that speculation.

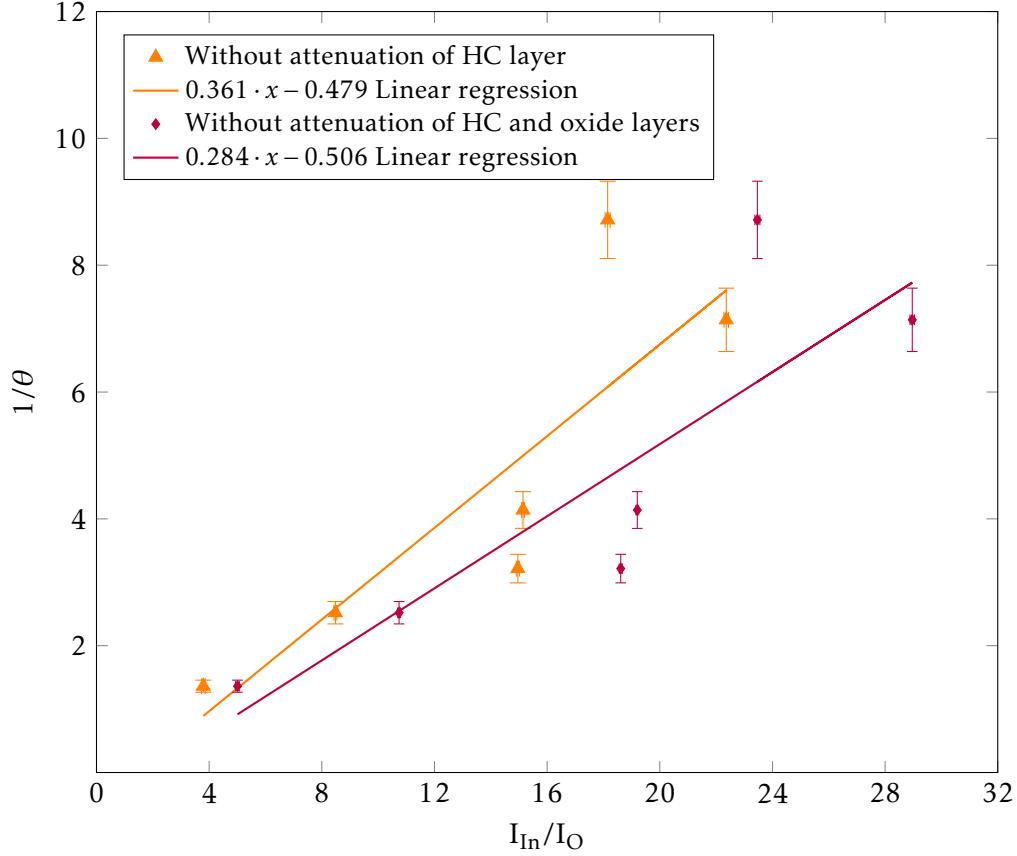


Figure 5.20: Calibration data of PET using the line intensities of indium without attenuation of the hydrocarbon (HC) layer (orange triangular marks) and using the line intensities of indium without attenuation of both overlayers (red diamond marks).

In the case of PET (Fig. 5.20), removing the attenuation caused by the overlayers produced an improvement in the slope but the intercept values got much worse. The data point corresponding to Sample 1 remains the larger reason for the lack of linearity, implying that the problem may be inaccuracy in the coverage measurement.

An important factor that may be affecting all the samples to some extent is a potential contamination layer on top of the plastics that is attenuating the signal from all the elements present in the sample. Only the overlayers directly on top of indium were accounted for in the attenuation removal calculations, since these were made under the assumption that there was no surface contamination over the plastic microparticles. However, even though the amount may be considered negligible, it is unlikely that there isn't any contamination at all.

CONCLUSIONS

Reference samples of the indium substrate and the industrial plastics were analysed with XPS. The indium spectra showed the presence of an oxide-hydroxide layer and a hydrocarbon contamination layer. The resulting spectra from the analysis of PVC, PA6 and PET showed very similar results to what was expected from literature. However, there was a fair amount of evidence of contamination and/or possibly additives. Because they are produced for industrial use, it is certain that they have some additives to enhance their properties, but it is not disclosed what those additives are or what they are made of.

To study how the surface coverage of microplastic in a sample can be measured by XPS, several samples of each plastic were prepared with different percentages of coverage and analysed with XPS. The goal was to perform calibrations that show the relationship between the coverage and the ratio of intensities of indium and the plastic (more precisely, the identifying element of the plastic). The lowest coverage was around 2.3% and it was still detected by the instrument, proving that XPS can be very sensitive to microparticles and a competent technique for MP analysis.

The line intensities were obtained from the resulting spectra and the coverage was estimated by taking photos of the samples with a phone camera and analysing them with an image analysis software. Near the end of the experimental period of the dissertation, an additional procedure was carried out, in which a few PVC, PA6 and PET samples were prepared with different percentages of coverage and photographed with a phone and with a portable microscope, and subsequently analysed with the software. The purpose of this was to see if the lack of quality of the phone camera was greatly impacting the coverage results. After the comparison between the results from the phone and the microscope, it was concluded that, in average, there was no indication that this was the case, although considerable uncertainty is introduced.

Under the proposition that the ratio of intensities should increase with coverage, it was demonstrated that linear dependency is expected between the ratio of the XPS line

intensities and the reciprocal of the coverage, and the results of the calibrations were consistent with that statement. For PVC, the results were quite linear. However, the intercept value was not 1, thus having no physical sense, which happened for all three plastics. The results for PA6 and PET showed non-linear behaviour for certain samples but overall retained an apparent sense of linearity as well.

It was demonstrated that, with the values of thickness of the top layers, it is possible to estimate what would be the line intensity of indium if the signal were not attenuated. After calculating the line intensity of indium without attenuation from the oxide-hydroxide layer and without attenuation from both overlayers, another calibration was performed to see if linearity would improve. For PVC, it did. Specifically removing the attenuation of the hydrocarbon layer significantly improved linearity, implying that the contamination layer on top of the indium substrate was the issue. Yet, for PA6 and PET, the results did not get better. For PA6, there was a substantial loss of linearity that suggests that there may be surface contamination. In PET's case, the intercept values got worse but, in general, the results showed the same non-linearity pattern, indicating that it's probably due to poor estimation of coverage for one of the samples.

Even though the calculations for the calibrations were made under the assumption that there is no surface contamination on top of the microplastics, it is unlikely that there is none at all. Therefore, it's a strong possibility that a contamination layer over the plastics is affecting all the samples to some (possibly negligible) degree by attenuating the signal intensity coming from the elements present in the plastic. In a future work, the same analysis could be done but taking the attenuation from all the elements present in the sample to study how linearity changes.

The XPS technique proved very effective for the identification of PVC, PA6 and PET, and it was able to detect the microplastics even with low surface coverage (2.3% for PVC, 13.7% for PA6 and 11.5% for PET). The fittings of the reference spectra were done mostly in a straightforward way, using literature data. At the same time, having reference samples allowed for a simple process of fitting the XPS spectra that resulted from the calibration samples, even the ones with lowest surface coverage.

The strategies used for quantification provided satisfactory results, such as relying on an element that is known not to be present in the substrate and, if possible, in the contamination layer. For PVC and PA6, the identification of the signal was straightforward because chlorine and nitrogen were related only to the respective plastic. For PET, however, we relied on oxygen for quantification, which is present in metal oxides, indium oxide and hydroxide in this case. So, there was a potential problem of resolving the O 1s contributions from PET and from indium. Unexpectedly, this was solved by itself by

differential charging: indium and the oxide-hydroxide layer showed little to no charging, in contrast to the PET particles. This effect made the process of resolving the two contributions rather simple. For that reason, the differential charging that is expected when working with XPS on microplastics should be seen as an opportunity and another strategy to separate the substrate and plastic signals.

When it comes to the preparation of the samples, simply pressing the microplastics onto the indium substrate worked quite well for the reference samples because the intent was to completely cover the substrate surface. However, the samples for the calibration required a more controlled method of preparation to achieve a uniform distribution of microparticles in the substrate. Using a suspension of isopropanol and the microplastics and then depositing them on the indium substrate with a dropper helped accomplish this. If working with real samples, i.e., environmental samples, the same method could be utilised for the smaller particles, such as 1 mm and below, after the filtration processes to remove organic matter, salts, etc.. For larger particles, the recommendation would be to clean them (with isopropanol or ethanol, for example) and then proceed to press them onto the substrate in order to fixate them. This can be difficult to achieve depending on their shape and size, so another method may be needed.

In a possible sequel to this work, it would be interesting to collect samples of ocean/river water or sand and proceed with an XPS analysis to find which plastics are present. Additionally, it could also be of interest to make a statistical analysis about the plastics found in each collecting point.

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A

IMAGES FOR CALIBRATIONS

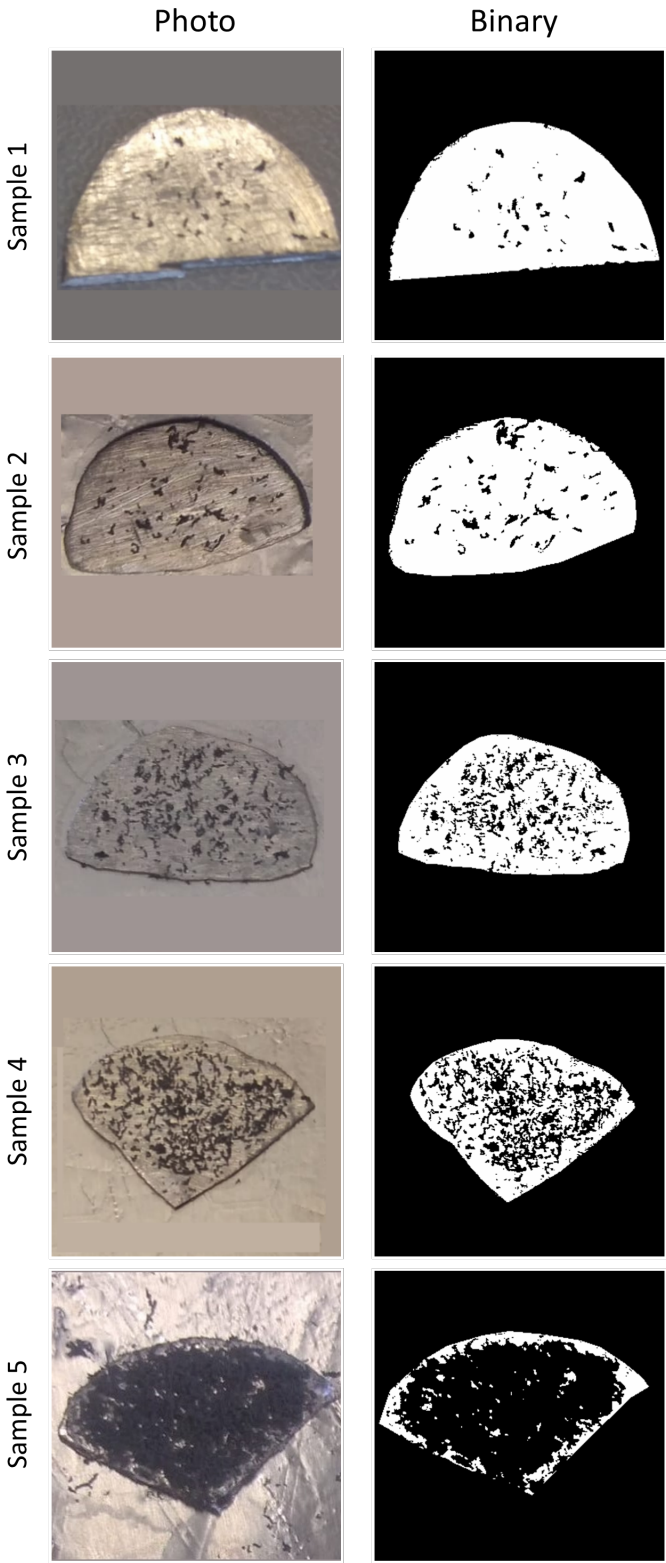


Figure A.1: Photos and binaries of the PVC samples used for calibration.

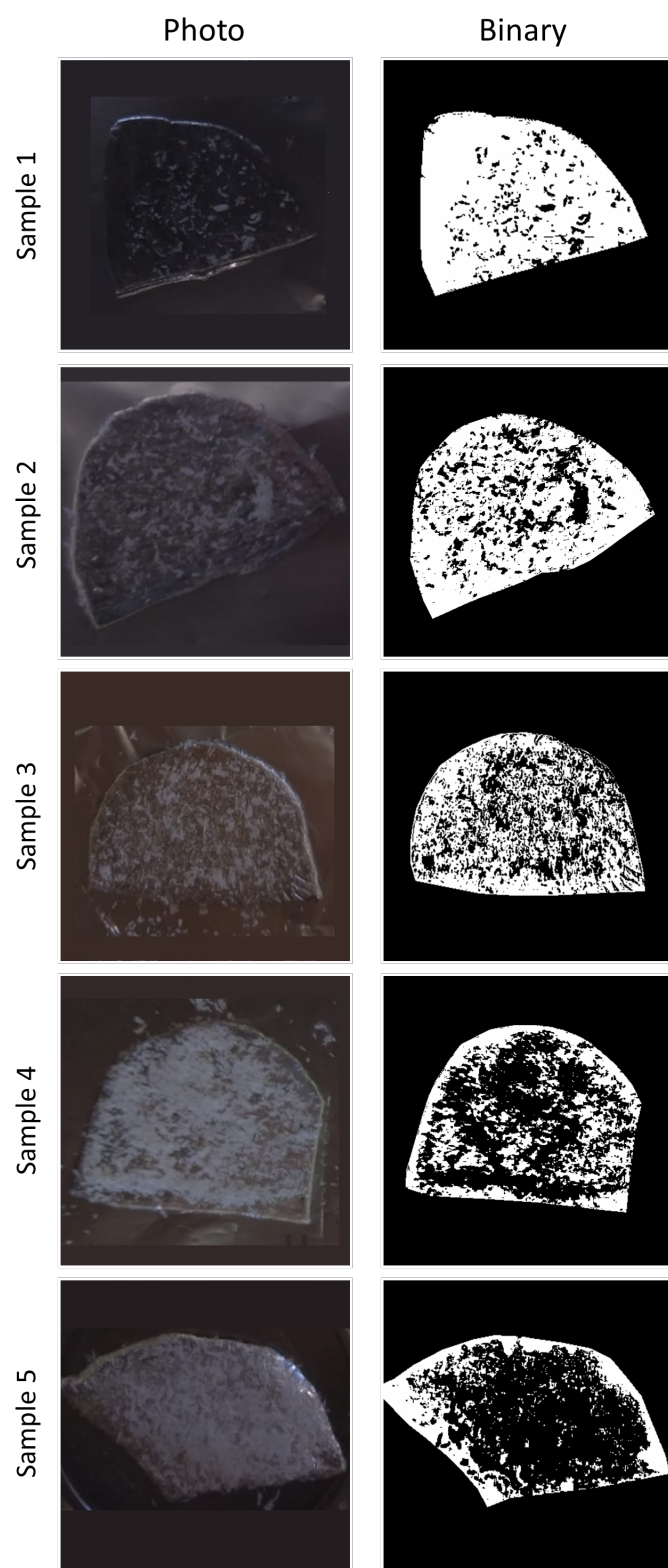


Figure A.2: Photos and binaries of the PA6 samples used for calibration.

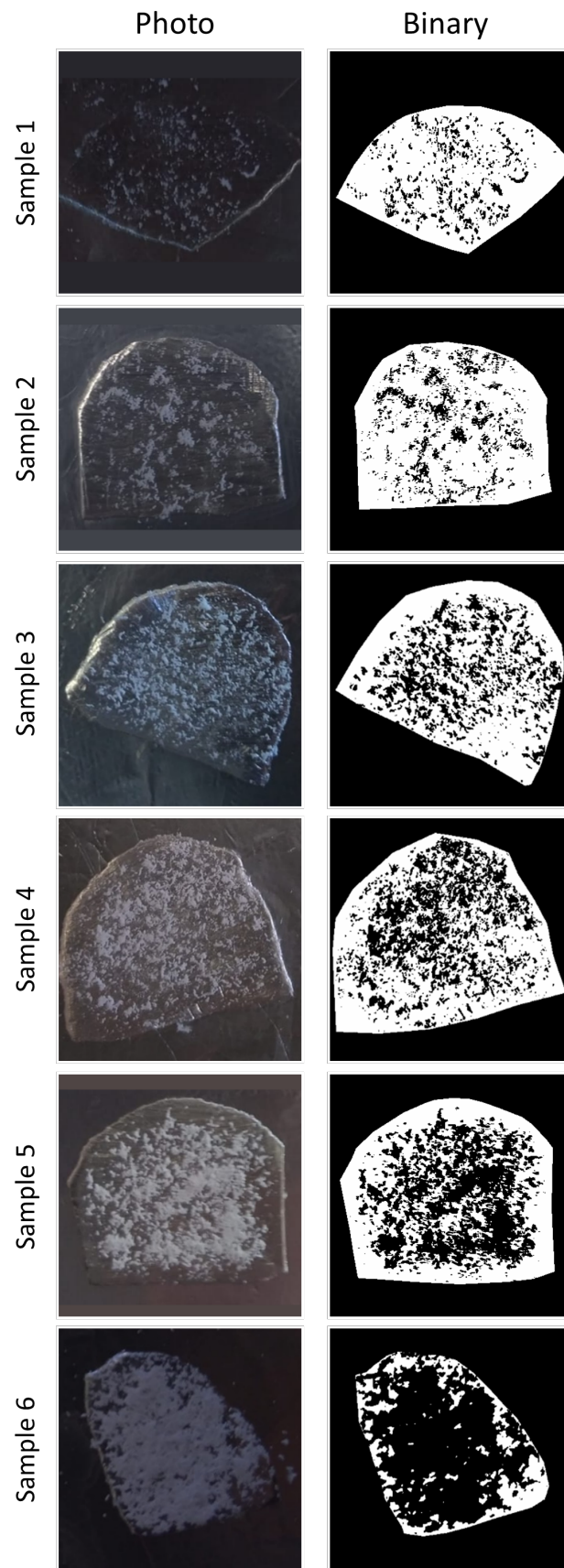


Figure A.3: Photos and binaries of the PET samples used for calibration.

| B

IMAGES FOR COVERAGE COMPARISON:
PHONE *VERSUS* MICROSCOPE

APPENDIX B. IMAGES FOR COVERAGE COMPARISON: PHONE *VERSUS* MICROSCOPE

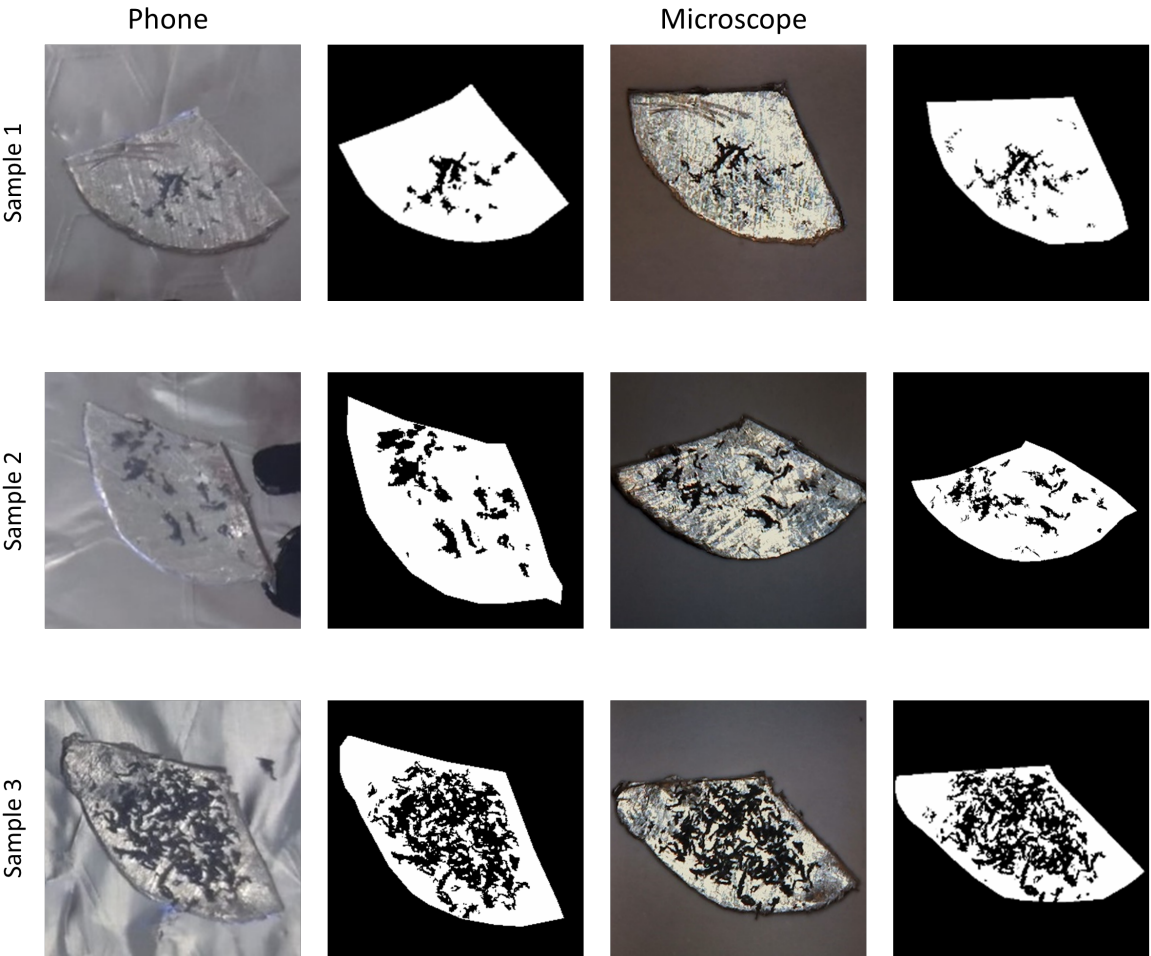


Figure B.1: Photos and binaries of three samples of PVC photographed with phone *versus* microscope.

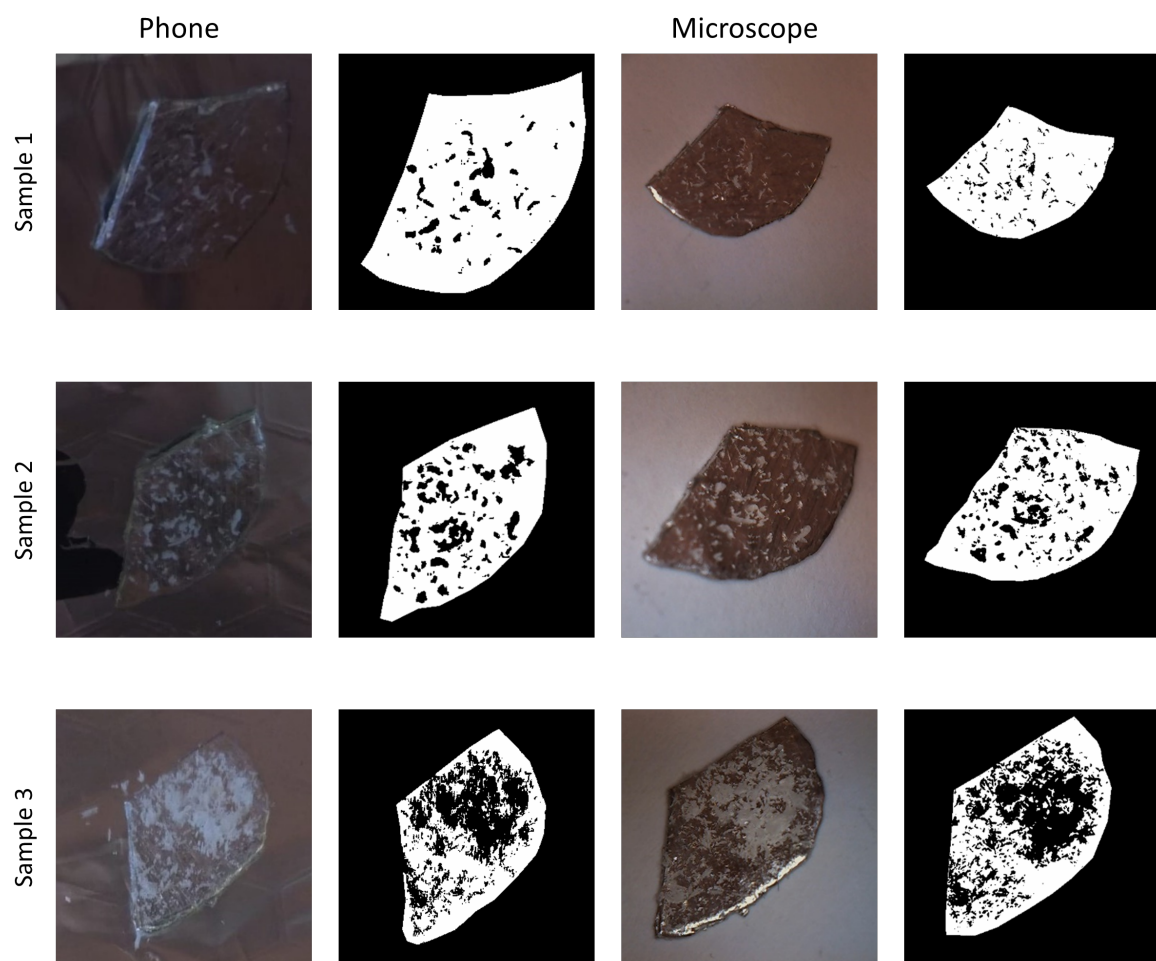


Figure B.2: Photos and binaries of three samples of PA6 photographed with phone *versus* microscope.

APPENDIX B. IMAGES FOR COVERAGE COMPARISON: PHONE *VERSUS* MICROSCOPE

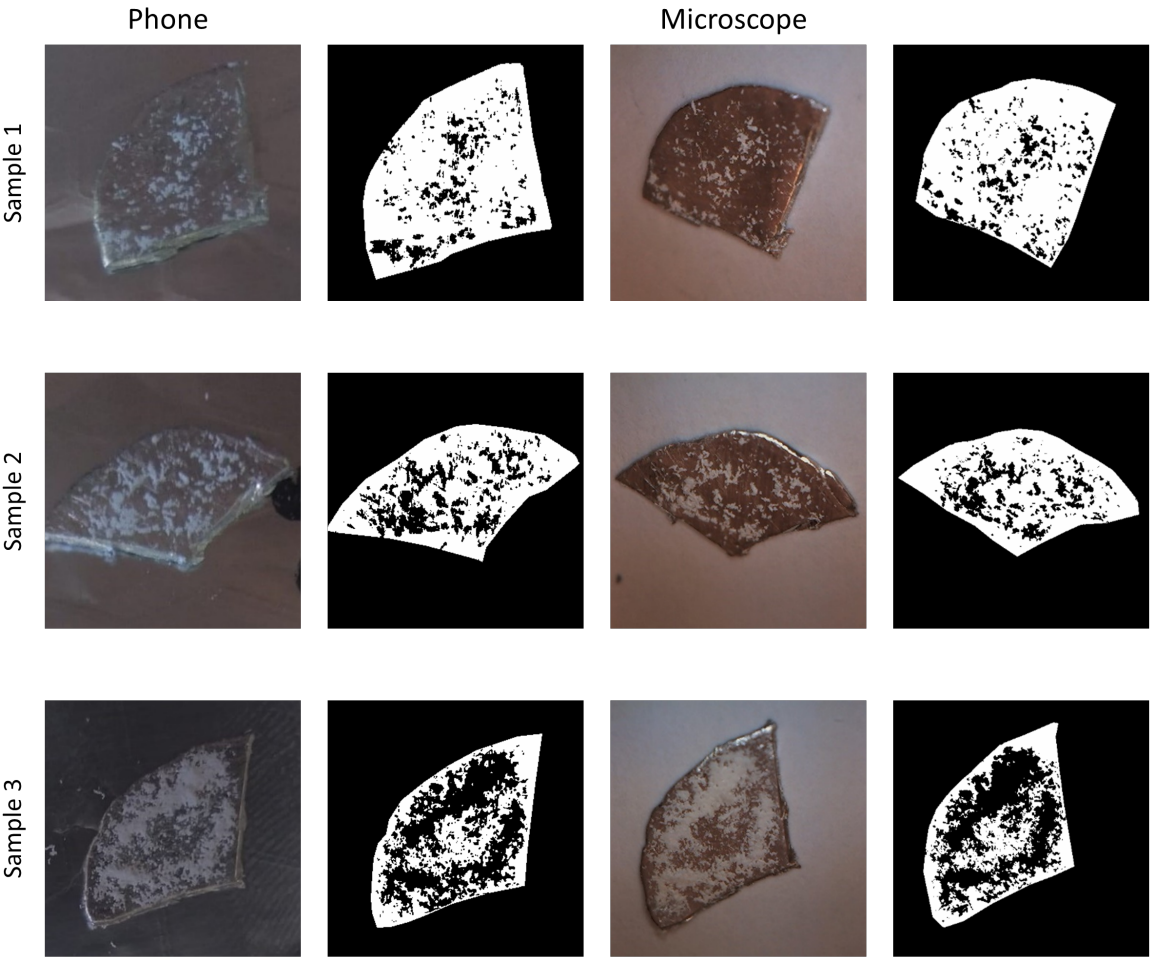


Figure B.3: Photos and binaries of three samples of PET photographed with phone *versus* microscope.



