

Faculté des bioingénieurs

Characterisation of Nano-structured High Entropy Alloys by ToF-SIMS

Auteur : Oscar LAURENT

Promoteur(s) : Prof. Damien DEBECKER (UCL/IMCN/MOST)

Prof. Arnaud DELCORTE (UCL/IMCN/BSMA)

Lecteur(s) : Prof. Christine DUPONT (UCL/IMCN/BSMA)

Prof. Thierry VISART DE BOCARME (ULB/CHEM/SIN)

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Part I

Introduction

1.1 Conventional Alloys

In the field of materials science, alloying has been a long-standing method of modifying and improving the properties of materials. Traditionally, alloys, defined as a metallic substance composed of two or more elements, have been created by adding small amounts of secondary elements to a primary element, such as iron in steels, with additional elements like carbon and chromium for strength and corrosion resistance, respectively. This primary-element approach is also reflected in the naming convention of alloys, including ferrous alloys, aluminium alloys, titanium alloys, and nickel alloys, among others. They are primarily situated at the corners of phase diagrams, occupying only a small portion of the design space and thereby limiting the scope for materials development. Information and understanding about alloys close to the corners and edges of a multicomponent phase diagram is well developed, with much less known about alloys in the centre of the diagram. This is shown schematically for the ternary and quaternary systems in Figure 1.1.

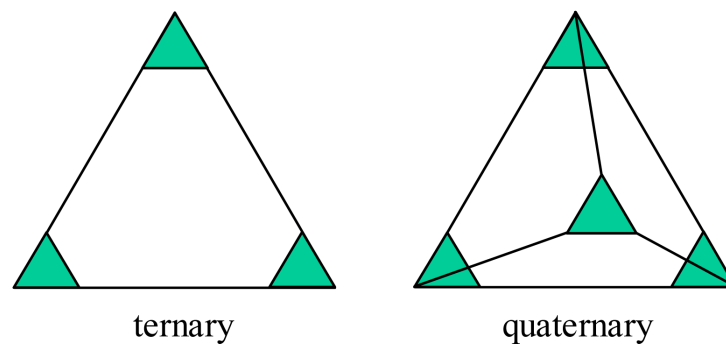


Figure 1.1: Schematic for ternary and quaternary systems, showing regions of the phase diagram which are relatively well known (green) near the corners, and relatively less well known (white) near the center. [1]

This primary element approach limits the total number of possible element combinations and, consequently, the range of alloys that can be explored. As a result, most of these combinations have already been identified and exploited, necessitating new methods to significantly expand the compositional space for investigation.

1.2 High Entropy Alloys

A promising alternative to the primary-element approach is the development of High Entropy Alloys (HEAs), which are characterised by multiple principal elements in relatively high concentrations, often equiatomic. This innovative approach deviates from traditional alloying practices and has garnered significant attention in recent years. The surge in research activity, particularly over the past five years, can be traced back to the publication of two seminal papers in 2004 [2], [3], where two groups independently proposed the study of a new class of alloys containing multiple elements in near-equiatomic concentrations.

Unlike conventional alloys, which are often limited to a small number of combinations of elements clustered around the corners or edges of phase diagrams, HEAs extend into the central region of the phase diagram, offering a much wider combination space (Figure 1.2).

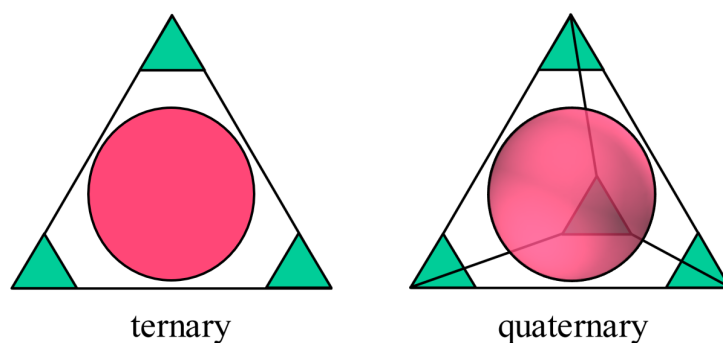


Figure 1.2: Schematic for ternary and quaternary systems, showing regions of the phase diagram of the conventional alloys (green) and the region of the HEAs near the centre (purple). Adapted from [1]

Because of the vast number of possible combinations, concentrated, multi-component alloys remain largely unexplored. However, this presents a promising opportunity to discover new alloys with useful properties.

When two pure elements, A and B, are combined to form an alloy, the resulting mixture may be one or more solid solutions or contains intermetallic phases (Figure 1.3). A solid solution is a homogeneous mixture of two or more elements in a single solid phase. On the other hand, intermetallic phases are compounds that have a specific stoichiometry and crystal structure, with the atoms arranged in a specific pattern.

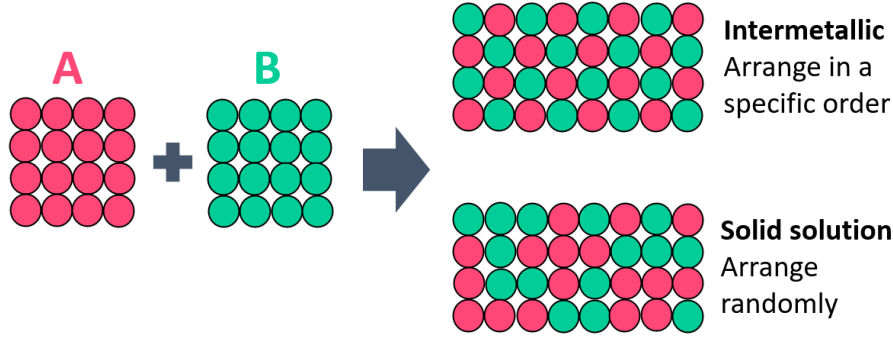


Figure 1.3: Possibilities of alloying for two pure element, A and B

The formation of either a solid solution or intermetallic phases depends on the relative free energies of the reactions (ΔG_{mix} and ΔG_f) involved.

$$A + B = AB_{solution} : \Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (1.1)$$

$$A + B = AB_{intermetallic} : \Delta G_f = \Delta H_f - T\Delta S_f \quad (1.2)$$

Where ΔG_{mix} , ΔH_{mix} , ΔS_{mix} are the Gibbs free energy, enthalpy and entropy of mixing, respectively; ΔG_f , ΔH_f , ΔS_f are the corresponding values for the formation of an intermetallic compound with AB stoichiometry and T is the absolute temperature.

At thermodynamic equilibrium, the phases present in the alloy depend on whether the Gibbs free energy of mixing (Eq. 1.1) is more or less negative than the free energies of formation (Eq. 1.2) of all possible intermetallic compounds comprising the elements A and B present individually or as mixtures. Entropy can stabilise a phase with a higher entropy, provided that the temperature is sufficiently high. For example, the melting phenomenon of a pure metal is due to the higher entropy of the liquid state relative to the solid state (according to Richard's rule, [4] at the melting point, the difference in entropy between the two states roughly equals the constant gas R).

Furthermore, if intermetallic compounds are not favoured and only a solid solution forms, the solid solution is not always strictly random because the different atomic species can cluster or order on the lattice, depending on whether ΔH_{mix} is positive or negative, respectively. Another possibility is that, instead of forming a single solid solution, the mixture decomposes into two solid solutions with different compositions, crystal structures, and/or lattice parameters.

The situation becomes increasingly more complex as more alloying elements are added ($A + B + C + \text{etc.}$) because the number of possible phases that can coexist correspondingly increases, as given by the Gibbs phase rule. If some of those phases are intermetallic compounds, they can be of several different types, even if we consider just the binary pairs (A-B, B-C, A-C, etc.). In reality, ternary and higher-order intermetallics can also form, rapidly increasing the number of possibilities. Some of the possible mixing reactions

are shown in Figure 1.4.

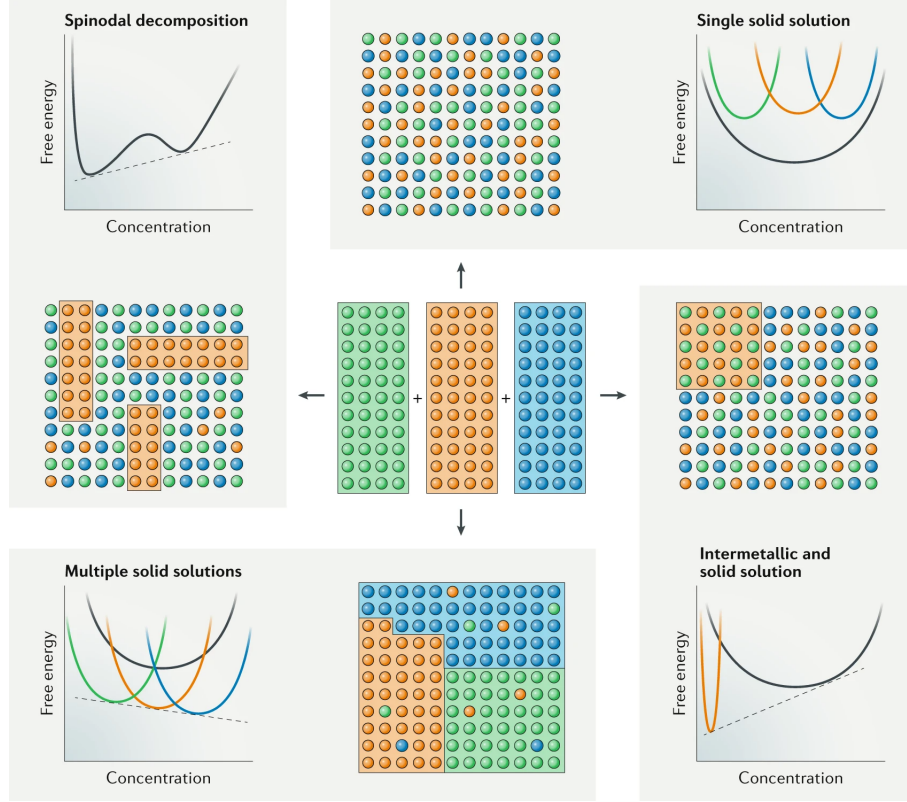


Figure 1.4: Possible mixing reactions for three alloying elements. Some of the possible reactions that can occur when three different elements, represented by the orange, blue and green spheres, are mixed in equal proportions, including spinodal decomposition, formation of single or multiple solid solutions or precipitation of an intermetallic compound in a solid solution. [5]

Yeh and al [2], were among the first scientists to study high entropy alloys and proposed that the increased configurational entropy of mixing in such alloys (as expressed in 1.1) could counteract compound formation (as expressed in 1.2). By incorporating more elements in near-equiatomic concentrations, solid solutions could be stabilised at the expense of intermetallics.

To simplify the problem, Yeh and colleagues assumed that the solid solution considered was ideal ($\Delta H_{mix} = 0$ in Eq. 1.1) and that the intermetallic compound was perfectly ordered ($\Delta S_f = 0$ in Eq. 1.2). The relative stability of the solid solution and intermetallic compound was then dependent on whether $-T\Delta S_{mix}$ (Eq. 1.1) was more negative than ΔH_f (Eq. 1.2). The ideal entropy of mixing was then described as follows.

$$\Delta S_{mix} = -R \sum x_i \ln(x_i) \quad (1.3)$$

Where R is the gas constant and x_i is the mole fraction of the i^{th} element. When assuming equimolar composition, this function yields values for ΔS_{mix} of $1.39R$, $1.61R$ and $1.79R$ for equiatomic alloys containing 4, 5 and 6 elements, respectively. This mean that, for HEAs,

the difference in entropy between solid solutions and intermetallic compounds is particularly large. For example, the configurational entropy of an equimolar quinary random solid solution is $1.61R$. This means that the entropy difference between an equimolar quinary solution and a completely ordered phase (whose entropy is negligible) is about 60% larger than the entropy difference of the melting case based on Richard's rule mentioned above (i.e. 60 % larger than the entropy difference between liquid and solid states of pure metals).

Based on this simplification, they concluded that, in alloys with a high number of principal elements (say, $n = 5$), the entropic contribution to the free energy ($-T_m\Delta S_{mix}$) at the melting temperature T_m is comparable to the formation enthalpies (ΔH_f) of most intermetallic compounds, thus suppressing their formation, except those with large heats of formation, such as strong ceramic compounds (oxides, carbides, nitrides and silicides).

Yeh and co-workers then defined high entropy alloys as those with **five or more elements in equiatomic concentrations forming a solid solution**. The high configurational entropy of these solid solutions pushes the mixing free energy toward negative values, allowing the mixing of metals that are normally immiscible in binary and ternary alloys [6].

To allow flexibility in alloy design, they relaxed the equiatomic requirement and permitted a range of molar concentrations from 5 to 35 % for each constituent element [7], [8]. However, this simple criterion based on the number of alloying elements is not sufficient to predict single-phase, solid-solution formation in multi-element alloys. The stating on whether or not an alloy is a HEA is then to be determined in the end only if it actually forms a solid solution; this highlights the importance of characterisation techniques that are able to describe the degree of atomic mixing in these complex systems. The concept of atomic mixing is defined as the degree to which the different components are, at the atomic scale, mixed together without preferential binding to a specific component, tending instead towards a random distribution of neighbouring atoms.

1.3 Properties of HEAs

The incorporation of a large number of elements into HEAs leads to several unique effects that are not observed in conventional alloys. These effects can be grouped into four core categories [9] that have been expressed as follows: (1) high entropy effects in thermodynamics, (2) sluggish diffusion in kinetics, (3) severe lattice distortion in structures, and (4) cocktail effects in properties.

- (1) **The high entropy effect** refers to the fact that when multiple elements are combined, they create a higher entropy than if only one element was present in the alloy. This means that these alloys have greater randomness and disorder compared to conventional single-component materials, which can lead to unique properties not found elsewhere. It is important to note that the degree of intimacy in the mixing of these elements is crucial in the manifestation of these high entropy effects [10].

- (2) **The sluggish diffusion effect** refers to the difficulty it is for atoms and molecules within an alloy to move due to their complex composition. This can lead to slower phase transformation rates, which, in turn, affects the properties of the material such as mechanical strength or corrosion resistance.
- (3) **The severe lattice-distortion effect** refers to the fact that because there are so many components in these alloys, each component can cause distortions or deformations of the crystalline structure (Figure. 1.5) which affects the overall structure of the material. This distortion is believed to be responsible for some of the unique properties of HEAs, such as high mechanical strength and low ductility at room temperature.
- (4) **The cocktail effect** is a figurative expression that describes how the combination of several materials together can create unique properties not found individually but instead created by this combination process itself. This is because the different components of an alloy interact with each other in ways that are difficult to predict, leading to unexpected and sometimes beneficial results [11].

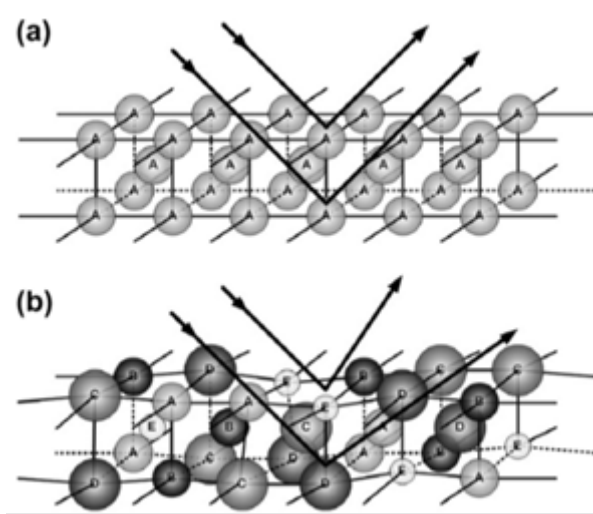


Figure 1.5: Schematic illustration of intrinsic lattice distortion effects on Bragg diffraction [12]: (a) perfect lattice with the same atoms; (b) distorted lattice with solid solutions of different-sized atoms, which are expected to randomly distribute in the crystal lattice according to a statistical average probability of occupancy. [13]

1.4 Applications

HEAs have received much attention in recent years due to their unique mechanical properties, which have been widely reviewed in the literature [5]. One of the key features of HEAs is their high strength and strain hardening ability [14]–[17], making them suitable for various structural applications. Additionally, HEAs have shown improved ductility, toughness, fatigue resistance, and high temperature strength compared to traditional

alloys [18]–[22], making them more resilient in demanding environments. Furthermore, the presence of multiple elements with different oxidation states in HEAs enhances their corrosion resistance [23]–[25], which can be further optimised by adjusting composition ratios or microstructure states [26]. These unique properties of HEAs make them promising candidates for a wide range of applications in various industries. Additionally, some HEA materials are biocompatible, making them suitable for use in medical implant devices such as stents or orthopaedic screws and plates [27], [28].

Finally, HEAs have been identified as promising candidates for various heterogeneous catalysis and electrocatalysis applications [6], [29]–[33]. The remarkable chemical and thermal stability of HEAs, along with their versatility to adjust the reactivity of active sites by adjusting the alloy composition, makes them ideal materials for the design of efficient catalysts [29], [30]. Reported applications of HEAs in catalytic and electrocatalytic reactions include ammonia decomposition [31], carbon oxide oxidation [34], reduction of carbon dioxide [35] and hydrogen and oxygen evolution reactions [36].

1.5 Bulk HEAs Synthesis

The first kind of HEAs made were mostly bulk solids, synthesised with shock methods. These protocols consist of rapid high-temperature heating of the precursor materials followed by fast cooling down. The high temperature (T) can promote uniform mixing of multiple elements, as indicated by the thermodynamic formula $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$. However, even at elevated temperature, phase separation can still occur during the long cooling process, ultimately resulting in heterogeneous structures [37]–[39]. Thus, to ensure uniform mixing of multiple elements into single-phase HEA, it is essential to combine high-temperature synthesis with a fast cooling rate, such as a fast quenching process.

1.6 Nanoscale HEAs Synthesis

In contrast to bulk HEAs, nanoscale HEAs, including HEA nanoparticles (NPs) and highly porous HEAs, exhibit a significantly increased surface area, making them highly promising for a wide range of catalytic applications [40]–[43]. To date, general synthetic strategies for HEA NPs catalysts can be categorised into four major categories, namely carbothermal, wet-chemistry solvothermal, and top-down methods. All of them will be described in details in this section.

1.6.1 Carbothermal Shock

High-temperature carbothermal shock (CTS) represents the first general method for the efficient and controllable synthesis of HEA nanoparticles with a single-phase structure and uniform dispersion [43]. This method involves a two-step process as shown in Figure 1.6a, where the metal salt precursors MCl_xH_y (M is Pt, Pd, Ni, Fe, Co, Au, Cu, or Sn,

among others) is loaded into a solution onto a conductive carbon support, such as carbon nanofibers. After drying, they are then flash heated at a temperature of approximately 2000 K and then rapidly cooled down. The duration of the shock is approximately 55 ms and ramp rates on the order of 10^5 K/s [44]–[46] as shown in Figure 1.6b. Despite being exposed to high temperatures that conventionally cause particle coarsening, the ultra-fast quenching allows the HEA NPs synthesised by CTS to have a narrow size distribution and are uniformly distributed throughout the carbon support [43]. High temperature, combined with the catalytic activities of the liquid metals, induces rapid particle fission and fusion events that result in uniform mixtures of multiple elements. The input electrical pulse parameters can be adjusted to produce phase-separated nanoparticles by reducing the cooling rate.

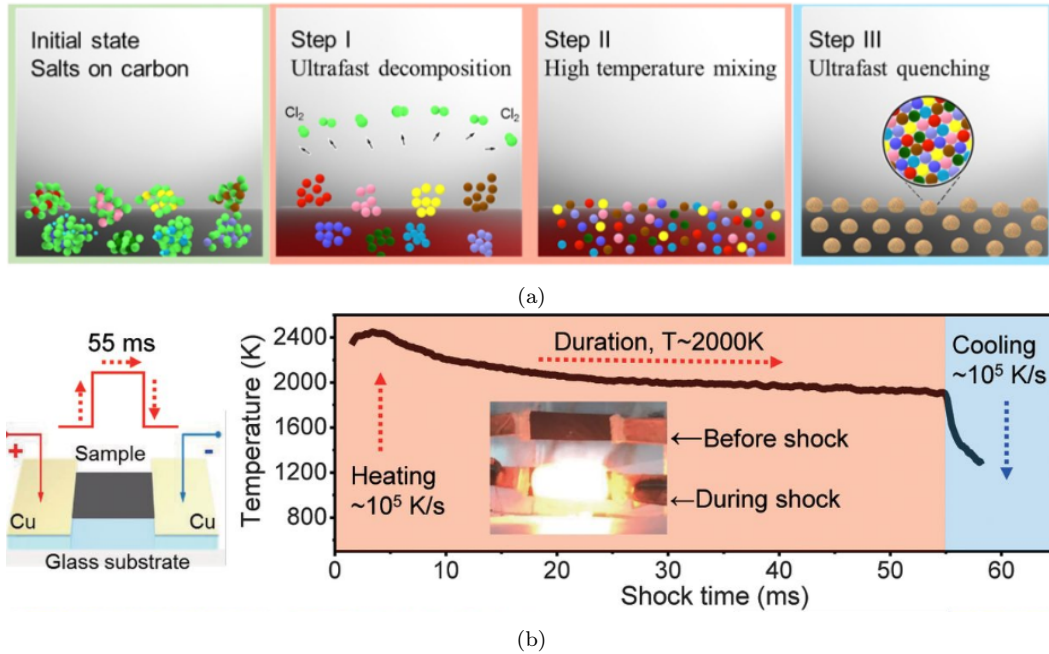


Figure 1.6: (a) Shock-type synthesis of HEA. (b) Sample preparation and the temporal evolution of temperature during a 55ms thermal shock [43].

1.6.2 Wet-Chemistry Methods

The wet-chemical approach is the most widely used method to synthesise HEA nanoparticles and nanocrystals, involving chemical reactions in the solution phase using precursors under appropriate experimental conditions without the need for complicated equipment. However, as a near-equilibrium approach, the wet-chemistry method exhibits some limitations for preparing homogeneous alloys with strongly immiscible elements, which can lead to phase separation and heterogeneity [47], [48]. In spite of this, wet-chemistry methods remain the most common approaches for the preparation of nanoparticles and nanocrystals. Therefore, for elemental combinations with slight immiscibility or good miscibility, preparing HEA nanoparticles by the wet-chemistry method shows superior features, that is, small size, precise morphology and uniform dispersion [32], [49]–[51].

1.6.3 Solvothermal synthesis

Solvothermal synthesis is defined as a chemical reaction that takes place in a solvent at a temperature higher than the boiling temperature of the solvent in a sealed vessel. For instance, Li *et al.* utilised a simple one-pot oil-phase synthesis method at atmospheric pressure to prepare PtNiFeCoCu nanoparticles (with a size of 3.4 nm) at around 220 °C [32]. In a similar study, Feng *et al.* produced ultra-small HEA nanoparticles (NiCoFePtRh) with an average size of 1.68 nm through chemical coreduction supported by carbon. The resulting ultra-small nanoparticles with high dispersion significantly improved the atom utilisation of noble metals [51].

1.6.4 Top-down Methods

In contrast to the above bottom-up methods, the top-down method refers to the synthesis of HEA catalysts by reducing bulk materials to nanoscale particles or high surface area materials [52]. Top-down methods, in general, are more scalable and simpler, but may lack precise control, as demonstrated in the bottom-up methods. For mechanical alloying, sputtering depositions, and dealloying, are widely used to synthesise highly porous or nanoparticle HEAs directly from bulk or thin-film samples. These methods are advantageous for producing highly porous HEA-based materials with elevated specific surface areas in an efficient and scalable manner.

1.6.4.1 Mechanical Alloying

Mechanical alloying exploits mechanical phenomena to initiate the alloying reaction. It involves solid-state reactions with no or minimal use of solvents. Pure metal powders are mixed and put into a high energy planetary ball miller (as shown in Figure 1.7) together with a grinding medium, usually stainless steel balls. Under the strong collision and agitation of steel balls, different metal powders undergo repeated cold welding, grinding, and rewelding processes [53]. This method avoids the need for a large number of metal salts and organic solvents typically used in traditional wet-chemical preparation, thereby reducing waste and avoiding the risk of chemical poisoning. The application of mechanical energy through methods such as extrusion, shear, and friction provides unique experimental conditions for chemical reactions at room temperature [54], [55]. As a result, mechanical alloying can achieve crystal structures that are not possible using traditional material preparation methods, making it an advantageous approach for the preparation of high entropy materials [35], [56].

For example, Lv *et al.* reported the synthesis of an AlCoCrTiZn HEA powder using mechanical alloying [57]. Using pure metal powders with the size of $\sim 40 \mu\text{m}$ as the precursor powders and n-heptane as the process inhibitor, the HEA powders are facilely prepared under the protection of an Ar atmosphere after ball milling for 60 h. These HEA powders are highly irregular in shape with a size of 0.5-10 μm , while the surface of the obtained powders is rough with abundant defects.

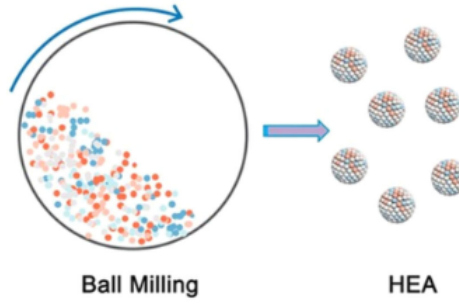


Figure 1.7: Schematic of the mechanical alloying process for the synthesis of HEAs [6]

1.6.4.2 Sputtering

The sputtering technique is frequently used in film preparation technologies to simplify the target preparation process. Adjusting the sputtering power in "multitarget sputtering" has been applied to prepare high entropy materials and obtain the required film. Using the sputtering technique, a range of multicomponent alloy systems have been successfully prepared.

Löffler *et al.* utilised combinatorial co-sputtering into an ionic liquid to prepare amorphous HEA nanoparticles (CrMnFeCoNi) with flexible size and composition [58]. They bombarded the element target with an Ar plasma and sputtered the metal atoms in the target into the ionic liquid rather than the substrates. These metallic atoms will then nucleate and grow in the ionic liquid to generate the corresponding HEA NPs as illustrated in Figure 1.8. The size of the nanoparticles could be adjusted by selecting a suitable ionic liquid, which served as a stabiliser and suspension medium due to its negligible vapour pressure. The composition of the HEA NPs is tunable by adjusting the sputtering flow of each of the primary elements. [58]

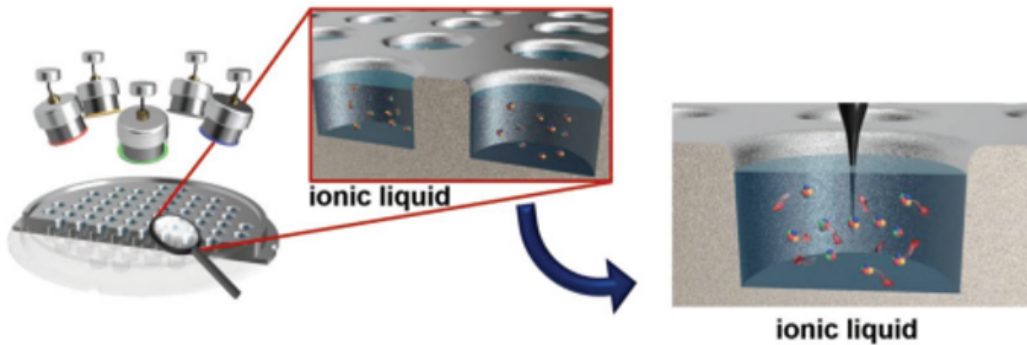


Figure 1.8: Synthesis of NPs by means of combinatorial co-sputtering into an ionic liquid, the different colors correspond to the different elements sputtered [58]

1.6.4.3 Spark Ablation

This synthesis method involves liquid-phase ethanol picosecond-pulsed laser ablation of CoCrFeMnNi HEA targets [59]. The process begins with a laser beam irradiating the surface of a bulk HEA target (Figure 1.9 a), forming a plume. This plume is then cooled and the ablated species are condensed, leading to the formation of a cavitation bubble

(Figure 1.9 b). The ablated species mixed with the liquid vapour inside the bubble, and as the bubble collapses, the condensed species is released as nanoparticles into the liquid (Figure 1.9 c).

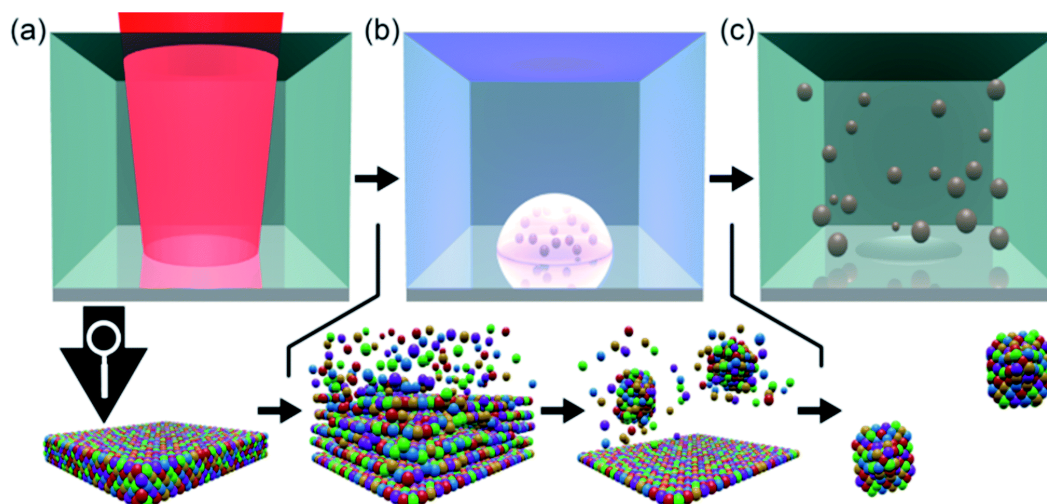


Figure 1.9: Schematic representation of the laser-based synthesis of HEA-NPs. (a) Ultrashort-pulsed laser irradiation of the bulk HEA. (b) The atomisation/ionisation of the bulk causing the formation of a plume, and subsequent nucleation and condensation of the ablated matter in the vapor phase of the liquid. (c) The colloidal high entropy alloy nanoparticles electrostatically stabilised in ethanol. [59]

1.6.4.4 Dealloying

Dealloying refers to the selective leaching of one or more components from a solid solution alloy or compound to produce a residual nanoporous structure. It is recognised as a facile method for the fabrication of bicontinuous nanoporous metals of tunable sizes [60]. Traditionally, dealloying is used mainly to prepare binary or ternary alloys, while multicomponent alloys are rarely involved due to the huge differences between metal atoms [61]–[63].

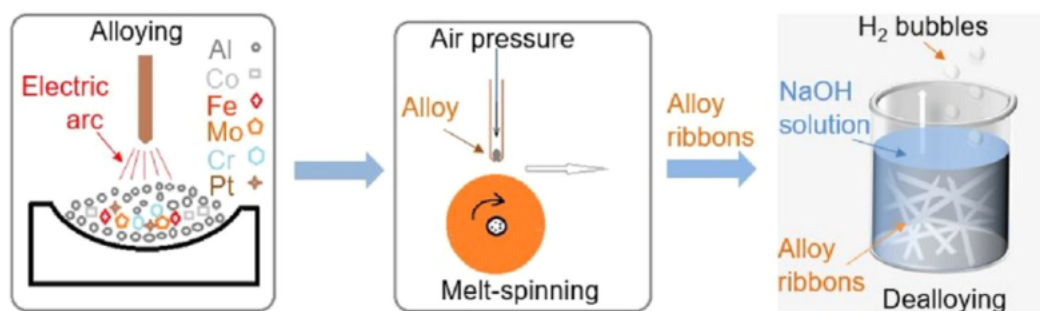


Figure 1.10: The pure metals compounds are melt into a HEA. This last one is then was prepared into ribbons by melt-spinning. The ribbons were dealloyed in NaOH at room temperature for 2 h until no obvious bubbles were generated. [64]

Jin *et al.* have successfully prepared highly porous HEA catalysts with a dealloying process illustrated in Figure 1.10. Precursor alloys consisting of AlCoFeMoCrPt were initially prepared by melting pure metals in an arc-melting furnace. The alloy ribbons

were fabricated using melt spinning, which involves casting molten metal by jetting it onto a rotating wheel or drum, which is cooled internally. The use of a NaOH solution for simple dealloying resulted in the efficient production of a hierarchical nanoporous HEA [64].

In addition to the methods listed above, other traditional nano alloy synthesis strategies such as microwave heating [65], solid-state reduction of molten salt [66], [67], fast-moving bed pyrolysis [68] and pulse laser [69], [70] have certain potential in the preparation of high entropy materials and are also worth exploring.

1.7 Emerging Bottom-up HEAs Fabrication Method Based on Spray Drying

Porosity is critical for catalytic applications as it maximises active surface area and optimises mass transport [71], [72]. Therefore, the fabrication of porous HEAs is particularly desirable. However, processing and shaping HEAs into architected materials relevant for catalytic applications remains an important challenge in the field. The realisation of porous HEAs with an elevated specific surface area is highly desirable, as has been demonstrated for other families of materials in the past decades [73]. Nevertheless, the fabrication of porous HEAs is currently arduous with the top-down and bottom-up approaches available.

To address these challenges, two methods based on spray drying have been developed for the synthesis of porous HEAs: (i) spray pyrolysis, which results in the formation of hollow nanoparticles. (ii) polymer templated synthesis that yields ordered macro and mesoporous nanoparticles with tunable porosity and high specific surface area.

1.7.1 Spray Pyrolysis

This synthesis method involves creating a stream of droplets as small as 1 μm in diameter containing metal chloride salts homogeneously dissolved in ethanol and citric acid, which serves as a blowing agent. Droplets are then carried by argon through the heated zone of a tubular furnace with a flow rate of 5 L min^{-1} . After being heated (below 100 $^{\circ}\text{C}$), ethanol evaporates rapidly from the droplet, resulting in the rapid formation of solid condensed particles containing uniformly mixed metal precursors and citric acid. When the temperature further increases to ~ 300 $^{\circ}\text{C}$, citric acid rapidly decomposes to produce CO_x and H_2O , which puffs the particle into a hollow structure [74]. As the temperature increases further to 1080 $^{\circ}\text{C}$, the metal chlorides decompose into metals, which are alloyed into one phase on the shell to complete the synthesis of hollow HEA nanoparticles. The whole process takes place in less than 1 s, a schematic of the process is provided in Figure 1.11. This synthesis method leads to the production of hollow HEA-NPs; the hollow structure enabling a high active sites per mass ratio.

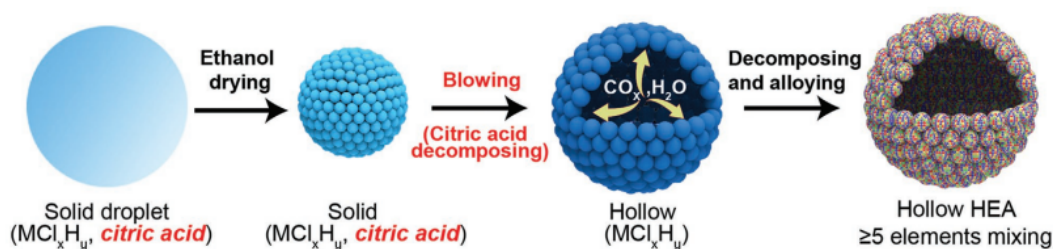


Figure 1.11: Schematic of the droplet-to-particle evolution in the formation of hollow HEA nanoparticles [74]

1.7.2 Polymer Templated Aerosol Synthesis

As was said previously, a significant challenge in the field of HEA catalytic applications is to process and shape HEA into architected materials [73]. To achieve optimal matter transport and maximise active surface area, porosity must be introduced at various scales [71], [72]. A crucial aspect for the application of HEA-based materials in this field is the development of feasible fabrication methods to shape them into intricate architectures without demixing or collapse. However, it is a difficult task with the conventional approaches described above. In addition, conventional methods described in Sections 1.5 and 1.6 often require the use of toxic solvents, high temperatures, or complex apparatus, which limit their practicality and scalability.

To overcome these challenges, the Faustini group has developed a soft-chemistry method for the synthesis of HEA-based porous materials [75]. This method enables the synthesis of macro and mesoporous HEA nanoparticles. The method is inspired by the templated sol-gel synthesis of porous metal oxides by spray-drying [76]–[79], which is a waste-free, environmentally-friendly, and easily scalable technique. This method has been particularly successful in synthesising heterogeneous powdery oxide catalysts with precise control over texture, composition, and surface properties [80].

With high surface area, thermal stability, and excellent control of texture, composition, and surface properties, the method is scalable and can be performed under mild conditions, making it an attractive option for large-scale production of porous HEAs for catalytic applications.

This method will be described in greater details, as it is the primary technique used for synthesising the samples analysed in this master thesis.

1.7.2.1 Synthesis of Mesoporous or Macroporous HEAs

The preparation of Mesoporous or Macroporous HEA NPs follows almost the same protocol. The choice of the templating particles is the key step in the resulting HEA structure. To obtain mesoporous HEA, polystyrene (PS) beads with an average size of approximately 30 nm are used as the templating agent. On the other hand, for the fabrication of Macroporous HEA, larger poly(methyl methacrylate) (PMMA) beads with

a diameter of around 300 nm are employed as the templating agent.

This method is straightforward in terms of operation, but involves complex mechanisms. (Figure 1.12 provides schematic illustrations of the process). First, the metal chloride precursors of five noble metals, namely $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$, PtCl_4 , and PdCl_2 , are dissolved in almost equimolar concentrations in deionised water. This mixture is then combined with an aqueous suspension of polymer latex, creating a latex-to-metal ratio of 50 wt %. One of the two different types of latex particles is employed as templating agents. Next, a spray-drying process is used to produce an aerosol of droplets containing latex particles and dissolved metal chloride salts. During water evaporation, the droplets are transformed into hybrid spheroidal microparticles, comprising organic latex beads embedded in an inorganic metal chloride salt matrix.

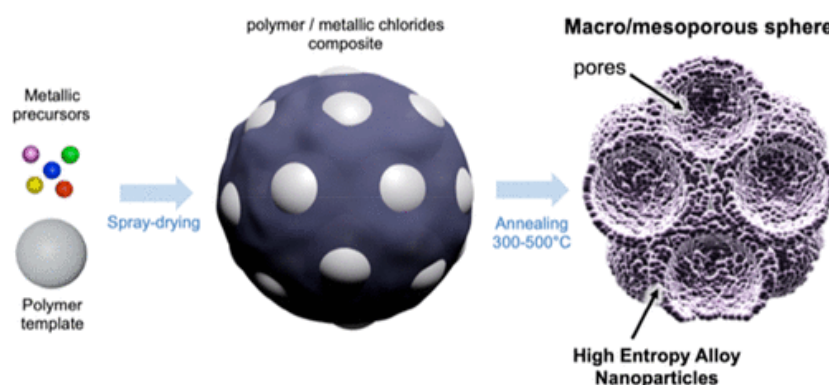


Figure 1.12: Scheme of the fabrication process of porous HEA-based particles by aerosol synthesis followed by thermal annealing [75].

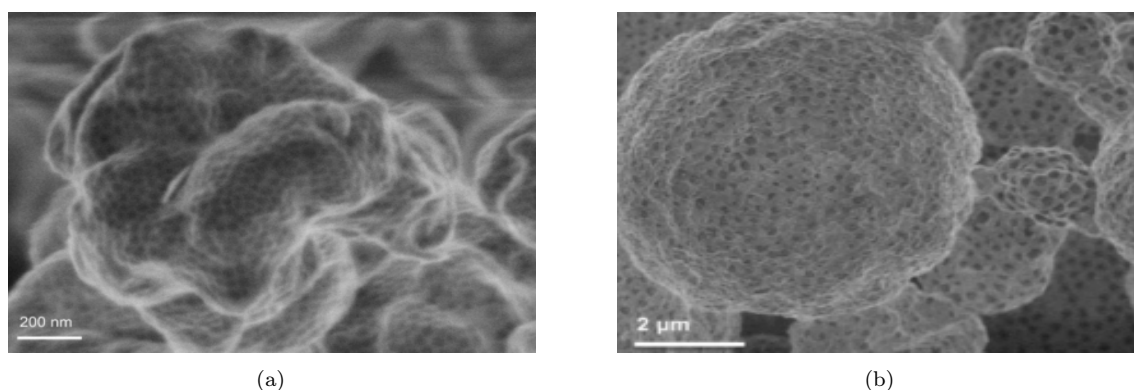


Figure 1.13: SEM pictures of the as-sprayed (a) PS-templated and, (b) PMMA-templated pristine powder. [75]

The resulting microparticles are thermally treated in Ar at 500 °C for 5 mins. During this treatment, the thermal decomposition of the polymer releases calibrated pores and helps to convert the chlorides into a Pt-Pd-Ru-It-Rh metal alloy (HEA). The resulting nanostructured particles were mesoporous or macroporous with pore size dependent on

the diameter of the polymer template beads used (Figure 1.13).

The crucial step in the process is the thermal treatment of the resulting hybrid spheroidal microparticles under an inert atmosphere of Ar at 500 °C. The PS beads-based particles results in the production of polydisperse mesoporous microparticles with an irregular "deflated" shape and pore size ranging from approximately 20-30 nm. A STEM analysis revealed that the pore walls were composed of crystalline nanoparticles of around 4-5 nm (Figures 1.14A, B, and C). Whereas, upon annealing the hybrid PMMA-templated particles under inert gas (Ar) at 500 °C, macroporous particles with ordered pores of approximately 200 nm were obtained (Figure 1.14 D and E).

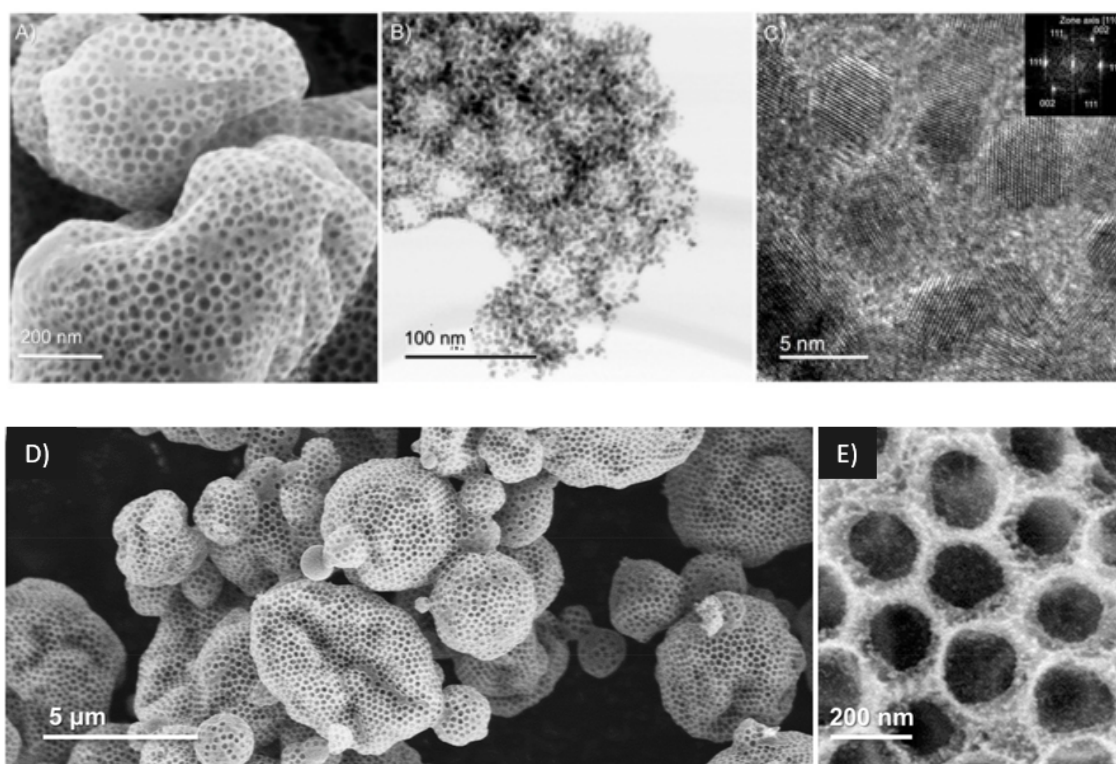


Figure 1.14: (A) SEM pictures of the mesoporous HEA-based particles surface. (B) STEM and (C) high-resolution STEM images. (D, E) SEM images of the macroporous HEA particles surface. [75]

The X-ray diffraction pattern (XRD) of the mesoporous sample corresponded to a face-centered cubic (fcc) metal phase (XRD in Figure 1.15A). The presence of a single crystalline phase suggested the formation of a homogeneous solid solution and hence the formation of a high entropy alloy. The pores of the macroporous sample formed a hexagonal close-packed (hcp) structure (Figure 1.14E), which was induced by the self-assembly of the PMMA latex beads in an hcp structure during water evaporation during the spray-drying process. XRD patterns corresponding to a single fcc phase are observed for particles annealed at 300 °C and above (Figure 1.15B).

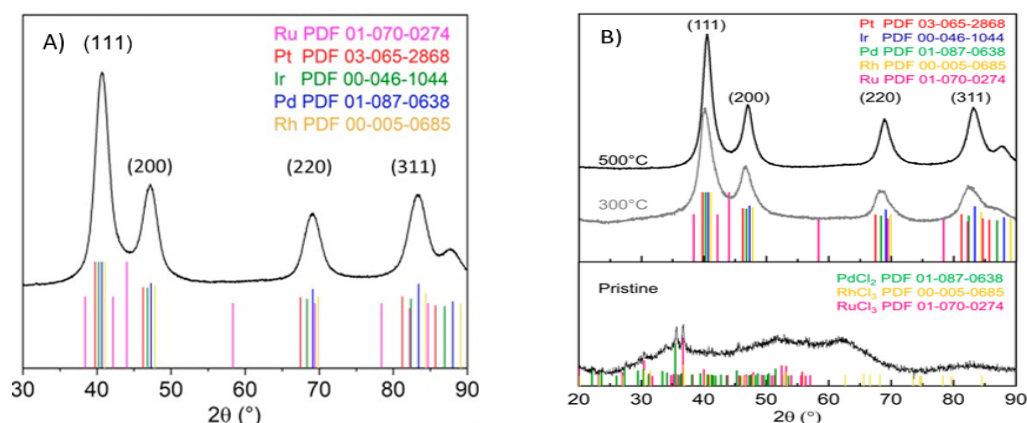


Figure 1.15: (A) X-ray diffraction pattern, which corresponds to a face centered cubic (fcc) structure of the mesoporous sample. (B) XRD pattern of the as-sprayed particles (pristine) and of the particles annealed at 300 and 500 °C under Ar for the macroporous sample. [75]

The elemental mapping obtained through STEM-EDX analysis for both the mesoporous (Figure 1.16 A-E) and the macroporous (Figure 1.16 F-J) suggested the homogeneous distribution of all elements within the porous structure, indicating the successful formation of a HEA. While those observations indicated a certain degree of homogeneity at the bulk level in both the mesoporous and macroporous samples, they serve only as an initial indicator; further atomic-scale analysis is necessary to definitively confirm the homogeneity of the high entropy alloy structure at the atomic level. It is an ambition of this master thesis work to explore new ways to characterise this level of homogeneity (see below).

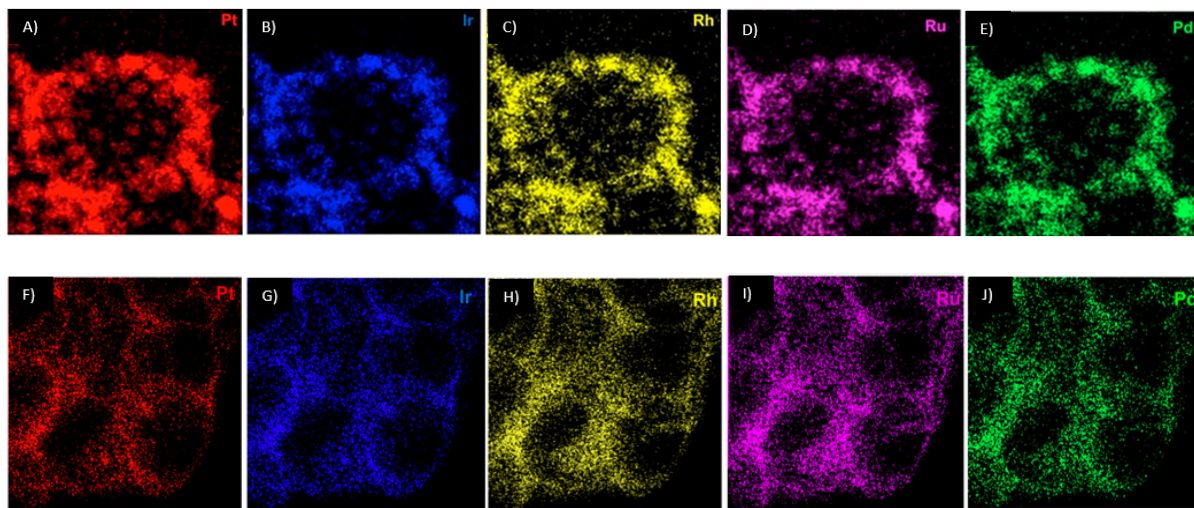


Figure 1.16: Elemental mapping (STEM-EDX) showing the distribution of Pt (red), Ir (blue), Rh (yellow), Ru (pink), and Pd (green) for (A-E) the mesoporous and (F-J) macroporous sample. [75]

1.8 Characterisation Techniques for HEAs

1.8.1 Conventional characterisation Methods

HEAs are usually made up of more than five elements, so it is significant to identify the nature, concentrations, and distribution of all elements. Inductively coupled plasma-optical emission spectrometry (ICP-OES), inductively coupled plasma atomic emission spectrometry (ICP-AES), or inductively coupled plasma mass spectrometry (ICP-MS) are widely used for quantitative analysis of the composition. It is noteworthy that ICP provides information for the bulk of the sample, so we can obtain the types and concentrations of all elements in HEAs [81]. ICP uses an inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element.

EDX, or Energy Dispersive X-ray Spectroscopy, is an additional characterisation technique commonly used to determine the elemental composition within a specific region of interest [82]. Linear scanning EDX spectrum and EDX mapping are frequently used to visually demonstrate the uniform distribution of all elements in high entropy alloys [83].

X-ray Photoelectron Spectroscopy (XPS) can measure surface composition and provide information on the chemical state of surface elements in HEAs [84]. By employing etching or sputtering techniques, the chemical composition of HEAs can be explored at different depths. For a more precise determination of the chemical state and coordination environment, X-ray absorption spectroscopy (XAS), including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), is widely utilised [85]. All of those methods are a subset of absorption spectroscopy which measure the absorption of radiation, as a function of frequency or wavelength, due to its interaction with a sample.

XANES provides information about the valence state of the elements, while EXAFS reveals details such as coordination atoms, coordination number, and bond length [86], [87]. These techniques enable the investigation of the atomic and local coordination environment of each element in HEAs, offering insights into their mixed state, as well as potential short-range or local ordering phenomena within HEAs [88].

To identify the microstructure of HEAs, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), scanning electron microscope (SEM), and transmission electron microscopy (TEM) are usually used to observe the surface morphology, particle size, and size distribution of HEAs [43]. These methods are microscopy techniques in which a beam of electrons is transmitted through a specimen to form an image offering insights into the surface morphology, particle size, size distribution and element distribution of HEAs. Specifically, Annular Dark-Field STEM (ADF-STEM) is highly effective in intuitively presenting the atomic structure of HEAs, clearly indicating the positions of different atoms. High Resolution Transmission Electron Microscope (HRTEM) is frequently utilised to observe lattice distortion and atom vacancies, which are typical characteristics of HEAs [89], [90].

As seen in the previous section, De Marco *et al.* used high resolution elemental mapping to demonstrate the uniform element distribution within the nanoparticles to further confirm the high entropy mixing without obvious phase or element segregations (Figure 1.14). But there are numerous other examples of the application of these electron-based characterisation techniques [30], [38], [51], [91].

Diffraction technology, particularly XRD, is extensively used in the study of crystal structures of HEAs [92]. This technique enables rapid determination of factors such as grain size, lattice parameters, and crystallinity in HEAs. XRD peaks can often shift toward either positive or negative positions relative to pure metal due to lattice distortions in HEAs. The degree of lattice strain can also be calculated based on the diffraction data [93], [94]. However, potential sensitivity limitations can make it challenging to identify possible impurity peaks. To address this issue, synchrotron X-ray-based techniques, which offer high light intensity, can be employed. These techniques can reveal the overall phase structure and potential immiscible phases and impurities with greater precision [88].

The case of De Marco *et al.* using XRD on nanoparticles to discern a distinct single phase face-centred cubic structure (Figure 1.15), as mentioned in the previous section, is a fitting example of this approach.

1.8.2 In Situ characterisations Methods

In addition, in situ characterisations techniques are typically carried out under real time reaction conditions to monitor dynamic changes. Tools such as in situ Transmission Electron Microscopy and in situ X-ray Diffraction are frequently employed to scrutinise the growth process and disclose the structural evolution of HEAs throughout their fabrication [90], [95], [96]. When HEA is synthesised with FeCoNiIrRu, researchers have been able to determine the phase transition from Co nanoparticles to face-centred cubic HEA (fcc) structured nanoparticles during the pyrolysis process [95].

Moreover, in situ XPS and XAS are often employed to track alterations in the chemical valence of HEAs throughout their utilisation [51], [97]. These real-time or in situ characterisations provide a more profound understanding of the structural modifications in HEAs under live conditions.

In addition to synthesis mechanisms, environmental TEM was used to examine the oxidation behaviour of HEA nanoparticles ($\text{Fe}_{0.28}\text{Co}_{0.21}\text{Ni}_{0.20}\text{Cu}_{0.08}\text{Pt}_{0.23}$). This process revealed that elements such as Fe, Co, Ni, and Cu diffused outward to form cavities, while non-reactive Pt remained in the core. The same group also studied the reduction behaviour of oxidised HEA nanoparticles in an H_2 environment at 400 °C. Copper oxide was fully reduced to copper nanoparticles, while Fe, Co, and Ni remained in their oxide phases, resulting in the separation of the HEA core and oxide shell (Figure 1.17) [98], [99].

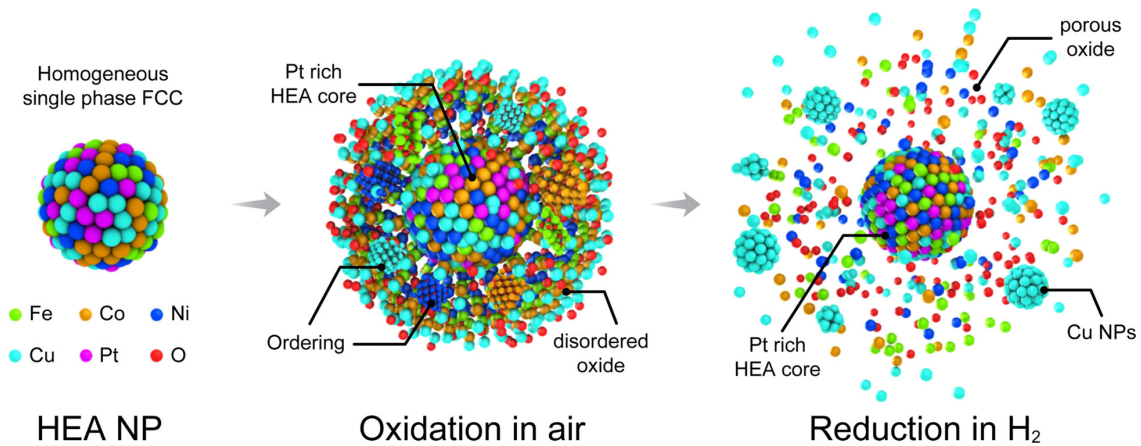


Figure 1.17: Schematic showing the reduction of oxidised HEA NPs at 400 °C. The oxidised HEA NPs have Pt rich HEA core with disordered oxide layer containing Fe, Co, Ni, Cu. During reduction in H₂, HEA core shrinks due to transition metals outward diffusion, with expansion of the oxide and segregation of oxidised Cu into reduced Cu NPs [99]

1.8.3 Atomic Scale Characterisation

The characterisation techniques outlined in Sections 1.8.1 and 1.8.2 effectively illuminate the alloy's mixing qualities, dynamic changes or oxidation behaviour; which is critical for alloy performance. However, these techniques do not provide direct atomic-scale evidence of inter-element mixing, a detail that remains elusive.

In this context, time-of-flight secondary ion mass spectroscopy (ToF-SIMS) is primed to solve some of the remaining challenges. This analysis uses a pulsed primary ion beam (for example, Bi⁵⁺) to bombard the sample surface and subsequently analyses the secondary ions emitted by high-resolution time-of-flight mass spectrometry. A comprehensive discussion of the ToF-SIMS method is provided in the next chapter.

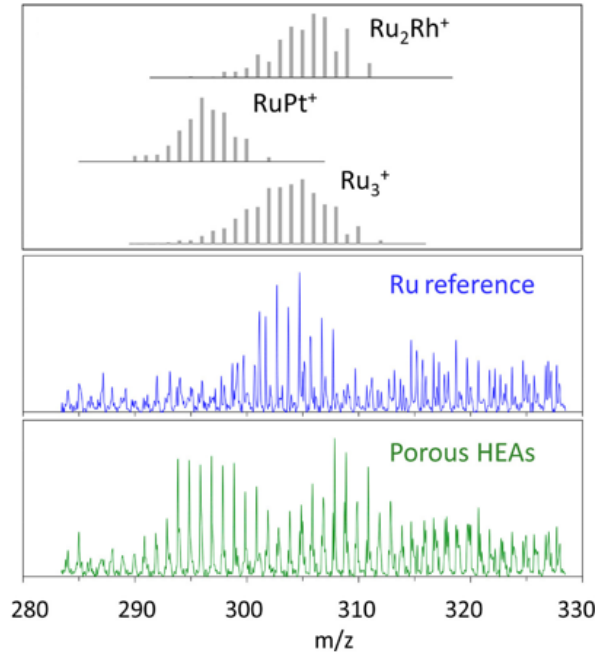


Figure 1.18: Part of the ToF-SIMS spectrum obtained on the macro- and mesoporous HEA-based particles (green) and on a reference Ru-based macroporous reference particle (blue). Histograms (gray) represent the theoretical isotopic distribution for Ru_3^+ , RuPt^+ , and Ru_2Rh^+ . [75]

The first example of the use of ToF-SIMS to characterise HEA was reported in the Faustini group study in 2022, in collaboration with the IMCN (UCLouvain), in charge of the ToF-SIMS measurements [75]. Analysis of a pure Ru reference sample allowed the detection of Ru_x^+ (with $x = \{1, 2, 3, 4\}$) ions, as expected. The natural isotopic distribution of Ru and the high mass resolution of the spectra enabled an unambiguous assignment of the nature of each ion. On the other hand, in HEA-based particles, some of the detected clusters are not attributable to monometallic clusters but rather to mixed metallic clusters, such as RuPd^+ , RuPt^+ , Ru_2Pt^+ , RuIr^+ , Ru_2Ir^+ , RuRhPt^+ , and others. However, in some regions of the spectra, the molecular signature of certain mixed clusters can be identified unambiguously. For example, Figure 1.18 shows a representative example of RuPt^+ and Ru_2Rh^+ .

These results provide first evidence of mixing of Ru-Pd and Ru-Rh, not only at the nanoscale as observed through STEM-EDX but also at the atomic level. In some cases, the theoretical isotopic distributions of these possible mixed clusters overlap, making it impossible to assign them definitively. Further efforts are needed to exploit the rich information gained from ToF-SIMS on these complex matrices.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has emerged as a powerful technique that has found widespread application in the characterisation of diverse materials, ranging from metals [100] to semiconductors [101], polymers [102], solid catalyst [103]–[106] and biomaterials [107]. Very recently, ToF-SIMS has also been used to study the surface properties of nano high entropy alloys [75]. In this section, the principles and key features of ToF-SIMS are covered.

2.1 Principle

ToF-SIMS can provide detailed chemical information about the top layers of a sample. The technique involves bombarding the sample surface with a pulsed primary ion beam under ultra-high vacuum conditions [108], generating secondary particles that include neutral atoms, molecular fragments, intact molecules, or ions that carry chemical information about the surface. The sputtering of material from the surface is the result of collision cascades initiated by primary ions striking the uppermost layer of the sample.

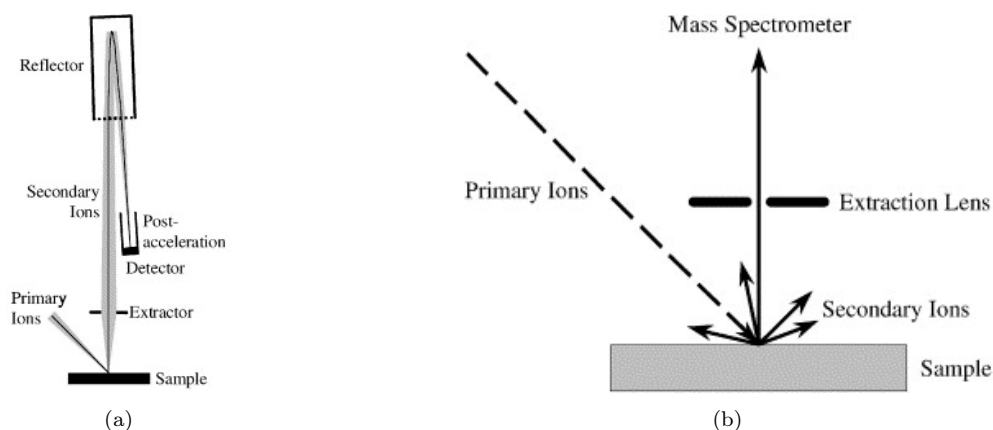


Figure 2.1: (a) A schematic ToF-SIMS instrument. (b) The principle of secondary ion mass spectrometry: On the sample surface, an energy-rich primary ion beam generates secondary ions, which are separated and detected with a mass spectrometer. [109]

Depending on the polarity of an applied electric field, positive or negative ions are extracted and then analysed in a Time of Flight (ToF) analyser [110]. The ToF analyser accelerates the secondary ions to a given potential so that all ions have the same kinetic energy. If all secondary ions have the same kinetic energy, the flight time of each ion is proportional to the square root of the mass to charge ratio (m/z) [110], [111] as shown in the equation 2.1. ToF SIMS measurements provide a spatial resolution of a few hundred nanometres and have a depth resolution of about 1 nm [112].

$$t = L \sqrt{\frac{m}{2zV}} \quad [\text{s}] \quad (2.1)$$

Where t is the measured flight time [s], V is the acceleration potential [V], z is the charge of the ion [C], and L is the flight path [m].

Despite the seemingly destructive nature of the technique, the dose of primary ions that impinge on the surface in routine analysis is very low, resulting in less than 1% of the atoms from the top layer being hit. The chance of a given location on the surface being impacted twice is close to zero, making the spectral information obtained from an undamaged surface [112]. The ToF analyser is capable of analysing the complete range of secondary ions, making it useful for both organic and inorganic samples.

As a result of the sputtering process, ions of the same mass have a distribution of initial energies, causing them to enter the tube with slightly different velocities. The reflectron, also known as the ion mirror, is used to compensate for this difference. It consists of a series of rings with a gradually increasing retarding field. The more energetic ions will penetrate further into the mirror before being reflected, ensuring that all ions of the same mass arrive at the detector simultaneously. One cycle of the ToF-SIMS instrument involves the primary ion beam pulsing, extraction, and charge compensation sequences, which occur within a small time window. The heaviest ion must reach the detector before the system starts a new cycle. ToF-SIMS is a costly analytical technique, primarily due to the requirement for a ultra high vacuum in the range of 10^{-9} mbar.

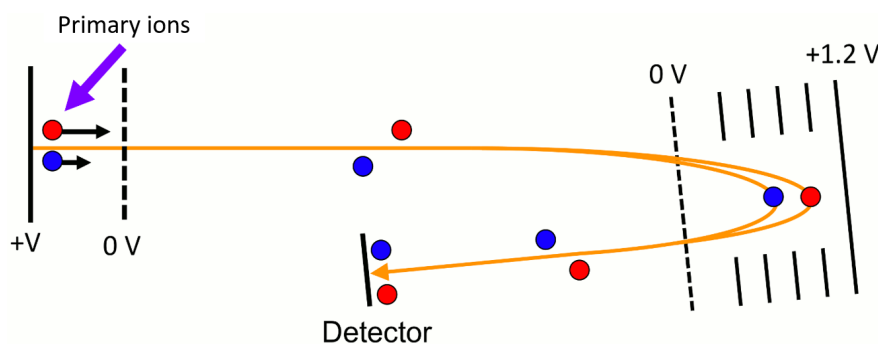


Figure 2.2: Schematic of a reflectron. The higher energy ion (red) takes a longer path but arrives at the detector at the same time as the lower energy ion (blue) of the same mass. Adapted from [113]

2.2 Modes of analysis

Depending on the type of sample and the desired information, various types of measurement and data acquisition can be performed using ToF-SIMS. In this work, only mass spectrometry will be conducted.

2.2.1 Mass Spectrometry

The most basic measurement possible by ToF-SIMS is called "Static measurement", as well known as "static SIMS". It consists of characterising a region ranging from $20 \times 20 \mu\text{m}^2$ to $500 \times 500 \mu\text{m}^2$ of the extreme surface of a material. The primary ion beam then strikes the sample at random points in the area of interest. To prevent surface damage, the dose of primary ions must be below the "static limit" of 10^{13} ions/ cm^2 , which is critical to avoiding decreases in sensitivity and preventing depth profiling [114]. The sample is bombarded with a short-time primary-ion pulse with typical lengths between several hundred picoseconds and a few nanoseconds. This is repeated every few hundred microseconds, resulting in a duty cycle of typically 10^{-5} s. The outcome is a spectrum showing all secondary ions as shown in Figure 2.3b.

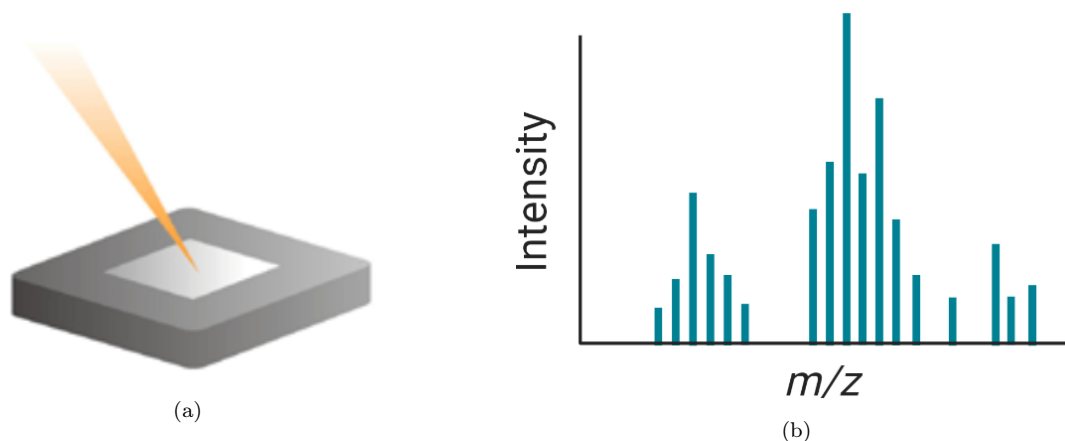


Figure 2.3: (a) Mass spectrometry acquisition schematic [115]. (b) Example resulting mass spectrum.

2.2.2 2D surface imaging

In this operational mode, the ion beam scans across the surface of the sample in small patches, and each patch is briefly analysed. The resulting data can be combined to generate a chemical map of the surface. Each pixel in the image corresponds to the intensity of a peak associated with a particular compound of interest as shown in Figure 2.4b. The colour scale is employed to display the number of ion counts detected from each pixel.

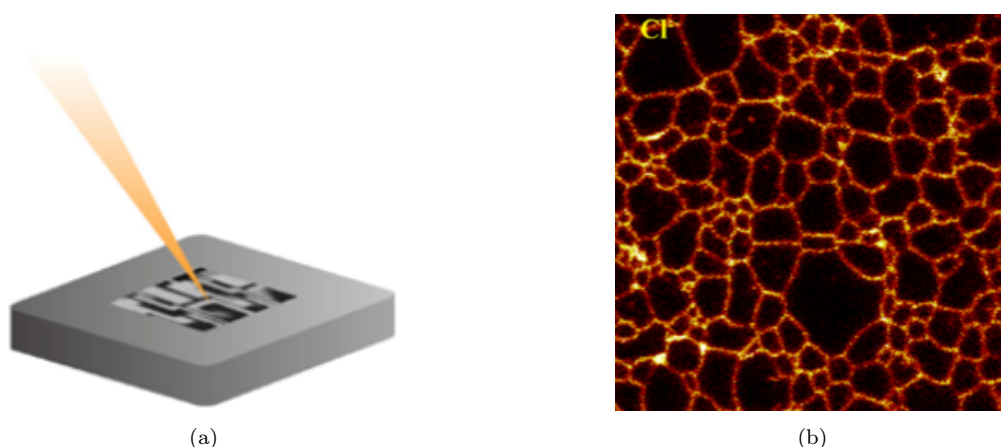


Figure 2.4: (a) Surface imaging schematic [115]. (b) Example of ToF SIMS 2D imaging of Cl^- negative ion from a Polycrystalline cadmium telluride (CdTe) thin-film [116].

2.2.3 Depth profiling

ToF-SIMS instruments are equipped with a primary ion source optimised for surface imaging analysis, typically ionised clusters of bismuth atoms. However, they also often have a second ion source, such as Cs^+ , O_2^+ or Ar_n^+ for ion sputtering to perform depth profiling. In dual-beam mode, the sputtering and analysis phases are alternated, and the signal intensities of selected molecular ions are measured as functions of sputter time, reflecting intensities versus sample depth. This allows for the determination of the location of molecules within the sample. Figure 2.5b provides an illustration of the analysis of passive films in HEA by measuring various types of oxides at different depths of the alloy. While the dual-beam experiment allows for separately optimising the analysis and sputtering processes, a disadvantage is that the material sputtered away during the sputtering phase may not be used for secondary ion detection. This method is termed "dynamic SIMS," in contrast to "static SIMS," which assumes that the surface is not damaged by the ion beam.

In molecular depth profiling, the subsurface damages induced by the impact of the ion beam are significantly reduced by the introduction of clusters such as Ar_x^+ in SIMS, preserving the molecular identity of molecules in the sample. This technique uses two ion beams alternately to analyse the surface and dig into the sample layer by layer in complex organic and biological samples.

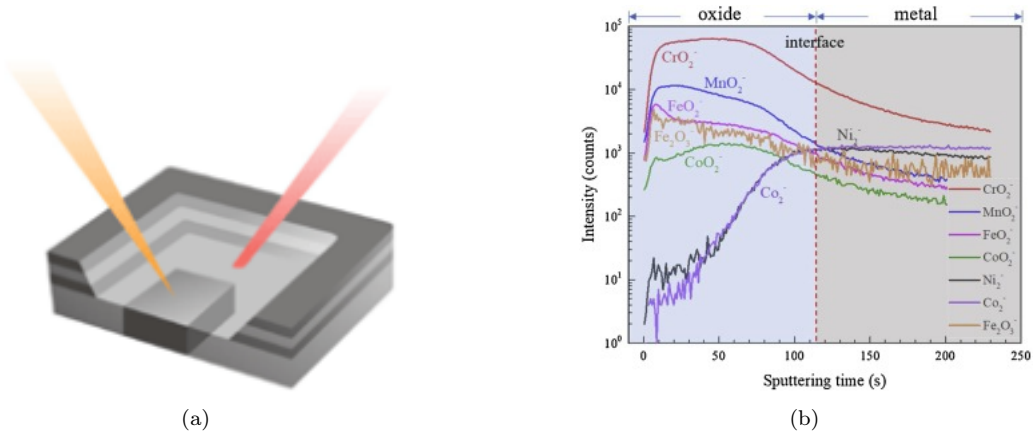


Figure 2.5: (a) Depth profiling schematic, the orange beam is the analytical beam and the red one is the sputtering beam [115]. (b) Example of ToF-SIMS depth profiles of the passive film pre-formed on CoCrFeMnNi HEA [117].

2.2.4 3D analysis

2D ion images can be acquired at different sputtering times, resulting in 3D representations of the sample. A 3D reconstruction can be achieved by combining multiple 2D images at different depths. This is done by combining two ion beams; one ion beam digs the surface and another beam maps the 2D distribution of ions; a single beam can also be used for both tasks. The resulting analysis is a complete 3D map of the analysed sample. This approach is useful in visualising the position, composition, and shape of features and defects in the sample. Figure 2.6 shows an example of ToF-SIMS 3D imaging to map the distribution and localisation of biomolecular species in the *Xenopus laevis* oocyte using this single-beam approach.

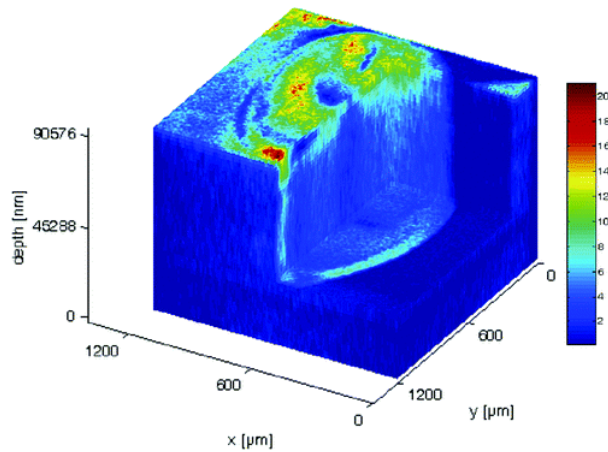


Figure 2.6: 3D biochemical image of freeze-dried oocyte, showing the distribution of the combined signal from amino acid fragments attributable to proteins [118].

2.3 Cluster ion beam

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has faced challenges in the analysis of organic systems, as atomic primary ion beams such as Ar^+ often result in low secondary ion yields and beam-induced damage effects. To mitigate these issues, cluster ion beams like Au_n^+ , Bi_n^+ , C_{60}^+ , Ar_n^+ have been used. These cluster beams distribute the energy among the atoms in the cluster, leading to a significant reduction in penetration depth and an increase in sputtering yield [112].

Conversely, atomic beams carrying the same overall energy penetrate deeper into the material as their atomic mass increases. Garrison et al. [119] have conducted a simulation of three cluster beams of Ar_3 , C_{60} , and Ar_{872} with the same energy of 20 keV. The results are represented in Figure 2.7.

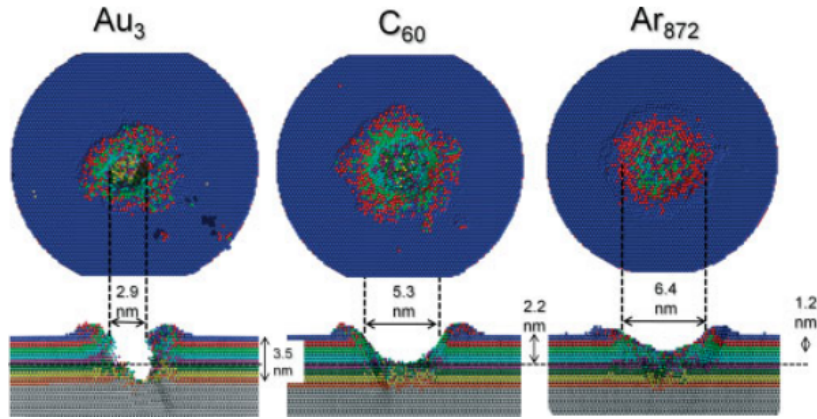


Figure 2.7: Top and cross-sectional side views of typical craters created by impact of 20 keV- Au_3 , C_{60} and Ar_{872} at normal incidence at a flat $\text{Ag}(111)$ surface at time of 30 ps. Color scheme depicts original location of atoms in a given layer. The cross-sectional view is 1.5 nm wide and is centered along the projectile impact point. [119]

Figure 2.7 shows that the shape and size of craters formed on a flat surface depend on the type of projectile used. The Au_3 cluster creates an elongated deep crater with a small opening, depositing a significant portion of its primary kinetic energy below the depth of the crater. This energy does not contribute to sputtering but leads to considerable interlayer mixing. In contrast, the C_{60} cluster forms a shallower and more azimuthally isotropic crater with a larger opening diameter. The shallowest and most laterally extended crater is formed by the Ar_{872} projectile.

Projectile-induced damage is well localised for C_{60} and Ar_{872} clusters, as the altered crystal volume is limited to a thin zone near the crater walls. This difference in the shapes of the crater is the result of the distinct initial conditions of the penetrating clusters. The gold atoms in Au_3 have a high kinetic energy and are heavier than the silver atoms, causing them to travel deeper into the sample and create disruption over a significant depth. This leads to an elongated crater shape and lower sputtering yield compared to C_{60} or Ar_{872} impacts.

The use of cluster-ion beams instead of atomic-ion beams also leads to lower fragmentation and higher ion yield. For example, the ion yields for Bi_5^+ clusters can increase by a factor of 100 to 1000 compared to their atomic equivalent Bi^+ . Moreover, cluster ion beams enable the sputtering of larger mass fragments, up to 10-12 kDa [112], [120].

The choice of primary ions can influence the fragmentation of the sample. Significant mixing caused by the Au_3 cluster results in deeper fragmentation and consequently smaller detected ions. The larger number of atoms in the C_{60} beam facilitates a more effective distribution of kinetic energy across the sample surface, leading to reduced disturbance within the layers and a subsequent decrease in fragmentation. This effect is even more pronounced for and Ar_{872}

In this work, four primary cluster ion beams have been used, specifically Bi_1^+ , Bi_3^+ , Bi_3^{++} , and Bi_5^+ . With an energy per atom of, respectively, 30, 10, 20 and 6 keV.

2.4 Data Treatment of ToF-SIMS Mass Spectra

ToF-SIMS mass spectra are highly informative because they allow for the simultaneous detection of an essentially unlimited range of masses. Both positive and negative secondary ion mass spectra can be obtained from ToF-SIMS, which allows for a more complete analysis of the sample composition. Positive spectra reveal information about cations, while negative spectra provide information about anions.

2.4.1 Quantification

ToF-SIMS analysis aims to quantitatively evaluate the mass spectra, by deducing the abundance of the secondary ion species and ultimately the concentration of the respective element or molecule in the target. However, only elemental or isotopic ratios can be determined in SIMS, and absolute concentrations cannot be obtained due to a lack of knowledge of sputter volumes, absolute ion yields, instrument transmission and detection efficiencies. For a quantitative analysis with ToF-SIMS, relative sensitivity must be determined. Therefore, carefully selected standards have to be analysed. Finally, the ionisation probability is strongly dependent on the charging state of the respective particle within the sample, that is, its chemical environment. This characteristic, known as the “matrix effect”, complicates the proper quantification of SIMS results.

2.4.2 Principal Component Analysis

The data interpretation challenge can be addressed using Principal Component Analysis (PCA). PCA is a well-established technique in multivariate data analysis, known for its robust statistical foundations [121]–[123]. Acting as a variable reduction tool, PCA is especially helpful when dealing with the extensive and intricate data sets generated by

ToF-SIMS. It produces two key outputs: scores and loadings.

Scores provide a new representation for the original data along the Principal Components (PCs), highlighting patterns and trends among the sample spectra. Each score point corresponds to a spectrum, and the distance between points illustrates their relative similarities.

The loadings, on the other hand, demonstrate how each original variable (m/z bins) contributes to each PC. They help interpret which variables are crucial in driving patterns seen in the scores.

The explained variance metric gauges how much information each PC or a set of PCs captures from the original data. The PCA process simplifies complex datasets, simplifying the identification of underlying patterns and trends and making it possible to more effectively understand the complex information derived from the sample's composition. For a detailed mathematical explanation, refer to Appendix A.1.

Part II

Objectives and Strategy

Objectives and Strategy

The main goal of this project is to gain a deeper understanding of High Entropy Alloys at the atomic scale and to investigate the atomic alloying formed between the constituent elements and explore their oxidation properties. In particular, this master thesis will investigate the ability of ToF-SIMS to bring new and useful information on these materials. The study will focus on macroporous HEA nanoparticles made of Ru, Rh, Ir, Pt, and Pd, as synthesised by De Marco *et al.* [75] To achieve these objectives, a comprehensive methodology will be used, including sample selection and characterisation, the use of ToF-SIMS, a sequential analysis approach and data analysis.

The research will concentrate on a five components HEA (Ru-Pt-Pd-Ir-Rh) and will use pure metals, binary, ternary, and quaternary alloys as benchmarks. The samples will be characterised using X-ray Diffraction (XRD) to identify their crystalline structure and CO oxidation catalytic tests to evaluate their catalytic properties. ToF-SIMS will be used as the primary analytical method of this thesis. It will be used to obtain atomic-scale information on the bonds and clusters formed by the elements within the HEA NPs, with the aim of unambiguously identifying clusters of different elements composing the HEAs, such as Ru-Pt, Ru-Pd, Ru-Pt-Pd, and others.

In order to reduce complexity and build a better understanding of the HEAs, a sequential approach will be adopted, starting with the ToF-SIMS analysis of pure Ru and binary alloys (i.e., Ru-Pt, Ru-Pd, Ru-Ir, and Ru-Rh), then leveraging the information obtained to understand more complex ternary alloys (i.e., Ru-Pt-Pd), and progressing to the analysis of quaternary alloys (i.e., Ru-Pt-Pd-Ir), and finally the targeted HEA (i.e., Ru-Pt-Pd-Ir-Rh). The conditions of the analysis (in particular, the nature and energy of the primary beam) will be varied with the idea of optimising the method for the detection of meaningful clusters (of large mass).

Taking into account the large amount of data generated by ToF-SIMS, statistical analysis methods may be employed to extract meaningful information and establish correlations. This will assist in interpreting the complex data obtained from the ToF-SIMS measurements.

By the end of this study, the expected outcome is to achieve a better atomic understanding of High Entropy Alloys, which will contribute to the understanding of their unique properties and potential applications in various fields.

Part III

Materials and Methods

HEA Synthesis Procedure

The subsequent protocol for HEA synthesis is based on the protocol established by De Marco *et al.* at Sorbonne University in Paris [75]. The description of this process remains faithful to its original methodology.

3.1 Materials

Palladium chloride (PdCl_2 , 96%), platinum chloride (PtCl_4 , 99%), iridium chloride hydrate ($\text{IrCl}_3 \cdot x\text{H}_2\text{O}$), and ruthenium chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$) were obtained from Sigma-Aldrich. Rhodium chloride hydrate ($\text{RhCl}_3 \cdot x\text{H}_2\text{O}$) was procured from Alfa Aesar. Pluronic (F127), methyl methacrylate, and styrene monomers were purchased from Sigma-Aldrich. deionised water was obtained using a Milli-Q system.

3.2 Synthesis of PMMA Latex Beads

Poly methyl methacrylate (PMMA) latex beads of approximately 300 nm in diameter were synthesised following the protocol of Hutton *et al.* [124]. The resulting PMMA latex suspension had a weight concentration of 11% in water.

3.3 Preparation of Stock Solutions

Separate stock solutions containing each metal chloride precursor in deionised water were prepared. $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$, and PtCl_4 were each dissolved in water at a concentration of 0.25% by weight (0.150 g of each metal salt in 60 g of water). A separate solution of PdCl_2 was also prepared at a concentration of 0.1% by weight (0.130 g of salt in 130 g of deionised water). The pH was adjusted between 1 and 2 by adding concentrated HCl. The solution was then filtered using a cellulose acetate syringe filter (0.2 μm) to remove undissolved aggregates.

3.4 HEA Synthesis

Equal volumes of each stock solution were mixed under magnetic stirring. A latex suspension of PMMA was added to this mixture to achieve a 50 wt% ratio of latex-to-metal salt. After 15 minutes of stirring, the suspension was processed using a Büchi B-290 mini spray dryer. The nozzle temperature was set at 150 °C, air flow at approximately 8 L/min, and the suspension flow at 3 mL/min. The aspirator flow rate was set to 0.45 L/min.

The resulting powders were annealed in a tubular oven under an Ar flow. To avoid oxidation, the oven was purged with Ar for 1 h before annealing. The temperature ramp rate was set to 5 °C/min, with the powders annealed at 500 °C for a dwell time of 5 minutes.

Table 3.1: Composition and mass available of the samples analysed in this work.

Composition	Composition ratio (%wt)	Mass (mg)
Ru ^a	100	-
Ru-Rh	80:20	10.3
Ru-Ir	80:20	7.0
Ru-Pd	80:20	10.9
Ru-Pt	80:20	16.0
Ru-Pt-Pd	60:20:20	12.2
Ru-Pt-Pd-Ir	40:20:20:20	35.8
Ru-Pt-Pd-Ir-Rh ^a	20:20:20:20:20	-

^aSample recovered from the work of De Marco *et al.* [75], not specifically made for this master thesis work.

4.1 Data Acquisition Conditions

The acquisition of ToF-SIMS data was carried out using an IONTOF V instrument (installed in 2010 from Münster, Germany). For static spectra acquisition, we employed the Liquid Metal Ion Gun (LMIG) source of Bi_n^+ ($n = 1, 3, 5$) in high current bunch mode, with a current range between 0.05 and 1 pA. The secondary ions were then drawn out via a reflectron-type ToF analyser perpendicularly to the surface of the sample.

Before the analyses, the samples are pressed onto a regular post-it chunk at a pressure of 1T for a few seconds and then mounted on an ION-TOF backmount sample holder. The latter is then inserted into a load lock, and the pressure is lowered to approximately $\sim 2 \cdot 10^{-6}$ mbar. Once the pressure is stabilised, the gate valve to the main analysis chamber is opened, allowing the sample holder to be transferred to the analysis chamber under a vacuum of 10^{-9} mbar. The sample is positioned on a manipulator table, which enables motion in the xyz planes. Video cameras (macro and micro) assist in positioning the sample accurately. Several preparatory steps are performed before conducting measurements, including activating the ion beams, loading the settings, centering the current in the Faraday cup, and adjusting the z position.

The Faraday cup, located on the sample holder, is designed to measure the current generated by the ion beams [125]. As ions enter the cavity, their charge is collected and subsequently measured using an ampere metre. Electrons and secondary ions are unable to escape the cavity due to the repelling force from the extraction voltage and the cavity's depth, which is significantly greater than its entry diameter. This ensures that the charge of the incident ion is accurately measured without interference from the charges of secondary species.

The actual data acquisition was performed over three distinct days, with each analysis probing a surface area of $150\mu\text{m} \times 150\mu\text{m}$. The operation was carried out using a cycle time of $150\mu\text{s}$ and an analysis time of 2 minutes for each sample, these parameters were specifically selected to optimise the detection of clusters of high mass. For each sample, the acquisition was performed in five separate repetitions for each primary ions species to provide substantial data for subsequent statistical analyses. Finally, analyses were carried out in both positive and negative ion modes. Switching between the two modes after the acquisitions were completed with all the primary ions species for one

sample. Throughout the acquisition process, there is a shift in the spectrum peaks, necessitating calibration. This calibration was carried out using CH_3^+ , C_2H_5^+ , C_3H_5^+ , and C_4H_7^+ peaks in positive mode, and CH^- , C_2H^- , C_3H^- , and C_4H^- peaks in negative mode.

In addition to the ToF-SIMS analyses conducted for this study, results from previous ToF-SIMS analyses performed one year prior on the same apparatus were also included. These previous analyses were performed on the pure Ru alloy and the five-component RuPtPdIrRh high entropy alloys. For these, only a single acquisition was made in each polarity for the primary ions of Bi_1^+ and Bi_3^+ . And for the Bi_5^+ primary ion, three acquisitions were undertaken in each polarity, however, no acquisitions were made for the Bi_3^{++} . All the acquisitions made and collected from other analyses in this master thesis are combined in Table 4.1.

Table 4.1: Experimental conditions and number of repetitions for the ToF-SIMS acquisitions.

Sample	Primary ions current measured (pA)				Number of Acquisitions				Polarity
	Bi_1^+	Bi_3^+	Bi_3^{++}	Bi_5^+	Bi_1^+	Bi_3^+	Bi_3^{++}	Bi_5^+	
Ru ^a	1.30	0.35	-	0.035	1	1	0	3	+/-
Ru-Pt	0.95	0.29	0.17	0.05	5	5	5	5	+/-
Ru-Pd	0.87	0.28	0.17	0.05	5	5	5	5	+/-
Ru-Rh	0.87	0.28	0.17	0.05	5	5	5	5	+/-
Ru-Ir	0.87	0.28	0.17	0.05	5	5	5	5	+/-
Ru-Pt-Pd	0.92	0.27	0.15	0.05	5	5	5	5	+/-
Ru-Pt-Pd-Ir	0.92	0.27	0.15	0.05	5	5	5	5	+/-
Ru-Pt-Pd-Ir-Rh ^a	1.30	0.35	-	0.035	1	1	0	3	+/-

^aMeasurement recovered from the work of De Marco *et al.* [75], not specifically done for this master thesis work.

4.2 Peaks Identification Procedure

The process for peak identification in this study was implemented with the aid of IONTOF SurfaceLab 7.2. Distinct peak lists for both the positive and negative spectra were created, but the procedure remained the same across the board.

During the peak list creation process, peaks were manually introduced one at a time. Before the addition of each peak, a thorough inspection of the isotopic distribution was

performed as a verification metric. During the peak addition process, the focus was placed on the identification of peaks corresponding to single ions, clusters, oxides, chlorides, or oxychlorides of the five components of the alloys: Ru, Pd, Pt, Rh, Ir and their mixtures. In addition to these, peaks indicative of classical organic contaminants (C_4H_7^+ , C_6H_5^+ , C_7H_7^+ , C_2H^- , C_3H^-) were also incorporated into the peak list. Additional prevalent contaminants discernible from the preliminary inspection of the raw spectrum, including K^+ , Na^+ , Ca^+ , Cl^- , F^- , and H^- , were also incorporated.

In instances where the isotopic distributions of two different ions (for example, Ion A^+ and Ion B^+) overlapped, it resulted in a peak that was actually a combination of signals from both A^+ and B^+ . In such a case, another peak at the further end of ion A^+ 's isotopic distribution, which didn't overlap with ion B^+ , was chosen as the representative peak for ion A^+ . A similar approach was used for ion B^+ , as illustrated in Figure 4.1. This strategy allowed for a more accurate and unambiguous identification of the respective peaks for each ion.

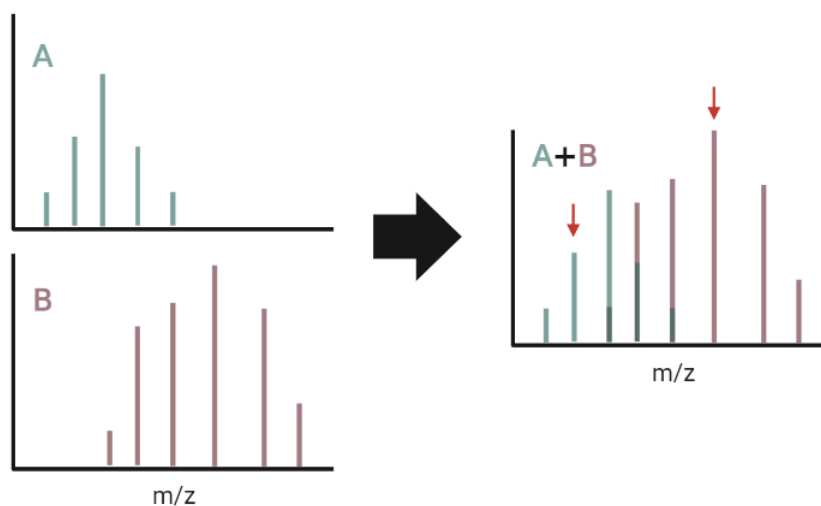


Figure 4.1: Schematic depiction of peak selection for two overlapping isotopic ion distributions, A and B. The designated peaks for A^+ and B^+ are highlighted with red arrows.

4.3 ToF-SIMS Spectra Treatment

The subsequent treatment of the compiled peak list grouped into a dataframe was carried out in R Studio (R version 4.2.3). Given that a uniform peak list per polarity was applied across all spectra, it is worth noting that specific peaks, identified at a certain mass and attributed to a certain alloy component, might coincide with peaks associated with different elements in other alloys due to similar masses. For instance, the Rh^+ peak at 102.92 amu, identified from the Ru-Rh sample and subsequently added to the peak list, will inevitably be applied to other samples (such as Ru-Ir) that do not contain Rh. In such cases, the labelled " Rh^+ " peak may register a non-null value for the Ru-Ir sample. This could occur either because the Ru-Ir spectrum might present a peak at this mass,

stemming from an unidentified source or due to the integration of random noise by the detector.

To address these issues, a correctional step was incorporated into the data treatment process. In the resultant dataframe, which contains all samples and their labelled peaks, the values of the peaks associated with an element not found in a given nominal sample composition were set to zero. This means, for instance, that the values for peaks such as Rh^+ , Rh_2^+ , RuRh^+ , and others involving rhodium will be set to zero for samples such as Ru, Ru-Ir, Ru-Pt, Ru-Pd, Ru-Pd-Pt, and Ru-Pd-Pt-Ir, which do not contain rhodium. This step ensures that the data accurately reflects the composition of the samples and removes potential artefacts due to coincidental mass matching or noise integration. This methodology was reciprocally applied for all elements across the different alloy samples.

Continuing the data treatment process, the corrected dataframe was subjected to a normalisation step. This step was necessary to account for potential variations in total ion yields among the samples. Specifically, the ion count of each column (corresponding to a distinct cluster identified in the peak list) was divided by the total ion count of the sample. The values in this normalised data frame represent the fraction of a specific cluster in relation to the total ion yield of the sample, providing a relative measure of cluster abundance and, thereby, mitigating any discrepancies resulting from different overall ion yields across samples.

The comprehensive process encompassing the peak identification and spectrum treatment steps is schematically illustrated in Figure 4.2.

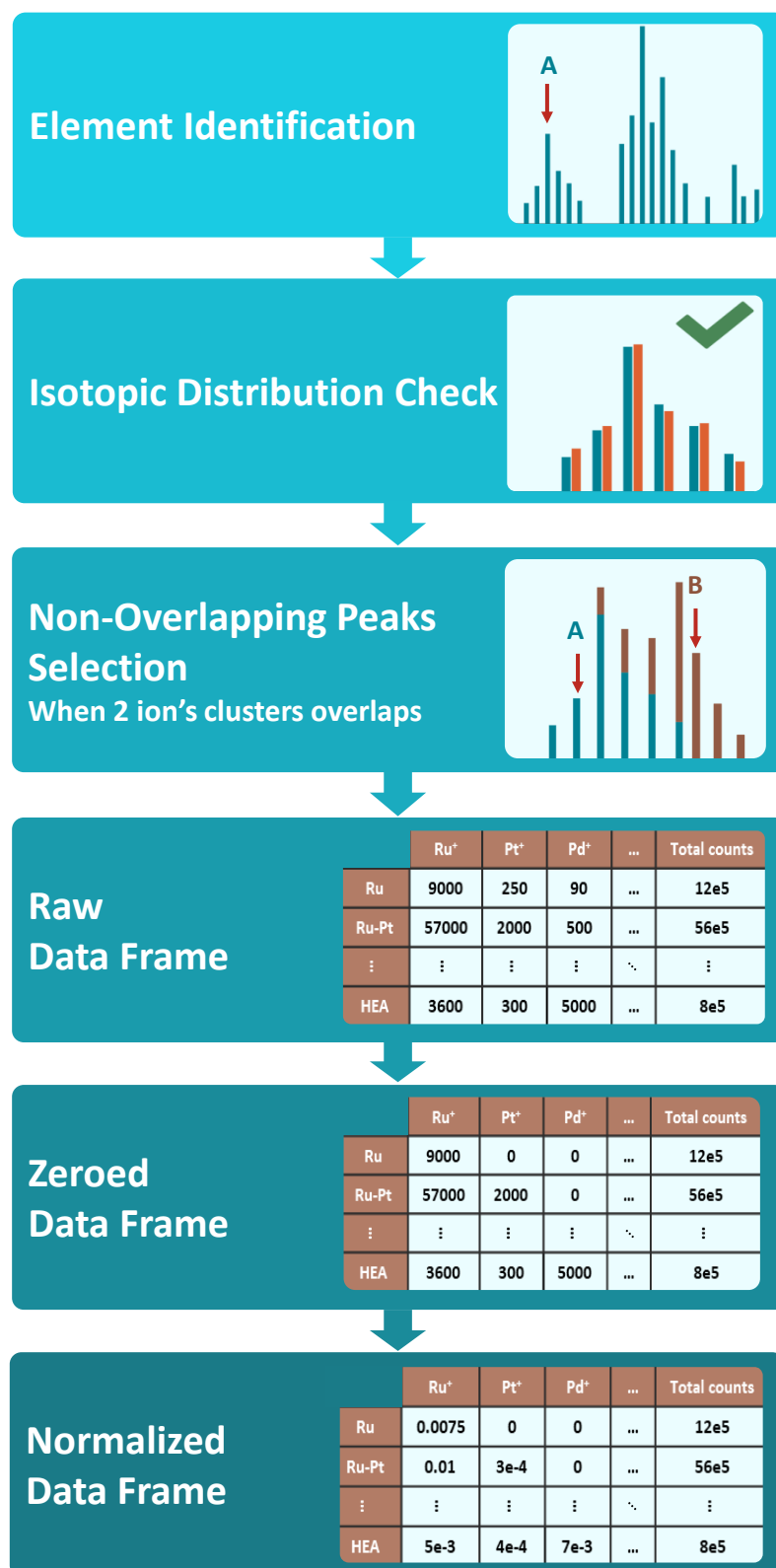


Figure 4.2: Peak identification and spectrum treatment workflow. Here the resulting data frame is the positive one but the same procedure has been apply for negative data.

5.1 CO Oxidation Capacities

Catalytic CO oxidation was performed using Catlab (Hiden) consisting of a temperature controlled microreactor in which the catalyst is fed with the reactive gas mixture. The equipment is connected to an in-line quadrupole mass spectrometer (QGA, Hiden) for gas analysis.

40 ml/min of 5% O₂ in helium and 5 ml/min of 20% CO in He are mixed to ensure an excess of oxygen (2 ml/min O₂ and 1 ml/min of CO diluted in He) to perform CO oxidation. An addition flux of 5 ml/min of pure Ar was added as an internal standard (except for Ru and Ru-Pt-Pd-Ir-Rh which were analysed last year). A temperature ramp (10 °C/ min) is applied from 50 °C to 250 °C and the evolution of the gas mixture is followed by mass spectroscopy.

For practical reasons, it was not possible to systematically load the same mass of catalyst in each test. Table 5.1 reports the actual sample mass and reaction conditions used for each CO oxidation reaction.

Table 5.1: Masses of catalyst loaded and experimental conditions during CO oxidation tests.

Sample	Mass loaded (mg)	Inlet flux (mL.min ⁻¹)			
		O ₂	CO	He	Ar
Ru ^a	10	2	1	42	0
Ru-Pt	9.2	2	1	42	5
Ru-Pd	4.9	2	1	42	5
Ru-Rh	8.2	2	1	42	5
Ru-Ir	8.7	2	1	42	5
Ru-Pt-Pd	9.2	2	1	42	5
Ru-Pt-Pd-Ir	9.1	2	1	42	5
Ru-Pt-Pd-Ir-Rh ^a	14	2	1	42	0

^aAnalysis recovered from the work of De Marco *et al.* [75], not specifically made for this master thesis work.

5.2 X-Ray Crystallography

The crystalline nature of the prepared catalysts was verified using X-Ray Diffraction (XRD), a technique that identifies crystalline phases based on the elastic scattering of photons through the sample's crystalline planes. In this study, two different diffractometers were used due to practical constraints.

The Ru and Ru-Pt-Pd-Ir-Rh samples were characterised by De Marco *et al.* [75] at Sorbonne University, using a Bruker apparatus with a Cu anode. Radiation emitted, with a wavelength of 1.54 Å, was produced under conditions of 40 kV and 30 mA. Powder diffractograms were recorded within a 2θ range between 10° and 90°, at a speed of 1.17°/min, and totalling 2258 steps

On the other hand, the samples synthesised specifically for this Master thesis; Ru-Pt, Ru-Pd, Ru-Ir, Ru-Rh, Ru-Pt-Pd, and Ru-Pt-Pd-Ir; were subjected to a different protocol. For these samples, XRD diffraction experiments were conducted at UCLouvain on a Bruker-D8 Advance diffractometer equipped with Bragg-Brentano geometry. This diffractometer used X-ray radiation generated by a copper anode, operating at 40 kV and 30 mA, with a $K\alpha$ wavelength of 0.154 nm. The diffractometer recorded within a 2θ range from 5° to 80°, proceeding in increments of 0.015° at a rate of 5.93°/min, resulting in a total of 5051 steps.

Regardless of the protocol, the sample powder was dispersed on a coated sample holder. LynxEye XE-T technology was deployed in the Bruker detector for the detection process. After data acquisition, the diffractograms were analysed using DIFFRAC.EVA software (version 4.2.1, 2016), with reference to the ICDD-PDF-2004 database, allowing the identification of crystalline phases.

Part IV

Results and Discussion

X-Ray Diffraction Results

6.1 Crystallite Size Results

The comparison of all XRD diffractograms as shown in Figure 6.1, reveals some interesting distinctions. One of the most noticeable differences is the breadth of the peaks. The Ru sample displays broader peaks compared to the narrow, well-defined peaks of the Ru-Rh or Ru-Ir samples.

This broadening can be interpreted in the light of Speakman's observations [126]. According to Speakman, peak broadening can be attributed to several factors, including a smaller crystallite size, an increased number of stacking faults, microstrain, and other defects in the crystal structure, as well as an inhomogeneous composition.

The Scherrer equation [127] was used to estimate the mean crystallite size. For the Ru sample, it was estimated to be about 3 nm.

In the case of binary alloys, it was observed that the introduction of Pt to Ru did not significantly alter the mean crystallite size, which is inferred from the comparable broadness of the XRD peaks. However, when Pd was added to the alloy, the XRD diffractogram demonstrated noticeably narrower peaks. Further narrowing of the peaks was seen upon the addition of either Rh or Ir. These narrower peaks suggest a greater mean crystallite size according to the Scherrer equation. The resulting estimations for the mean crystallite size for Ru-Pt, Ru-Pd, Ru-Rh and Ru-Ir samples are respectively 4.5, 6, 9 and 9 nm. Thus, the incorporation of Pt, Pd, Ir, or Rh into the Ru-based alloys seems to affect the crystallite size. The intensity of this effect varies with the element added and can be classified as follows: $\text{Ir} \simeq \text{Rh} > \text{Pd} > \text{Pt}$.

When examining the ternary, quaternary, and quinary alloys, the situation is slightly different. The ternary alloy initially appeared to exhibit broader peaks on the XRD diffractogram, suggesting smaller crystallites. However, as discussed in the following section, the coexistence of two phases within the material complicates the interpretation.

In contrast, the XRD diffractogram for the quaternary alloy clearly demonstrates wider peaks, indicating smaller crystallites compared to the binary alloys. The trend of decreasing crystallite size persists in the quinary alloy. Specifically, the full quinary alloy exhibits the broadest peaks, corresponding to a mean crystallite size of about 3 nm, which is consistent with the findings reported by De Marco *et al.* [75], in their study on mesoporous HEA.

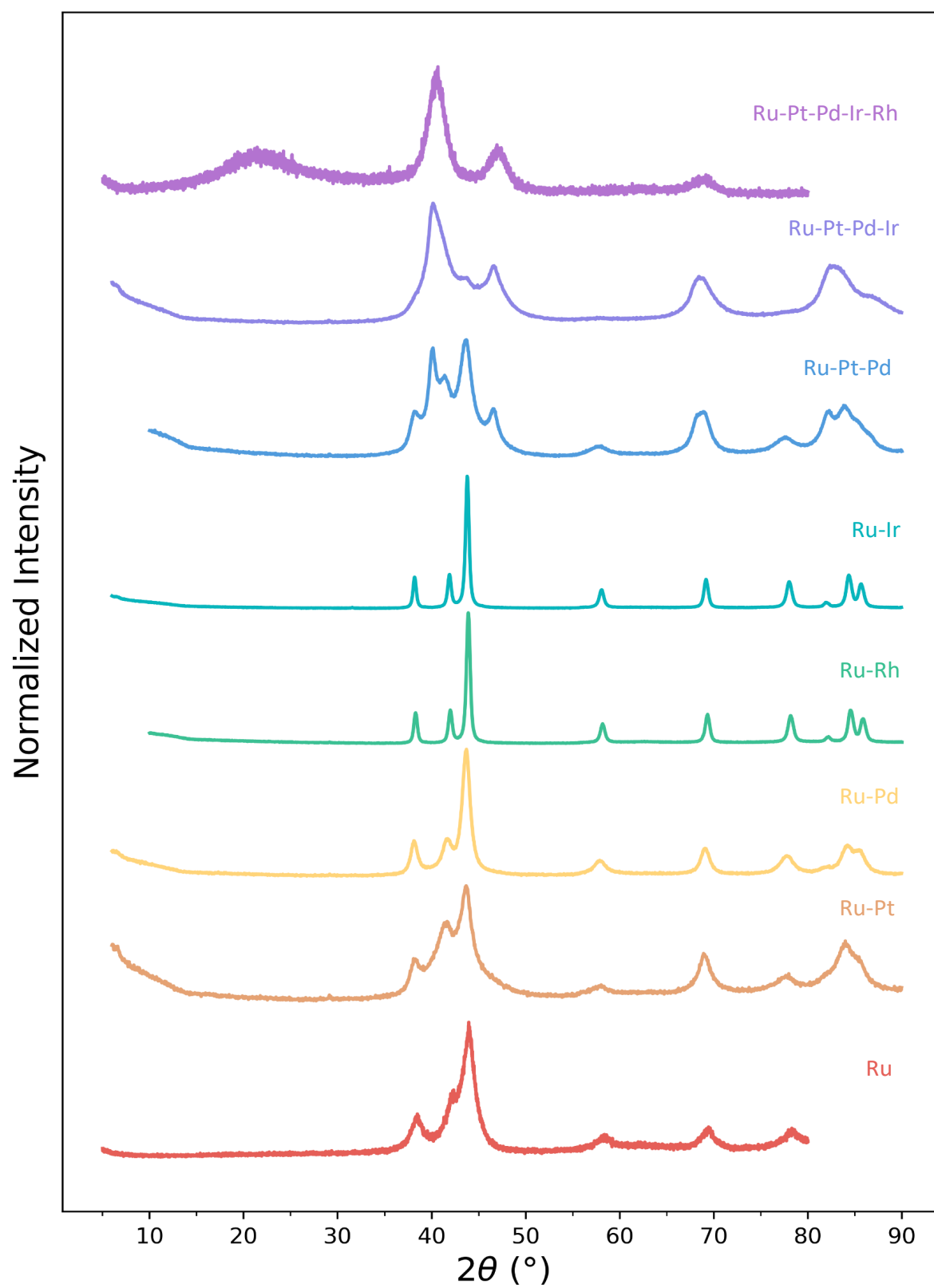


Figure 6.1: Diffractograms of the different alloys

6.2 Crystalline Phases Results

The evolution of the crystalline phases presents a discernible pattern in the context of these materials. Starting with the Ru sample, we observe a strong correlation with the Hexagonal Close Packed (HCP) phase of Ru, as illustrated in Figure 6.2. Interestingly, this pattern extends to all binary samples (Figures 6.3, to 6.6), though a minor shift toward smaller theta values is discerned.

The observed shift implies a subtle disturbance in the HCP phase of Ru. According to Bragg's law [128], smaller theta values are indicative of larger interplanar distances (i.e. the distances between successive layers of atoms) compared to the theoretical HCP phase of Ru. Consequently, the addition of another element to the Ru base appears to increase the distance between crystal layers while preserving the HCP crystal structure.

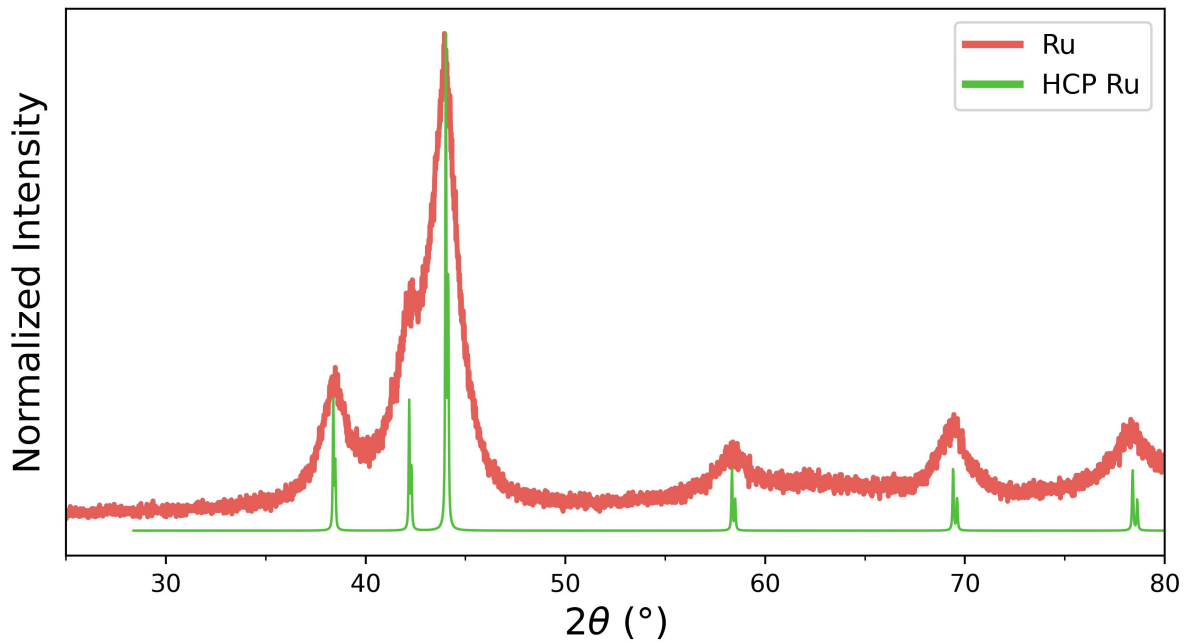


Figure 6.2: Diffractograms of the Ru alloy. Ru hcp phase ID : PDF 06-0663

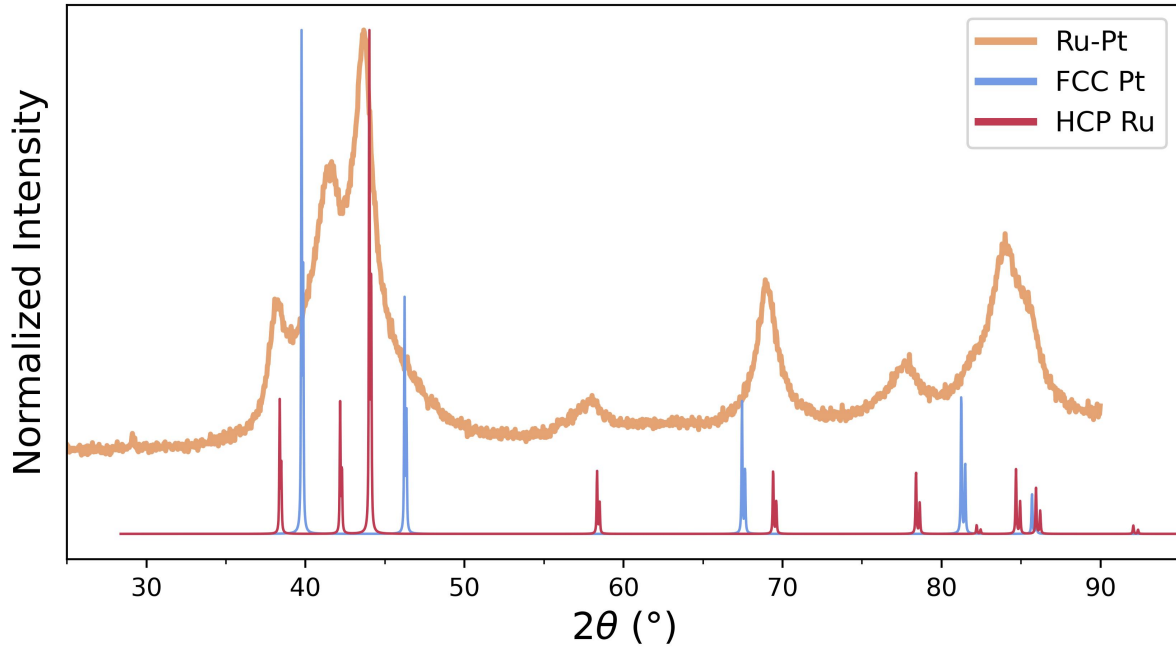


Figure 6.3: Diffractograms of the Ru-Pt alloys with its component's phases. Ru hcp phase ID : PDF 06-0663, Pt fcc Phase ID : PDF 87-0644.

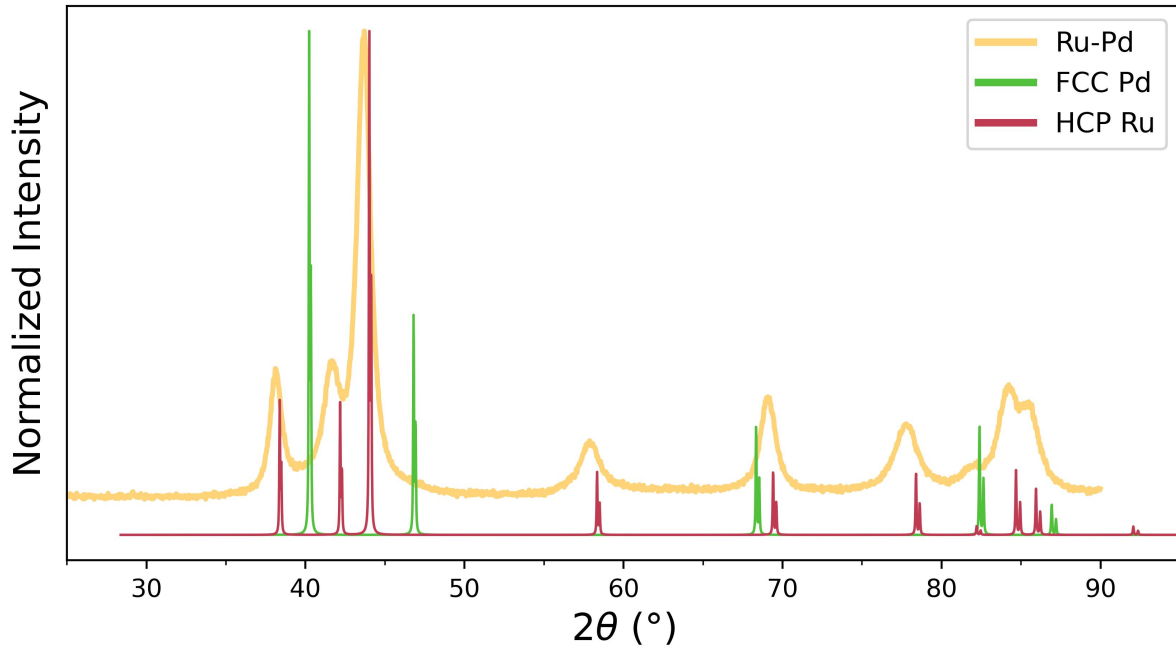


Figure 6.4: Diffractograms of the Ru-Pd alloys with its component's phases. Ru hcp phase ID : PDF 06-0663, Pd fcc phase ID : PDF 87-0638.

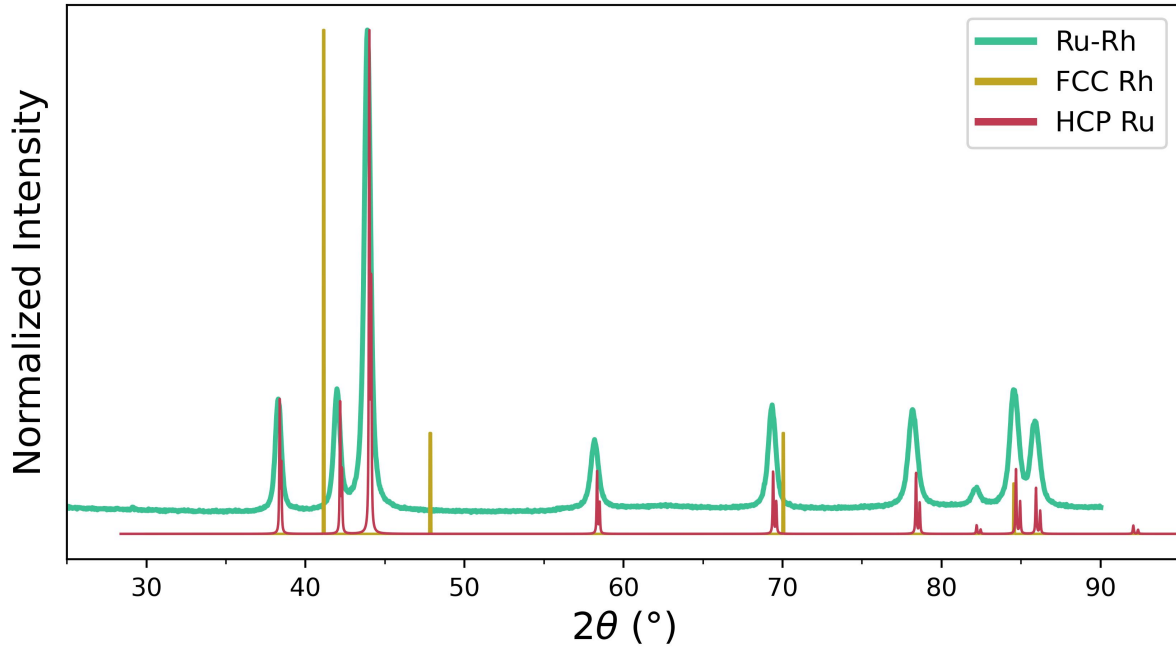


Figure 6.5: Diffractograms of the Ru-Rh alloys with its component's phases. Ru hcp phase ID : PDF 06-0663, Rh fcc phase ID : PDF 88-2334.

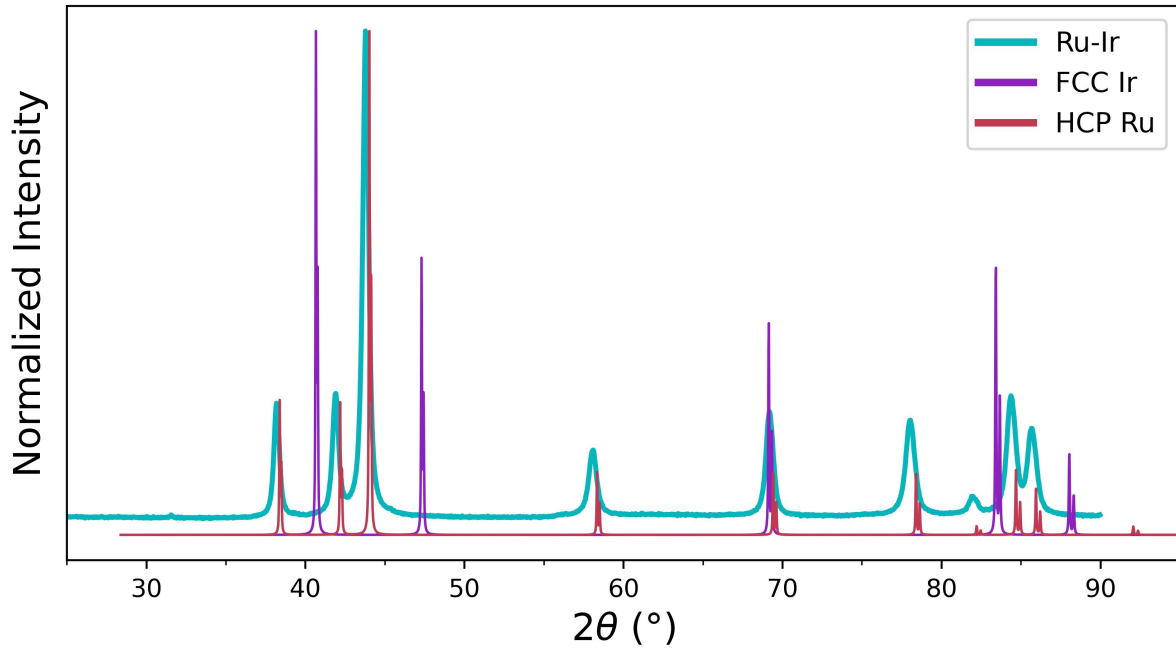


Figure 6.6: Diffractograms of the Ru-Ir alloys with its component's phases. Ru hcp phase ID : PDF 06-0663, Ir fcc phase ID : PDF 46-1044.

Upon examination of the XRD diffractograms of alloys composed of more than two constituents, additional patterns emerge. For the ternary alloy, we can identify a combination of the Hexagonal Close Packed (HCP) phase corresponding to Ru and the Face-Centered

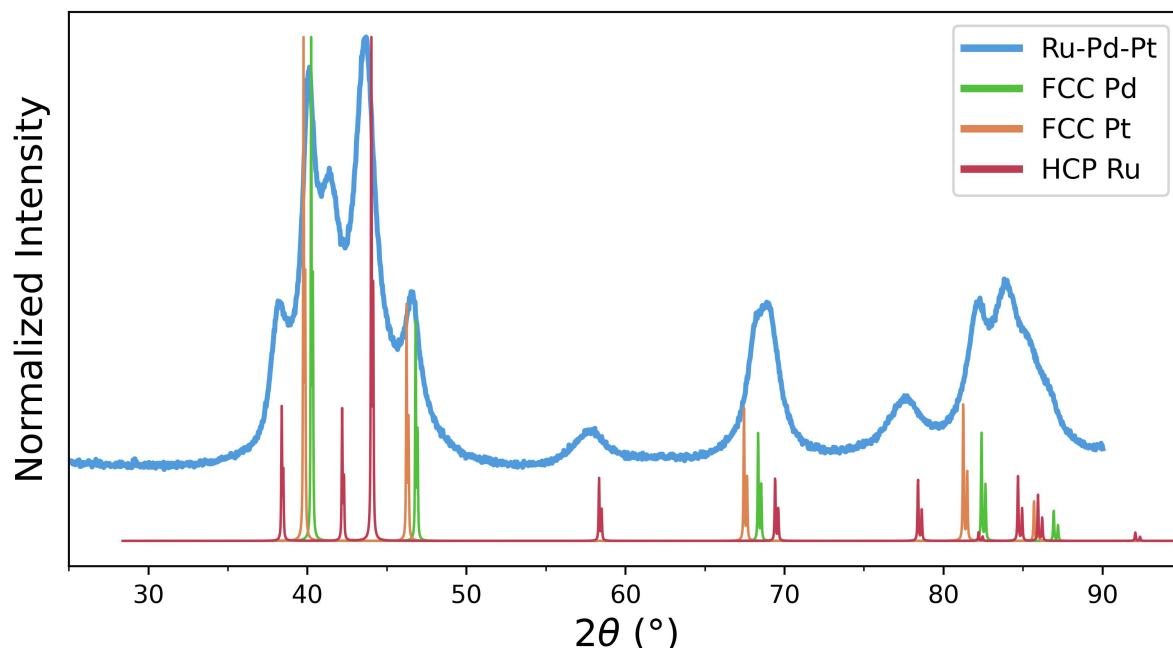


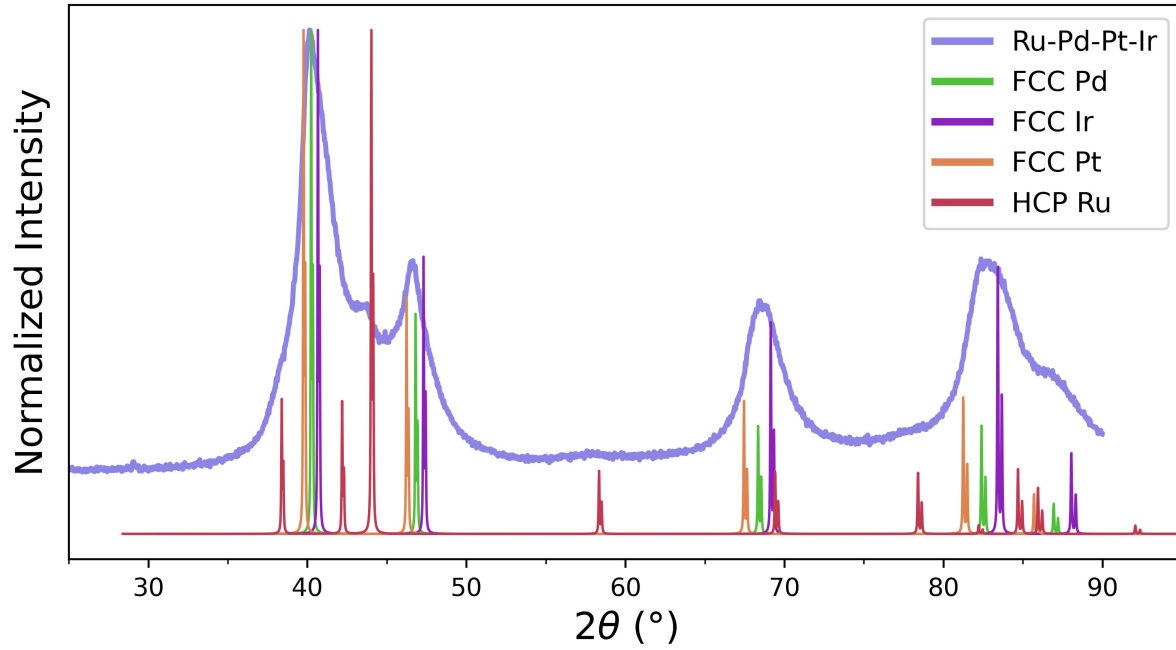
Figure 6.7: Diffractograms of the Ru-Pt-Pd alloy with their component's phases. Pt fcc Phase ID : PDF 87-0644, Pd fcc phase ID : PDF 87-0638

Cubic (FCC) phase corresponding to Pt and Pd, as illustrated in Figure 6.7.

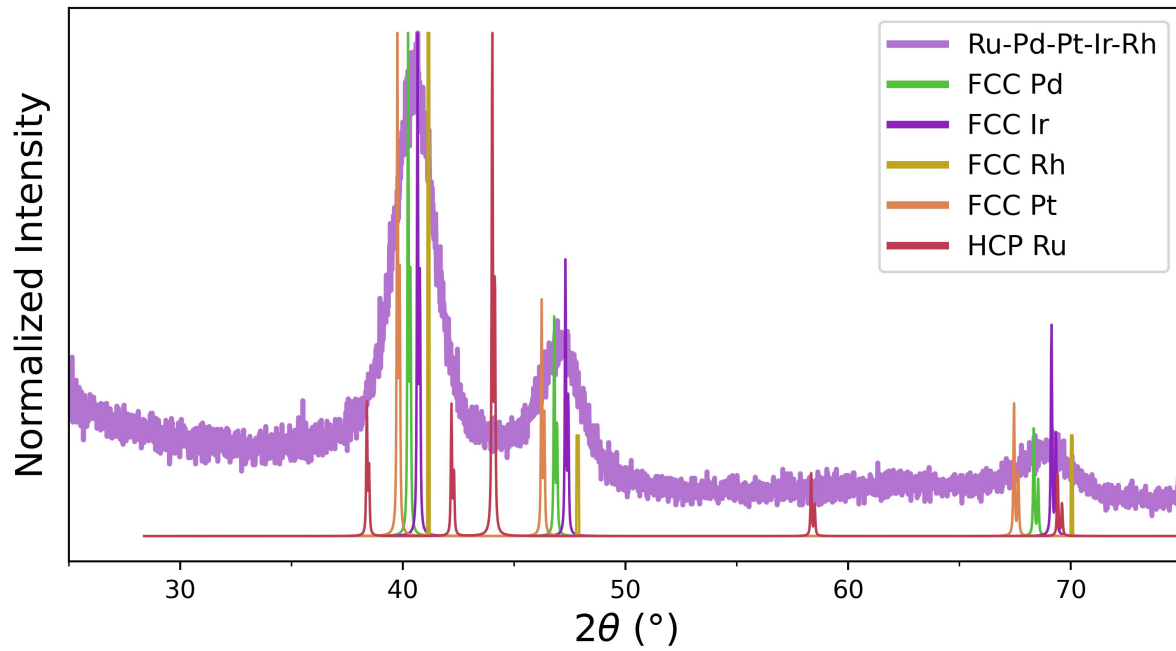
This suggests that in this ternary alloy, Ru maintains its native HCP phase while Pt and Pd adopt an FCC phase. The combination of the theoretical FCC Pt and Pd phases seems to align well with the diffraction pattern. But the HCP Ru phase appears to shift towards smaller theta values compared to the binary alloys, indicating a more pronounced widening of the crystal layers of this phase.

A modification in the phase behaviour is noticed when we progress to the quaternary alloy. The HCP phase associated with Ru is no longer discernible, leaving only the FCC phase corresponding to Pt, Pd and Ir (Figure 6.8a). The diffraction pattern is still aligned with the combination of the theoretical FCC phases of the three elements. This modification in the phase landscape is consistent with the quinary alloys, where the FCC phase persists (Figure 6.8b).

These observations suggest an intriguing relationship between the number of components in an alloy and the evolution of phase behaviour. In the case of ternary alloys, two distinct phases are observed, suggesting a lack of homogeneous blending. However, when the number of components increases to four or five, a shift towards a single FCC phase is noted, implying likely homogeneity. This transformation in phase behaviour indicates that the increased entropy generated by the mixing of four or five elements promotes intermixing, leading to a single, presumably homogeneous phase. It underscores the profound role of compositional complexity and entropy in phase evolution and stabilisation within these alloys.



(a)



(b)

Figure 6.8: Diffractograms of the (a) Ru-Pt-Pd-Ir and (b) Ru-Pt-Pd-Ir-Rh alloy with their component's phases. Ru hcp phase ID : PDF 06-0663, Pt fcc Phase ID : PDF 87-0644, Pd fcc phase ID : PDF 87-0638, fcc Ir phase ID : PDF 46-1044, fcc Rh phase ID : PDF 88-2334

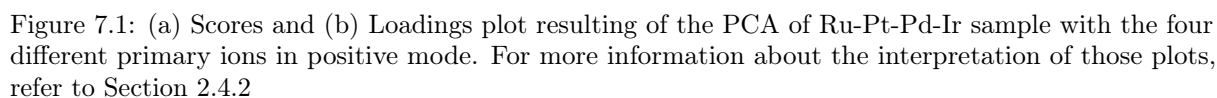
7.1 Primary Ion Optimisation

As stated earlier in section 2.3, the choice of primary ion considerably influences the yield of specific secondary ions. Given that the purpose of this work is to examine the homogeneity of the sample, the analysis focuses on all types of high mass cluster ions of Ru, Pt, Pd, Ir, and Rh and their combinations. The task is to identify the primary ion that will enhance the presence of these cluster ions, and to this end, a Principal Component Analysis is performed.

For this analysis, the positive spectrum of the Ru-Pt-Pd-Ir sample from the normalised data frame was selected. The decision to select the positive spectrum of the Ru-Pt-Pd-Ir sample from the normalised data frame for this analysis is based on its complex composition and the depth of available data. As seen in Table 4.1, five replications were carried out for this sample, each time with a different primary ion. This provides a richer dataset for analysis. On the other hand, in the preliminary work by De Marco *et al.*, the Ru-Pt-Pd-Ir-Rh sample was tested only three times with Bi_5^+ , and once each with Bi_1^+ and Bi_3^+ .

The choice of the positive spectrum was significant, as metal-based clusters show the best yield in this mode. Once these data were isolated, each variable underwent a scaling operation. Scaling is a necessary preprocessing step to ensure that all variables are weighted equally during PCA. This is done by dividing each cluster count by the standard deviation of this specific cluster. Without scaling, variables with larger value ranges, such as Na^+ or K^+ , could potentially dominate the analysis, thereby minimising the contribution of variables with smaller value ranges.

The resulting scores and loadings of the normalised and scaled positive spectrum are illustrated in Figures 7.1a and 7.1b. Reviewing the score plot, we observe that the Bi_5^+ and Bi_3^+ primary ions score highest on the first principal component (PC1). This component is strongly associated with the expression of most metal clusters such as Ru_2^+ , RuPt^+ , RuPtPd^+ , among others. On the contrary, Bi_1^+ yields the lowest score on PC1, indicating a lower expression of high-mass metal clusters when using this primary ion. Furthermore, the negatively associated loadings on PC1 correspond to individual metal ions such as Ru^+ , Pd^+ and their derived species (RuO^+ , PdO^+ , RuNa^+ , etc.). This implies that these ions are less expressed or their detection is less favoured when Bi_5^+ or Bi_3^+ are employed.



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have lower scores on PC1, while those with lower energy per atom have higher scores. Since high-mass secondary cluster loadings on this PC1 are predominantly positive, this implies that the yield of high-mass secondary clusters decreases with increasing energy of the primary ion. This aligns with the intuition that a high-energy primary cluster would cause more fragmentation, resulting in smaller secondary clusters.

These observations suggest that Bi_5^+ and Bi_3^+ are optimal for the detection of high-mass metal clusters. Giving its slightly higher score on PC1, Bi_5^+ was selected as the primary ion for further analyses.

7.2 Preliminary SIMS Analyses

As an initial analysis, the adjusted total count was evaluated. This metric is defined as the total count of secondary ions from each sample divided by the primary ion current actually delivered for each primary ion beam (available in Table 4.1). It is important to mention that the Ru and Ru-Pt-Pd-Ir-Rh alloys are not included due to limited repetitions, which could compromise the data validity.

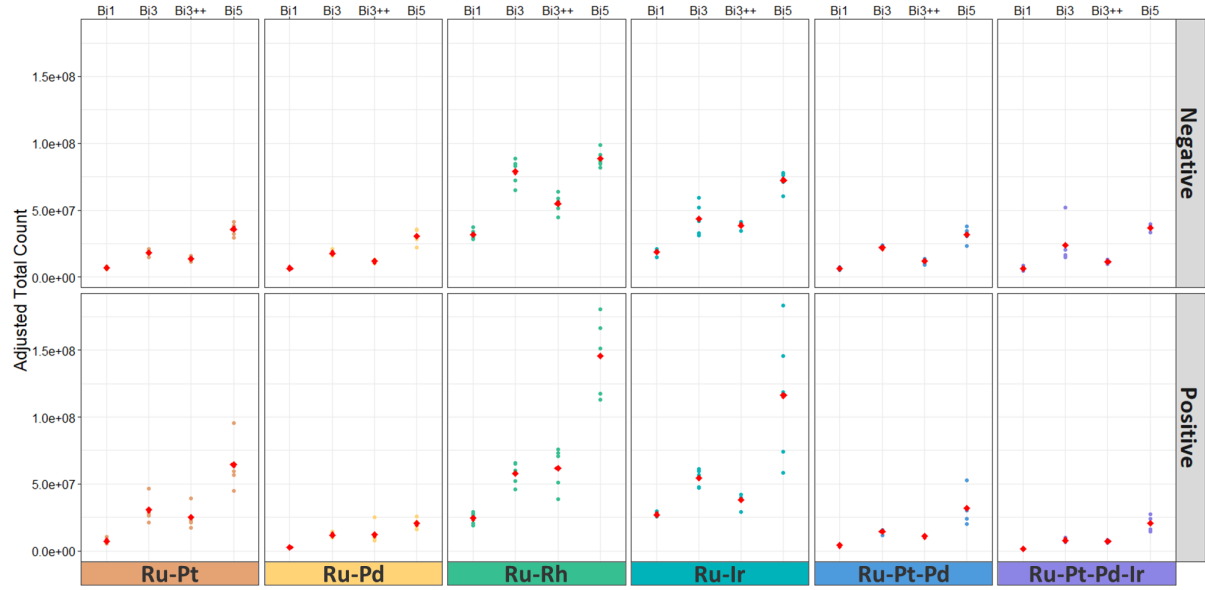


Figure 7.2: Adjusted Total Counts of the five samples in positive and negative mode with all the primary ions.

Figure 7.2 reveals that the adjusted total count with Bi_5^+ as primary ions consistently yields the highest number of secondary ions in all samples, regardless of the operating mode, either negative or positive. This finding is consistent with the existing literature on the subject [119], [120].

Further analysis of Figure 7.2 indicates that the Ru-Ir and Ru-Rh samples produce significantly more ions in both polarities compared to the other samples. Upon examination of the raw spectra provided in Figures A.1 and A.2 available in the Appendix A.2, it can be discerned that this elevated yield is primarily due to contaminants such as Cl^- , Na^+ , H^- , and K^+ . Intriguingly, these peaks appear to be correlated. This suggests that these contaminants may come from a single source. Furthermore, examination of the spatial distribution (Figure A.3, also available in the Appendix A.2), indicates a homogeneous distribution of these contaminants. This evidence points to the possibility of a common contamination source, potentially a metallic precursor, or a handling error during sample manipulation.

The hypothesis that could explain the source of this contamination stems from the different chemical precursors used in the synthesis of these alloys. The chloride precursors of Ir and Rh are hydrated, while those of Pd and Pt are not. The information provided by the precursor supplier includes a mention of "trace metals" in the description of these hydrated species, whereas no mention of such "trace metals" is found for the precursor of Pd nor Pt. Therefore, it is plausible that the contaminant ions, specifically K^+ , Na^+ or Cl^- , might originate from hydrated species of $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ and $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$.

7.3 Binary and Ruthenium Cluster Ratios

To examine the hypotheses of metal integration in the Ru phase (as discussed in chapter 6), two evaluation metrics were used for all binary alloys (Ru-Pt, Ru-Pd, Ru-Ir and Ru-Rh): the Binary Cluster Ratio (BCR) and the Ruthenium Cluster Ratio (RCR).

The Binary Cluster Ratio quantifies the extent to which the two elements in a binary alloy form binary clusters relative to their individual occurrences. The formula for a binary alloy Ru-M is expressed as follows:

$$BCR_{Ru-M} = \sum_a \sum_b \left[\frac{\text{Ru}_a \text{M}_b^+}{\text{Ru}^+ + \text{M}^+} \right] \quad \forall a, b = 1, 2, 3, \dots \quad (7.1)$$

In this equation, $\sum_a \sum_b \text{Ru}_a \text{M}_b^+$ represents the sum of the counts of all the binary cluster ions of Ru and the element M, while Ru^+ and M^+ are the counts of the respective individual ions of Ru and the elements M.

On the other hand, the Ruthenium Cluster Ratio (RCR) provides a measure of the tendency of Ru to form clusters with more than two atoms, relative to the sum of individual ion of Ru and M. The RCR is expressed as follows:

$$RCR = \sum_n \left[\frac{\text{Ru}_n^+}{\text{Ru}^+ + \text{M}^+} \right] \quad \forall n = 2, 3, \dots \quad (7.2)$$

In this equation, Ru_n^+ represents the count of all Ruthenium clusters of more than one atom, while Ru^+ and M^+ are, respectively, the count of individual Ruthenium ions and the count of the other element ions.

This metric aids in determining whether the trends observed in the BCR results are attributable to mixing of alloy constituents, or are primarily influenced by other phenomena such as some differences in the yields of the samples. If the BCR truly reflects the degree of mixing within the sample, an inverse relationship with the RCR is anticipated. This expectation is rooted in the supposition that low BCR values, potentially indicative of reduced mixing, should coincide with an increased frequency of homonuclear Ru clusters, thus increasing the RCR. Conversely, if the RCR does not exhibit this inverse correlation with the BCR, it suggests the presence of other influencing factors, which weakens the conclusion that can be drawn from the BCR alone.

The statistical significance of the BCR and RCR was assessed using an Analysis of Variance (ANOVA). This statistical tool provides a robust method to compare the means of independent groups, in this case, the different alloys [129], [130]. The results are presented in Table 7.2.

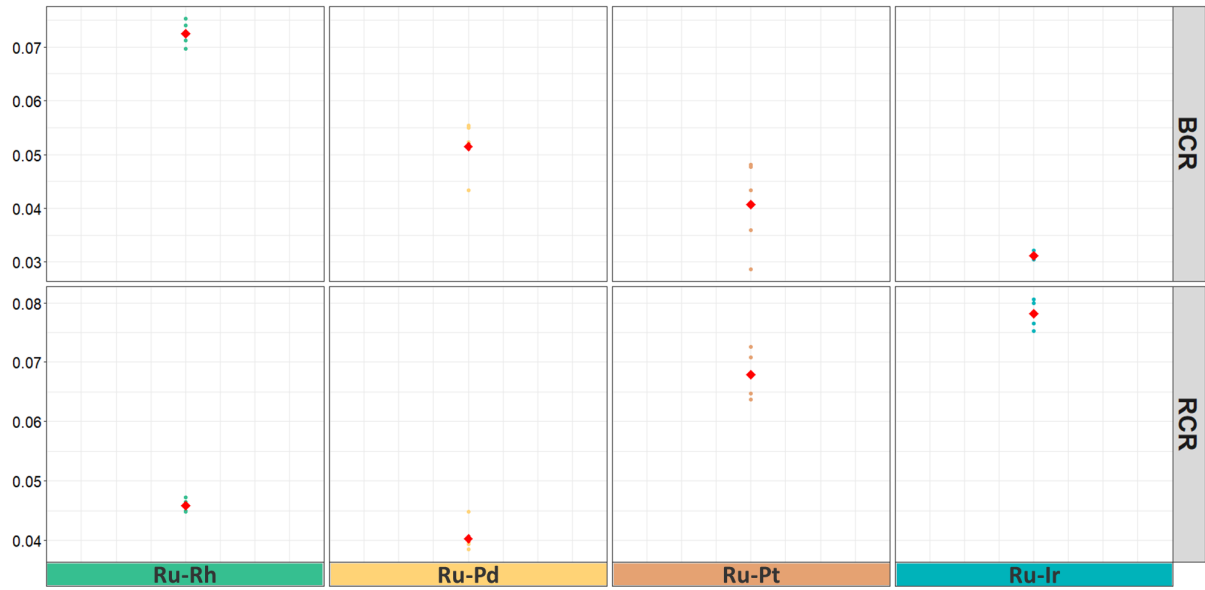


Figure 7.3: Comparison of the different Binary and Ruthenium Cluster Ratios for the four binary samples with Bi_5^+ in positive mode.

Table 7.1: Mean and standard deviation values of the binary and ruthenium cluster ratio with Bi_5^+ in negative mode.

Sample (10^{-3})	BCR	RCR
Ru-Rh	72.5 ± 2.2	45.8 ± 1.0
Ru-Pd	51.4 ± 4.9	40.3 ± 2.5
Ru-Pt	40.8 ± 8.3	67.9 ± 3.8
Ru-Ir	30.2 ± 0.7	78.2 ± 2.2

The results of the BCR and RCR analyses present significant differences among the four samples, as shown by the ANOVA results in Table 7.2. The obtained p-value suggests that the disparities in the BCR and RCR values across the alloys are statistically significant. And the η^2 in the table which is defined as:

$$\eta^2 = \frac{SSE_{\text{effect}}}{SSE_{\text{total}}}$$

Where SSE_{effect} is the sum of squares between the groups (the variability due to interaction between the groups) and SSE_{total} is the total sum of squares (the total variability in the data). This metric measures the degree of association between the independent variable (the type of alloy in this case) and the dependent variable (the BCR or RCR values). With a value of 0.96 and 0.98, it indicates a very strong association, suggesting that, respectively, 96% and 98% of the variance in the BCR or RCR values can be attributed to the type of alloy.

The trends for BCR and RCR are well inversely related, as depicted in Figure 7.3, corroborating that these ratios logically reflect the degree of blending in these alloys. Therefore, in light of the BCR and RCR results, the alloys can be organised according to their mixing efficiency as follows: $\text{Ru-Rh} > \text{Ru-Pd} > \text{Ru-Pd} > \text{Ru-Ir}$.

Table 7.2: Resulting table of the ANNOVA test on the BCR for the four binary samples with Bi_5^+ in positive mode.

Ratio	DF numerator	DF denominator	F_{obs}	p-value	η^2
BCR	3	16	63.85	4.2×10^{-9}	0.92
RCR	3	16	237.83	1.8×10^{-13}	0.98

Although the inverse trend between BCR and RCR holds, it is worth noting that for RCR, the distinction between the Ru-Rh and Ru-Pd samples is less pronounced. The RCR value for Ru-Rh is slightly higher than that for Ru-Pd, contrary to the clear hierarchy

seen in the BCR values. However, given the general trend and the high value of η^2 for the RCR, this minor inconsistency does not undermine the overall interpretation of the BCR results.

7.4 Hetero and Iso Atomic Cluster Ratios

In an effort to understand degree of atomic mixing within these alloys, two other metrics have been developed: the Hetero Atomic Cluster Ratio (HACR) and the Iso Atomic Cluster Ratio (IACR). However, the application of these two metrics across all samples presents a significant challenge due to the varying compositions of these alloys.

HACR was initially conceived to be the division of the sum of all clusters composed of at least two different elements into the sum of all individual ions (Ru^+ , Pt^+ , Pd^+ , Ir^+ , Rh^+). However, this approach would entail two major problems.

Firstly, the introduction of new elements within the alloys could markedly influence the denominator, and by extension, the calculated HACR. For instance, the addition of Pd from the Ru-Pt sample to the Ru-Pt-Pd sample leads to the apparition of Pd^+ ions in the denominator. Likewise, the addition of Ir from the Ru-Pt-Pd sample to the Ru-Pt-Pd-Ir sample would introduce the individual ions Ir^+ , thereby further contributing to the denominator. Since the individual ions of these elements could have very different yields, these changes could instigate a profound shift in the HACR. This could make the HACR heavily dependent on the mere presence or absence of specific elements, thereby detracting from its intended purpose of evaluating atomic-scale interactions.

Secondly, the representation of some elements, such as Rh, in the alloys is restricted to only a couple of samples. This poses a problem when it comes to evaluating the effect of increased compositional complexity on atomic-scale interactions. Specifically, considering Rhodium-based clusters for the calculation of the HACR could potentially yield skewed results due to the limited dataset. Therefore, failing to provide a sufficiently accurate depiction of the effect of increasing elemental complexity on atomic-scale interactions.

To address these challenges, the HACR was adjusted to only include ions that can be found in at least three different samples, ensuring a more reliable comparison. In the denominator, only individual ions present in all compared alloys, and in the same proportion across all of them, were included. This approach limited the choice to only three samples: Ru-Pt-Pd, Ru-Pd-Pt-Ir, and Ru-Pt-Pd-Ir-Rh, and necessitated the use of Pt^+ and Pd^+ ions in the denominator. Indeed, Ru's proportion varies, starting at 60% in the Ru-Pt-Pd alloy, then dropping to 40% in the Ru-Pt-Pd-Ir alloy, and finally to 20% in the Ru-Pt-Pd-Ir-Rh alloy. The numerator was made up of the sum of the ions Ru_aPt_b^+ , Pd_aPt_b^+ , Ru_aPd_b^+ and $\text{Ru}_a\text{Pt}_b\text{Pd}_c^+$. Thus, the HACR is expressed as :

$$HACR = \sum_a \sum_b \sum_c \left[\frac{\text{Ru}_a\text{Pt}_b^+ + \text{Pd}_a\text{Pt}_b^+ + \text{Ru}_a\text{Pd}_b^+ + \text{Ru}_a\text{Pt}_b\text{Pd}_c^+}{\text{Pt}^+ + \text{Pd}^+} \right] \quad \forall a, b, c = 1, 2, \dots$$

Therefore, this ratio represents the prevalence of clusters with at least two different components in relation to the individual ion yield. In this context, a higher HACR implies a higher degree of mixing at the atomic scale.

Similarly, the IACR was computed by adding the sum of the iso atomic clusters of Pt and the iso atomic clusters of Pd to the same denominator as for the HACR. Therefore, it can be defined as:

$$IACR = \sum_n \left[\frac{Pt_n^+ + Pd_n^+}{Pt^+ + Pd^+} \right] \quad \forall n = 2, 3, \dots$$

The IACR, like the RCR, serves as a verification tool to discern whether variations in the HACR are indeed indicative of atomic interactions within the clusters or merely artefacts of the overall yield. A high IACR would suggest a greater occurrence of iso atomic clusters in the sample, which could mean a lower level of atomic-scale interaction between different elements in the alloy, providing an inverse trend similar to the RCR.

Those two metrics have been applied to the ternary, quaternary and quinary samples, adopting the same Bi_5^+ primary ion and positive mode as in previous analyses. This consistent approach was selected as this primary ion and mode have exhibited the best yield for high-mass ions. The results of the HACR and IACR values are graphically depicted in Figures 7.4, while Table 7.3 provides a detailed representation of the mean values alongside their standard deviation and the results of the ANOVA analysis for each individual cluster. For the HACR, a graphical representation of the mean composition of each cluster in the HACR is provided in Figure 7.5.

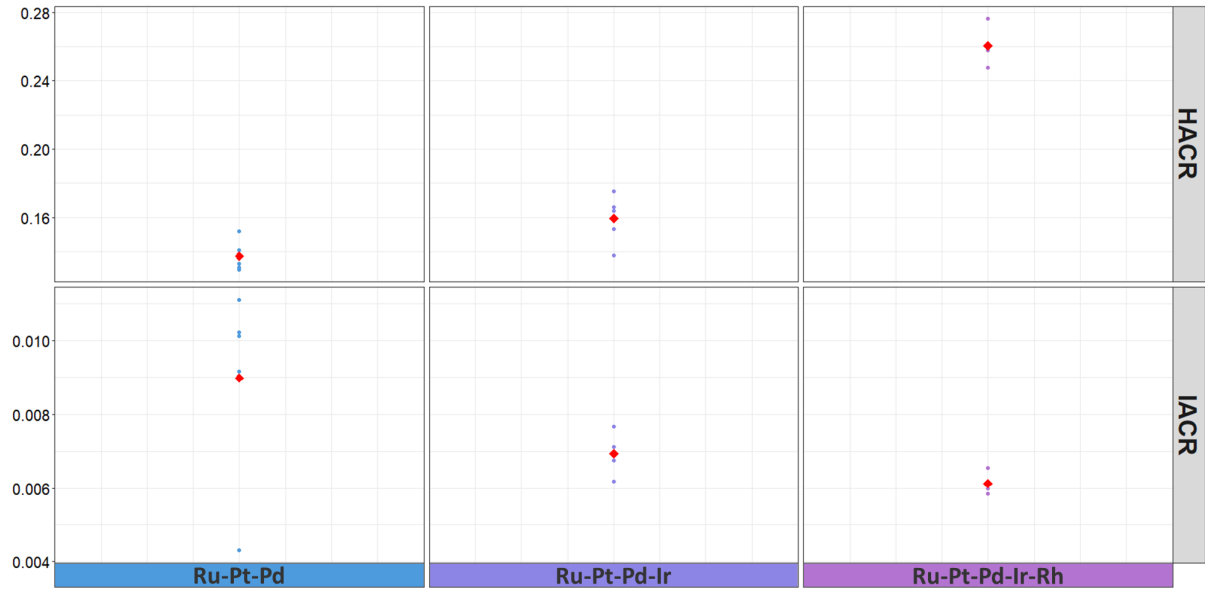


Figure 7.4: Hetero and Iso Atomic Cluster Ratio across the three samples in positive mode with Bi_5^+

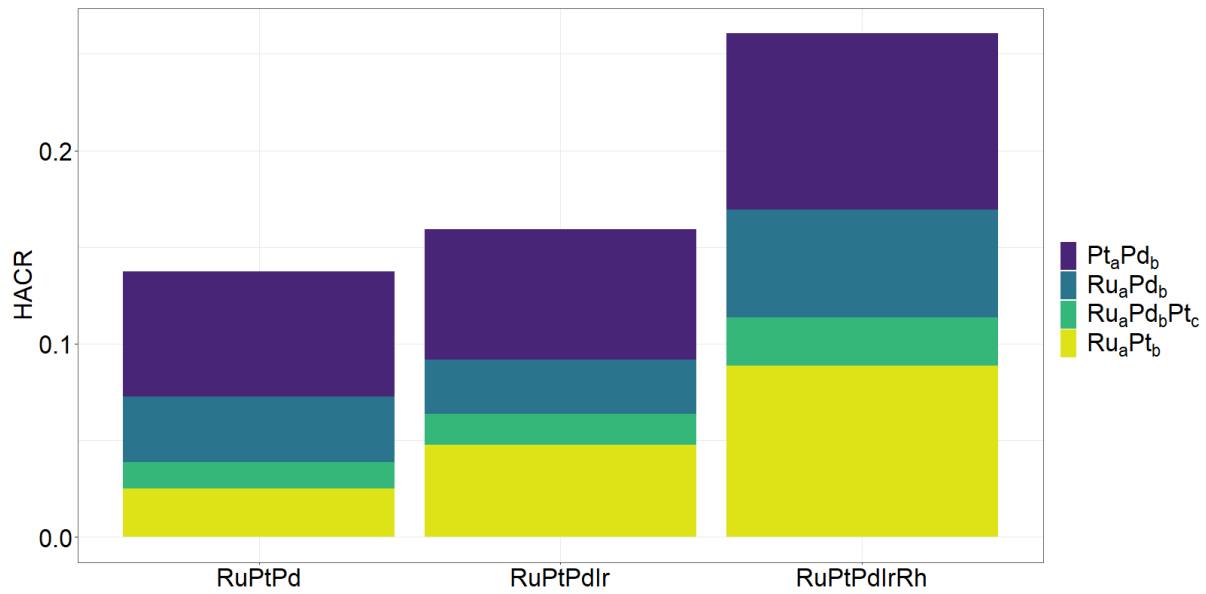


Figure 7.5: Mean composition of Hetero Atoms Clusters Ratio across the 5 acquisitions made in Bi_5^+ in positive mode.

Table 7.3: Mean and standard deviation values of all the different cluster composition of the HACR with Bi_5^+ in negative mode. Note that all the values displayed in the first sub table are multiply by 10^3 from their real value

Sample (10^{-3})	HACR				IACR
	Ru _a Pd _b	Ru _a Pt _b	Pt _a Pd _b	Ru _a Pt _b Pd _c	Pt _n +Pd _n
Ru-Pt-Pd	33.7 ± 2.1	24.9 ± 1.6	63.9 ± 6.4	13.5 ± 1.2	9.0 ± 2.7
Ru-Pt-Pd-Ir	27.7 ± 3.6	47.3 ± 6.1	67.0 ± 6.4	15.7 ± 1.8	6.9 ± 0.5
Ru-Pt-Pd-Ir-Rh	88.0 ± 1.5	55.2 ± 4.1	90.4 ± 8.4	24.6 ± 2.8	6.1 ± 0.4

ANNOVA results (-)

DF numerator	2	2	2	2	2
DF denominator	10	10	10	10	10
F _{obs}	73.1	228.8	15.7	35.1	50.1
p-value	1.1×10^{-6}	4.5×10^{-9}	8.3×10^{-4}	3.0×10^{-5}	6.2×10^{-6}
η^2	0.936	0.979	0.758	0.875	0.909

From the information presented in Figures 7.3, all the clusters examined for the HACR or the IACR contribute significantly. However, the extent of their contributions varies significantly. Despite these differences, a discernible pattern is observed with the HACR

generally increasing along with the number of components in the alloy. Simultaneously, an inverse pattern is seen with the IACR, which tends to decrease as the number of alloy components increases. This reciprocity in the trends of HACR and IACR further validates the results, indicating a genuine enhancement in atomic interactions with greater compositional complexity. Thus, the observations collectively suggest that an increase in the number of alloy components increases the degree of atomic mixing.

Interestingly, the contribution from the Ru_aPd_b^+ cluster does not follow this upward trend. Instead, it initially decreases in the Ru-Pt-Pd-Ir alloy before increasing again in the five-element HEA. This anomaly could potentially be attributed to the addition of iridium in the Ru-Pt-Pd-Ir alloy, which may negatively impact the interaction between the Ru and Pd elements. However, the introduction of Rh in the five-element HEA appears to mitigate this effect, as evidenced by the subsequent increase in the contribution of the cluster Ru_aPd_b^+ .

7.5 Oxidation Ratio

As mentioned in Section 1.4, HEAs often display superior oxidation resistance compared to conventional alloys. In an attempt to quantify this trait using ToF-SIMS data, a new metric, the Oxide Ratio (OR), was formulated. The OR is defined as the ratio of the sum of all oxide ions to the sum of all primary ions. For example, for the full five-component HEA, the OR is expressed as :

$$OR_{\text{Ru-Pt-Pd-Ir-Rh}} = \sum_x \left[\frac{\text{RuO}_x^- + \text{PtO}_x^- + \text{PdO}_x^- + \text{IrO}_x^- + \text{RhO}_x^-}{\text{Ru}^- + \text{Pt}^- + \text{Pd}^- + \text{Ir}^- + \text{Rh}^-} \right] \quad \forall x = 1, 2, \dots$$

This ratio represents the propensity of the metal components of the alloy to form oxides. Furthermore, by individually examining each component in the numerator, it becomes possible to discern which metallic component is most susceptible to oxidation and how varying chemical conditions may influence this propensity. The OR was thus applied to all samples in the negative ion mode, as this mode is known to yield oxide ions more effectively.

The OR (made up of its oxide components, namely RuO_x , PtO_x , PdO_x , IrO_x , RhO_x) was applied to all spectra with Bi_5^+ as the primary ion. This choice was guided by consistency, echoing the strategy used during the BCR analysis. Subsequently, the mean values of the OR and individual oxide components were calculated for each alloy. These data are conveniently tabulated in Table 7.4 and graphically represented in Figure 7.6. Similarly to BCR, the statistical significance of the OR was assessed using an ANNOVA test, and the result can be found in Table 7.5.

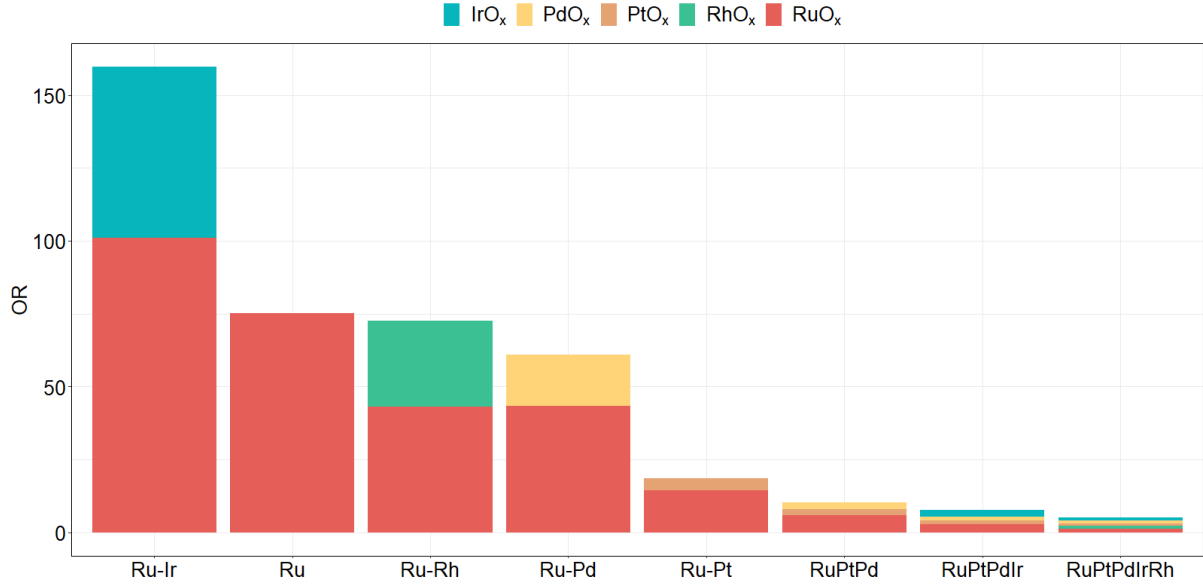


Figure 7.6: Mean composition of the oxide ratio across the 5 acquisitions made in Bi_5^+ in positive mode.

The results of the OR analysis offer some compelling insights. A marked decrease in the OR is observed when the number of elements in the alloy reaches three, suggesting a correlation between oxidation resistance and the number of components of the alloy. These findings are statistically reinforced by the p-value and η^2 values presented in Table 7.5. In particular, the quinary alloy (which complies with the definition of a HEA) shows the lowest OR value, confirming – at the atomic level – a property that is well documented [131]–[133].

Table 7.4: Mean and standard deviation values of all the different oxide composition of the Oxidation Ratio with Bi_5^+ in negative mode.

Sample (-)	RuO _x	PtO _x	PdO _x	IrO _x	RhO _x
Ru	89.20 ± 24.31	-	-	-	-
Ru-Pt	14.30 ± 4.74	4.24 ± 0.97	-	-	-
Ru-Pd	35.40 ± 3.87	-	14.50 ± 1.24	-	-
Ru-Ir	101.10 ± 6.72	-	-	58.70 ± 3.97	-
Ru-Rh	43.20 ± 4.94	-	-	-	29.40 ± 2.57
Ru-Pt-Pd	5.74 ± 1.06	1.83 ± 0.34	2.26 ± 0.21	-	-
Ru-Pt-Pd-Ir	2.70 ± 0.33	1.41 ± 0.17	1.07 ± 0.12	2.44 ± 0.45	-
Ru-Pt-Pd-Ir-Rh	1.14 ± 0.01	0.85 ± 0.05	0.79 ± 0.04	1.18 ± 0.04	0.85 ± 0.04

An interesting aspect to note from the data is the higher prevalence of oxidation in the Ru-Ir, Ru, and Ru-Rh samples. These three alloys tend to be the most oxidised among

the group. This observation aligns with the inherent chemical characteristics of Ru, Ir, and Rh. These elements are known to be highly oxophilic or have a more pronounced tendency to form oxides than Pd or Pt. Specifically, the oxophilicity values for Ru, Ir, and Rh are 0.4, 0.4, and 0.3 respectively, which are significantly higher than those for Pt and Pd, which are 0.1 and 0.0 respectively [134]. This greater propensity to form oxides may be contributing to the elevated levels of oxidation observed in these alloys.

Table 7.5: Resulting table of the ANNOVA test on the OR for the all samples with Bi_5^+ in negative mode.

DF numerator	DF denominator	F_{obs}	p-value	η^2
7	13	20.294	1.66×10^{-6}	0.926

Another intriguing aspect of the data is the higher proportion of Ru oxides in the Ru-Ir alloy compared to the pure Ru alloy, although the latter has a higher percentage of Ru (100% vs. 80% in the Ru-Ir alloy). This suggests that the presence of Ir enhances the oxidation of Ru. However, another explanation could be attributed to statistical variation. With a standard deviation of 24.3 in the Table 7.4, the measurement of Ru oxides is the most variable among all values. Therefore, the seemingly "low" value of 89.2 for Ru oxides in the pure Ru sample could be the result of this significant statistical variation.

Finally, analysis of the oxide distribution as the alloy complexity increases reveals an intriguing pattern. As elements are added to the alloy, there is a trend towards a more uniform distribution of different metal oxides. For instance, the proportion of IrO_x decreases from 36% in the Ru-Ir alloy to 33% in the Ru-Pt-Pd-Ir alloy, and further to 24% in the full five-component HEA. This trend suggests that as the number of components in the alloy increases, the distribution of oxides increasingly mirrors the proportion of the respective components in the alloy (detailed in Table 3.1).

CO Oxidation Results

In the CO oxidation process, CO molecules first adsorb onto an active site on the catalyst surface, forming adsorbed CO, symbolised as $\ast\text{CO}$. Simultaneously, O_2 molecules adsorb to a different active site to form adsorbed oxygen, represented as $\ast\text{O}_2$.



For the oxidation of CO to CO_2 to occur, these active sites need to be close enough for the transfer of an oxygen atom from $\ast\text{O}_2$ to $\ast\text{CO}$, thereby transforming CO into CO_2 .



These reactions indicate that the spatial arrangement and proximity of these active sites significantly influence the oxidation process. The overall reaction can be represented as follows:



CO oxidation tests were performed on all samples to evaluate their catalytic abilities involving this chemical reaction.

The quantity of CO_2 produced by each sample under a flow of CO and O_2 in He was monitored during a temperature ramp. From the maximum CO_2 signal obtained under these conditions, the percentage of CO oxidised at any given temperature could be calculated. Traditionally, the T°_{50} metric, defined as the temperature at which 50% of CO is oxidised, is usually used as a benchmark [135]–[137] and thus will be used to compare the results of this work with those from the scientific literature. However, due to differences in sample masses placed in the reactor (Table 5.1), the T°_5 metric, defined as the temperature at which 5% of CO is oxidised, was also used to allow more reliable comparisons between samples from this work.

In these tests, the mass spectrometer monitored three primary species: O_2 (32 uma), CO_2 (48 uma), and $\text{CO} + \text{N}_2$ (28 uma). To compensate for potential variations in gas pressure within the reactor, the raw signals of these species were normalised to the carrier gas signal. For tests conducted last year, He served this normalising function. However, for the tests carried out this year, Ar was introduced. Owing to its greater molecular weight compared to that of helium, Ar stabilises the vacuum created by the pumping system and hence was used as the normalising standard for this year's samples.

Comprehensive graphs showcasing the three signals for each sample are available in the Appendix A.3. However, for a concise summary, the plots showing the normalised CO_2 signal for all samples are provided in Figure 8.1.

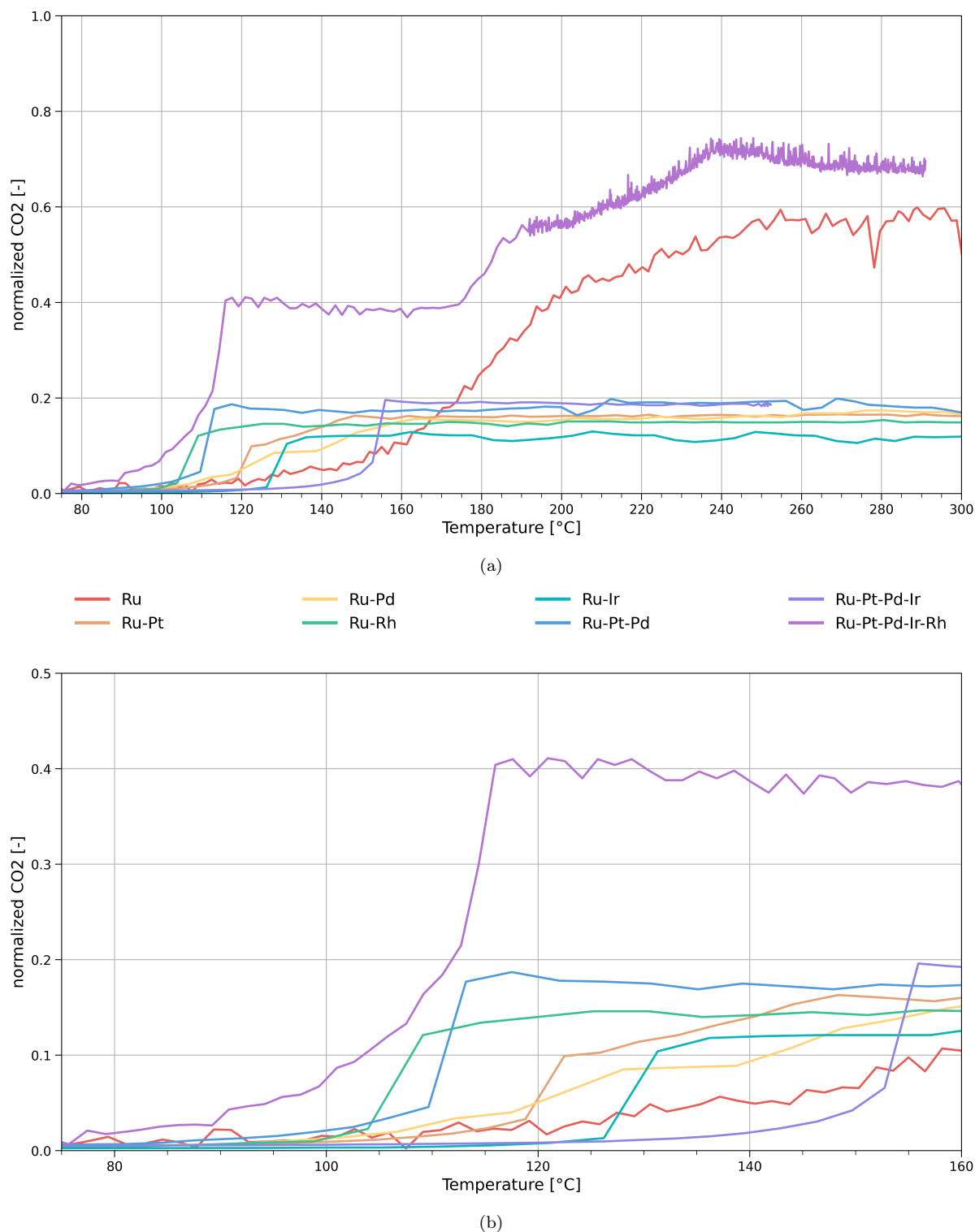


Figure 8.1: Full range and zoomed plot of normalised signal of CO_2 for all samples.

Table 8.1: T_{50}° and T_5° values of alloys for CO oxidation.

Sample	T_{50}° (C°)	T_5° (C°)
Ru	179	112
Ru-Pt	122	97
Ru-Pd	128	96
Ru-Rh	109	94
Ru-Ir	131	121
Ru-Pt-Pd	113	88
Ru-Pt-Pd-Ir	156	126
Ru-Pt-Pd-Ir-Rh	116	91

Observations of the T_{50}° values from Table 8.1 reveal that binary alloys systematically exhibit lower T_{50}° values in comparison to the pure elements (Ru, Pd, Pt, Rh, Ir) impregnated on Alumina (Al_2O_3), according to data from Akil *et al.* [135] with T_{50}° values of 268, 194, 164, 236, and 236 °C respectively. However, the differences in experimental conditions between this work and the cited study must be kept in mind when interpreting these comparisons.

However, when comparing binary alloys, the Ru-Ir sample stands out with a T_5° value of 121°C. This is significantly higher than the other binary alloys, which have T_5° values around 95 °C, and even exceed the T_5° value of the pure Ru sample, which is 112 °C. T_5° values, a different trend emerges as the complexity of the alloy increases. The incorporation of Ir into the Ru-Pt-Pd alloy results in an increase in the T_5° value from 88 °C to 126 °C.

For the non-binary alloys, the ternary Ru-Pt-Pd alloy exhibits an even lower T_5° value of 88°C, which is, intriguingly, lower than the T_5° of the full five elements HEA, which stands at 91°C. However, the introduction of Ir into this ternary alloy to form the quaternary Ru-Pt-Pd-Ir alloy results in a significant increase in the T_5° value, reaching 126°C, the highest value among all alloys tested. Interestingly, the inclusion of Rh into the quaternary alloy to form the HEA induces a reduction in the T_5° value to 91°C, nearly reversing the impact of the addition of Ir. However, the mechanism behind these considerable fluctuations in T_5° values requires further investigation and discussion.

In this section, the teachings of the results presented above will be used to tentatively understand some of the most interesting effects related to the atomic mixing in alloys and high entropy alloys. Special focus will be placed on the possible correlations between some of the indicators expressed from ToF-SIMS and the catalytic performance in CO oxidation.

9.1 Discussion on Binary Alloys

From the results of the Oxidation Ratio, Ir shows a strong tendency to form oxides, thus attracting oxygen to it. Conversely, the small Binary Cluster Ratio value of the Ru-Ir sample indicates that Ir does not tend to mix extensively with Ru. Ruthenium, on its side, is recognised for its favourable bond with CO [138], [139]. This propensity leads to the expectation that in this Ru-Ir sample, a significant proportion of the active sites hosting carbon monoxide (*CO from Equation 8.1) will likely be composed of Ru atoms. Likewise, due to the strong oxidation tendency of Ir, a considerable part of the active sites that host oxygen (*O from Equation 8.2) would be on Ir atoms.

It is important to note that ruthenium also exhibits a tendency to form oxides, as evidenced in the Oxidation Ratio results. Therefore, Ru would indeed form active sites with O. However, the high affinity of Ir for oxygen means that Ir competes with Ru for O. Consequently, this competition could reduce the oxygen available to Ru for the oxidation reaction.

The spatial segregation between Ru and Ir as indicated by the low BCR value, combined with their preferential binding to carbon monoxide and oxygen, respectively, may lead to a scenario in which there is a significant spatial distance between carbon monoxide at the *CO site and oxygen at the *O site. This is of considerable importance, as the proximity of these two active sites is crucial for effective catalytic activity, as mentioned in Chapter 8. Consequently, the oxidation reaction is less efficient, has a lower overall oxidation activity, and a higher T°_5 value than pure Ru for CO oxidation.

On the other hand, according to the OR results, Rh also manifests a strong tendency to form oxides and, hence, attracts oxygen. However, the BCR value shows better mixing between Rh and Ru. This improved mixing could reduce the likelihood of creating localised "oxygen traps" that can hinder access to O for the CO oxidation reaction. As a result, more oxygen is readily available for CO oxidation to occur, resulting in superior catalytic

activity demonstrated by the lower T_5° value observed for the Ru-Rh sample, compared to pure Ru. An illustrated comparison of those two scenarios is provided in Figure 9.1.

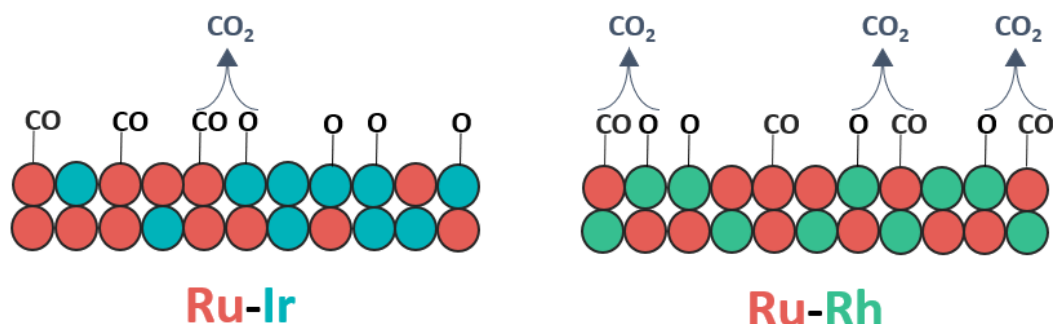


Figure 9.1: Schematic illustration of the proposed CO oxidation reaction for the relatively not well mixed Ru-Ir sample and the relatively well mixed and Ru-Rh sample. Note here the "oxygen traps" in right side of the Ru-Ir sample.

Similarly, the samples of Ru-Pd and Ru-Pt exhibit very similar T_5° values (96 °C for Ru-Pd and 97 °C for Ru-Pt) to those of the Ru-Rh alloy. However, the OR reveals that both Pd and Pt have a lower propensity to form oxides compared to the propensity of Rh. Among the two, Pd has a higher inclination to form oxides compared to Pt. This pronounced tendency in the Ru-Pd sample may lead to the formation of the so-called oxygen traps, which have been mentioned above, thereby limiting its availability for the CO oxidation reaction.

In contrast, Pt's lesser inclination toward forming oxides reduces the likelihood of these "oxygen traps" in the Ru-Pt sample, making oxygen more accessible for the CO oxidation process.

The similarity between the T_5° values despite the differences in oxygen attraction can be rationalised by considering the Binary Cluster Ratio. The Ru-Rh sample exhibits a higher BCR value than the two others, indicating a relative better mixing between Ru and Rh, which may mitigate the impact of "oxygen traps". The same applies to the Ru-Pd sample, which has a higher BCR value than Ru-Pt, compensating for the negative impact of oxygen adhesion on the T_5° values.

In contrast, the relatively less mixed Ru-Pt sample might be less affected by heterogeneity, as Pt does not tend to sequester oxygen as strongly as Pd. Therefore, the disparity in oxygen attraction does not significantly affect oxygen availability for the * CO sites.

In summary, the interaction between the contrasting tendencies of these two factors - the Oxidation Ratio and Binary Cluster Ratio - seems to balance out, leading to similar observed T_5° values for these three samples.

9.2 Discussion on Three-, Four-, and Five-Component Alloys

The three-component alloy presents some intriguing characteristics that deserve specific attention. It exhibits the smallest T_5° value of all alloys, reaching 88 °C. It is also the only alloy to combine a Faced Centered Cubic phase of Pt and Pd with a Hexagonal Close Packed phase of Ru.

From the High Atomic Cluster Ratio, a high presence of Pt_aPd_b clusters is observed, suggesting that Pt and Pd are more closely arranged in this sample. This proximity is likely to be within the FCC phase, leading to the inference that the concentration of Pt and Pd into this specific phase significantly benefits the CO oxidation reaction.

Moreover, the literature indicates that Pt has the tendency to bond with CO [140], [141], similar to Ru. Considering that Pt also has the ability to bond with CO, it could form $*CO$ active sites in the FCC phase, analogous to Ru in other alloys. While Pd would form $*O$ active sites within this arrangement. The proximity of $*CO$ to $*O$ in the FCC phase could create a favourable environment for CO oxidation.

For the four-component alloy, with the addition of Ir into the alloy, the HCP Ru phase disappears, resulting in only one FCC phase that matches those of Pt, Pd, and Ir. The similarity in the value of the Pt_aPd_b cluster in the HACR for the Ru-Pt-Pd-Ir sample with the Pt_aPd_b cluster value of the Ru-Pt-Pd one leads to the hypothesis that Ru and Pt still exist in the same FCC phase together, while Ir remains in its own separate FCC phase. The stronger oxidation attraction of Ir appears to capture oxygen, making it less available for Pd to form a $*O$ site near a $*CO$ site formed by Pt. This negative impact on the CO Oxidation reaction can be observed at the relatively high T_5° value of 126°C.

Table 9.1: Mean and standard deviation values for the different proportions of oxide components in the Oxidation Ratio with Bi_5^+ in negative mode.

Sample (%)	RuO_x	PtO_x	PdO_x	IrO_x	RhO_x
Ru-Pt-Pd	58.4 ± 12.7	18.6 ± 4.1	23.0 ± 3.4	-	-
Ru-Pt-Pd-Ir	35.4 ± 5.1	18.5 ± 2.7	14.0 ± 1.9	32.0 ± 6.4	-
Ru-Pt-Pd-Ir-Rh	23.7 ± 0.5	17.7 ± 1.1	16.4 ± 0.9	24.5 ± 0.9	17.7 ± 0.9

This claim is supported by the percentage values of each oxide component in the Oxidation Ratio. Table 9.1 shows that the proportion of PdO_x clusters for the Ru-Pt-Pd sample is 23% of the five metal oxides in the OR, whereas for the Ru-Pt-Pd-Ir sample, it drops to 14%. This indicates that the addition of Ir indeed influences the proportion of Pd that forms oxide and thus has a potential impact on the formation of $*O$ site for the

CO Oxidation reaction.

In the case of the five-component HEA, the addition of Rh presents intriguing results. Higher HACR values suggest a more cohesive mixing of the components within the alloy. The analysis of the proportion of oxides in the OR further reveals a more balanced distribution among the five constituent elements. Specifically, the proportion of PdO_x clusters increases from 14% to 16%, while that of IrO_x decreases from 32% to 24%. These changes suggest a mitigation of the "oxygen traps" effect previously caused by Ir in the quaternary alloy. A more harmonious interaction between the elements occurs, resulting in a closer placement of the CO and O active sites. This enhanced proximity promotes better CO oxidation activity, leading to a lower T_5° value of 91°C. This value represents a notable decrease relative to the Ru-Pt-Pd-Ir sample.

Overall, in alloys with three or more components, it is hypothesised that the CO Oxidation reaction primarily takes place at the active sites formed by Pt and Pd. The presence of Ir, with its strong oxygen attraction combined with the relative lack of mixing, might give rise to what have been termed "oxygen traps", where oxygen is concentrated, limiting its availability for the formation of active sites for CO oxidation. It is important to emphasise that these conclusions remain speculative, contingent upon the assumptions and interpretations made from the data, and further investigation may be needed to validate these insights.

Part V

Conclusions and Outlooks

This Master thesis aimed to gain a deeper understanding of High Entropy Alloys at the atomic scale, investigating the atomic alloying formed between the constituent elements and exploring their oxidation properties.

The binary samples XRD diffractograms revealed that the mean crystallite sizes for Ru, Ru-Pt, Ru-Pd, Ru-Rh, and Ru-Ir are 3, 4.5, 6, 9 and 9 nm, respectively. These results indicate that the incorporation of Pt, Pd, Ir, or Rh into the Ru-based alloys significantly influences the crystallite size. The effect's intensity varies depending on the added element and can be classified in the following order: $\text{Ir} \simeq \text{Rh} > \text{Pd} > \text{Pt}$.

Furthermore, the analysis revealed that the mean crystallite size of around 3 nm of the full five-element HEA was already achieved with the four-element Ru-Pt-Pd-Ir alloy.

Comparison of the diffractograms of Ru and the binary samples with the theoretical crystalline phase of their constituents provided further insight. The addition of another element to the Ru base appears to increase the distance between the crystal layers while preserving the HCP crystal structure. For the three-element Ru-Pt-Pd alloy, two distinct phases were observed. One HCP phase of the Ru and another FCC phase matching those of Pt and Pd.

For the four-element Ru-Pt-Pd-Ir alloy, only one FCC phase matching the ones of the Pt, Pd and Ir was observed. A similar observation applies to the five-element HEA, where the FCC phase is consistent with the individual phases of Pt, Pd, Ir and Rh.

The results of the Principal Component Analysis performed on the ToF-SIMS data for the quaternary alloys revealed specific insights into the experimental conditions required for optimal results. Specifically, to achieve the best yield of the high-mass clusters, the utilisation of primary ions Bi_5^+ or Bi_3^{++} must be used.

Based on these insights, five specific metrics were formulated to analyse the ToF-SIMS data from the samples.

The first two metrics, known as the Binary Cluster Ratio and Ruthenium Cluster Ratio, were applied exclusively to binary samples. These metrics were tasked with measuring the degree of mixing between the two components of an alloy. This analysis showed that the two constituents of a binary alloy do not mix equally. The hierarchy of mixing among the binary alloys was identified in the order $\text{Ru-Rh} > \text{Ru-Pd} > \text{Ru-Pt} > \text{Ru-Ir}$.

The subsequent two metrics, named the Hetero Atomic Cluster Ratio and the Iso Atomic

Cluster Ratio, were specifically applied to the three-, four-, and five-component alloys. These metrics were designed to measure the degree of global atomic mixing among all the components of the alloy. A correlation was found between the number of components and the degree of mixing at the atomic scale in the samples. Specifically, the degree of atomic mixing increased with the addition of more components.

The final metric, called the Oxidation Ratio, was applied to all samples and was designed to represent the propensity of the metal components of the alloy to form oxides. A significant decrease in the Oxidation Ratio was observed with the addition of more components, along with a more homogeneous distribution of the proportion of oxides among components.

CO oxidation tests were also performed on all samples to evaluate their reactivity. The ordering of the T_5° values obtained from these tests, from highest to lowest, is Ru-Pt-Pd-Ir > Ru-Ir > Ru > Ru-Pt $\simeq$ Ru-Pd $\simeq$ Ru-Rh > Ru-Pt-Pd-Ir-Rh > Ru-Pt-Pd.

Finally, based on CO oxidation tests and insights from the five metrics, two central hypotheses were proposed.

First, it is suggested that the CO oxidation reaction predominantly takes place at sites containing Pt and Pd atoms. The close proximity of these two elements within the FCC phase of the ternary alloy is believed to significantly enhance the CO oxidation reaction.

The second hypothesis relates to the role of Ir. Specifically, when Ir is alloyed in a relatively low-mixed environment, it may lead to the formation of "oxygen traps." These traps could sequester most of the oxygen within the alloy, consequently limiting its availability for CO oxidation.

Interesting outlooks emerge from the conclusions of this study to investigate HEA in ToF-SIMS.

The need for quantifying the atomic mixing of an alloy with ToF-SIMS presents a complex challenge because of the lack of consistency of secondary ion yields across samples. To navigate this, one approach could be to conduct experiments with alloys of known atomic mixing, synthesised under the same conditions. These known values could be correlated with the ToF-SIMS data, which would establish benchmarks for comparison with other alloys.

Furthermore, the study of different HEA samples with steady composition but varying entropy might lead to isolating the mixing effect, providing insight into how individual elements interact within the alloy. This refined understanding could reveal the nuanced role entropy plays in determining the properties of the alloy, such as its reactivity, structure, and oxidation resistance.

The hypotheses drawn from the CO Oxidation performances need further investigation as well. Analysing a Pt-Pd sample could help determine whether the theory that CO oxidation occurs mainly with Pd and Pt holds true. This analysis would either confirm or challenge the understanding developed from this study.

In addition, using techniques such as Atom Probe Tomography, which offers both 3D imaging and atomic scale chemical composition measurements, has already been used on HEAs [142], [143] and could provide more nuanced insights into the reaction sites and confirm or infirm the just-mentioned Pt/Pd hypothesis as well as the proposed phenomenon of "oxygen traps".

Part VI

References and Appendices

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A.1 PCA

The data are collected in a matrix $\mathbf{X}$ with I rows ($i = 1, \dots, I$; here ToF-SIMS spectrum) and J columns ($j = 1, \dots, J$; here m/z bins), therefore of size $I \times J$. Individual variables (columns) of $\mathbf{X}$ are denoted by $\mathbf{x}_j$ ($j = 1, \dots, J$) and are all vectors in the I -dimensional space. A linear combination of those variables can be written as

$$\mathbf{t} = p_1\mathbf{x}_1 + \dots + p_J\mathbf{x}_J \quad (\text{A.1})$$

Here $\mathbf{t}$ is now a new vector in the same space as the $\mathbf{x}_j$ variables (because it is a linear combination of these). In matrix notation, this becomes:

$$\mathbf{t} = \mathbf{X}\mathbf{p} \quad (\text{A.2})$$

With $\mathbf{p} = [p_1, \dots, p_J]$ and p_j being the coefficient for the j^{th} variable. Since the variation of the matrix $\mathbf{X}$ can be seen as information, it seems reasonable to have as much as possible of that variation also in $\mathbf{t}$. The variation within $\mathbf{t}$, represented by its statistical variance, $\text{var}(\mathbf{t})$, is maximised by choosing optimal weights $p_1, \dots, p_J$. However, arbitrarily increasing an optimal weight can significantly inflate the variance of $\mathbf{t}$. Hence, to ensure a valid problem, the weights need to be normalised, which is achieved by requiring their norm (the sum of squared values) to be one, symbolised by $\|\dots\|$. Using equation A.2 and $\text{var}(\mathbf{t}) = \mathbf{t}^T\mathbf{t}$, the formally stated problem evolves as follows.

$$\max_{\|\mathbf{p}\|=1} \{\text{var}(\mathbf{t})\} = \max_{\|\mathbf{p}\|=1} \{\mathbf{t}^T\mathbf{t}\} = \max_{\|\mathbf{p}\|=1} \{\mathbf{p}^T\mathbf{X}^T\mathbf{X}\mathbf{p}\} \quad (\text{A.3})$$

A more insightful evaluation of $\mathbf{t}$ summarising power is achieved by determining how well $\mathbf{t}$ can substitute for $\mathbf{X}$. This is achieved by projecting the $\mathbf{X}$ columns onto $\mathbf{t}$ and computing the residuals of that projection. This process involves regressing all variables of $\mathbf{X}$ on $\mathbf{t}$, utilising the standard regression equation.

$$\mathbf{X} = \mathbf{t}\mathbf{p}^T + \mathbf{E} \quad (\text{A.4})$$

Where $\mathbf{p}$ is the vector of regression coefficients and $\mathbf{E}$ is the matrix of residuals. Therefore, this regression equation can be used to judge the quality of the summariser $\mathbf{t}$ by calculating:

$$\frac{\|\mathbf{X}\|^2 - \|\mathbf{E}\|^2}{\|\mathbf{X}\|^2} 100\% \quad (\text{A.5})$$

This is referred to as the percentage of explained variation of $\mathbf{t}$.

If the percentage of explained variation of equation A.5 is too small with only one linear combination $\mathbf{t}_1 \mathbf{p}_1$, the extension of equation A.4 adding more linear combination leads to:

$$\mathbf{X} = \mathbf{t}_1 \mathbf{p}_1^T + \mathbf{t}_2 \mathbf{p}_2^T + \dots + \mathbf{t}_K \mathbf{p}_K^T + \mathbf{E} = \mathbf{T} \mathbf{P}^T + \mathbf{E} = \hat{\mathbf{X}} + \mathbf{E} \quad (\text{A.6})$$

where

$$\mathbf{T} = [\mathbf{t}_1, \dots, \mathbf{t}_K] = \begin{bmatrix} t_{1,1} & \dots & t_{1,K} \\ \vdots & \ddots & \vdots \\ t_{I,1} & \dots & t_{I,K} \end{bmatrix} \quad \mathbf{P} = [\mathbf{p}_1, \dots, \mathbf{p}_K] = \begin{bmatrix} p_{1,1} & \dots & p_{1,K} \\ \vdots & \ddots & \vdots \\ p_{J,1} & \dots & p_{J,K} \end{bmatrix}$$

$\mathbf{T}$ is a matrix where each column in $\mathbf{T}$ represents the k^{th} principal component (PC) for $k = 1, \dots, K$ and each row ($m = 1, \dots, M$) stands for an individual measured spectrum. These spectra are commonly referred to as objects or individual samples, so the scores in the PC highlight the relationships between these samples.

The loading vectors, which are the columns of the matrix $\mathbf{P}$ (of size $J \times K$), capture the relationships between variables, such as the mass channels in ToF-SIMS. The purpose of these loading vectors is to articulate the connections between the different variables in the data.

Thus, the element $t_{i,k}$ of the $\mathbf{T}$ matrix represents the score of the i^{th} spectra on the k^{th} PC. And the element $p_{j,k}$ of the $\mathbf{P}$ matrix is the loading the j^{th} variable for the k^{th} PC.

$\hat{\mathbf{X}}$ is a data model that can be viewed as the best rank-one estimate of the original data because it captures the largest possible variance in the data set. K represents the total number of PCs in the model. Typically, K is larger than one but much smaller than J , meaning that a considerable reduction of variables took place.

A.2 Raw Spectrum

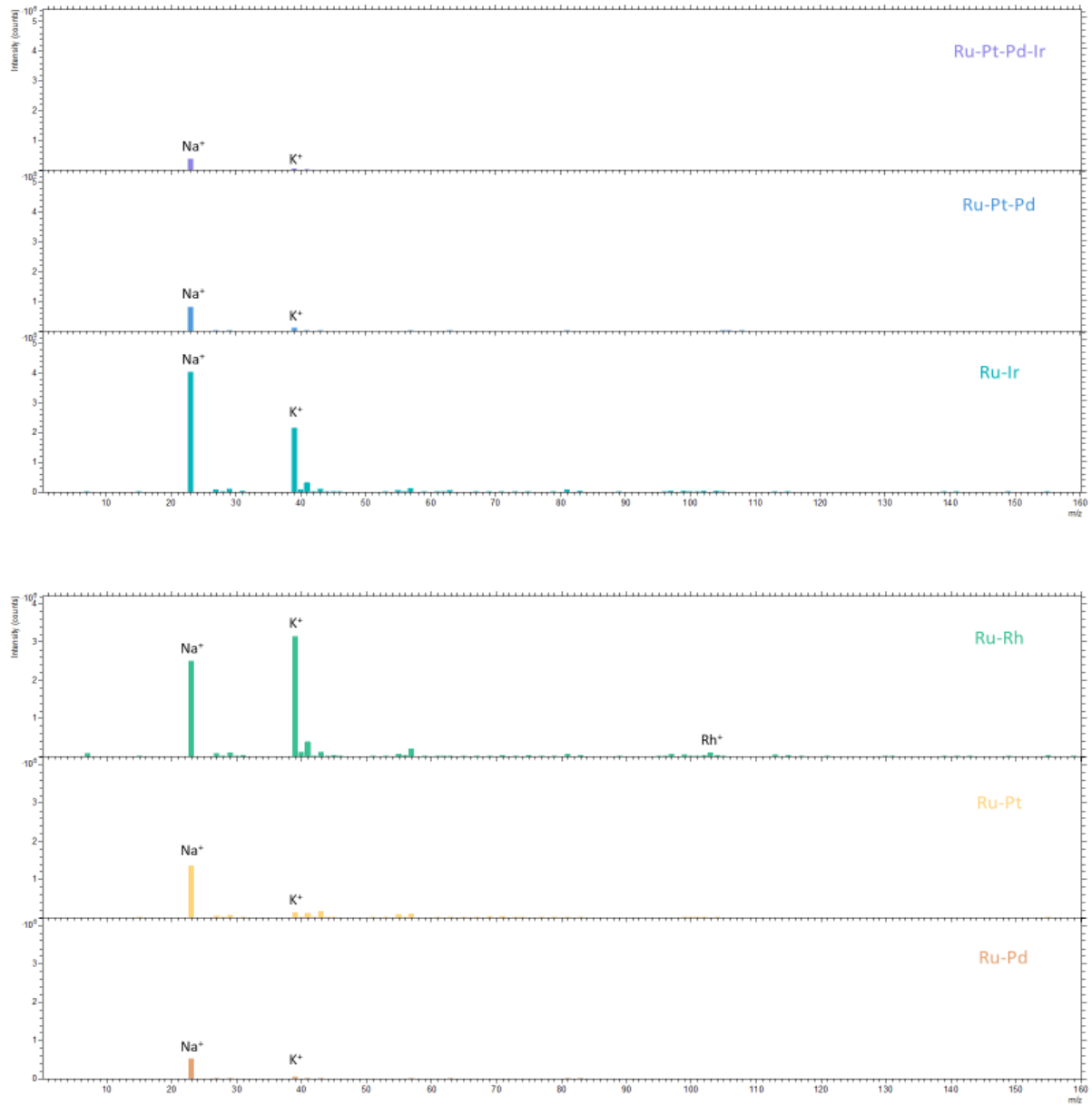


Figure A.1: Raw spectrum of the six sample analysed during this master thesis in positive mode with Bi_5^+ .

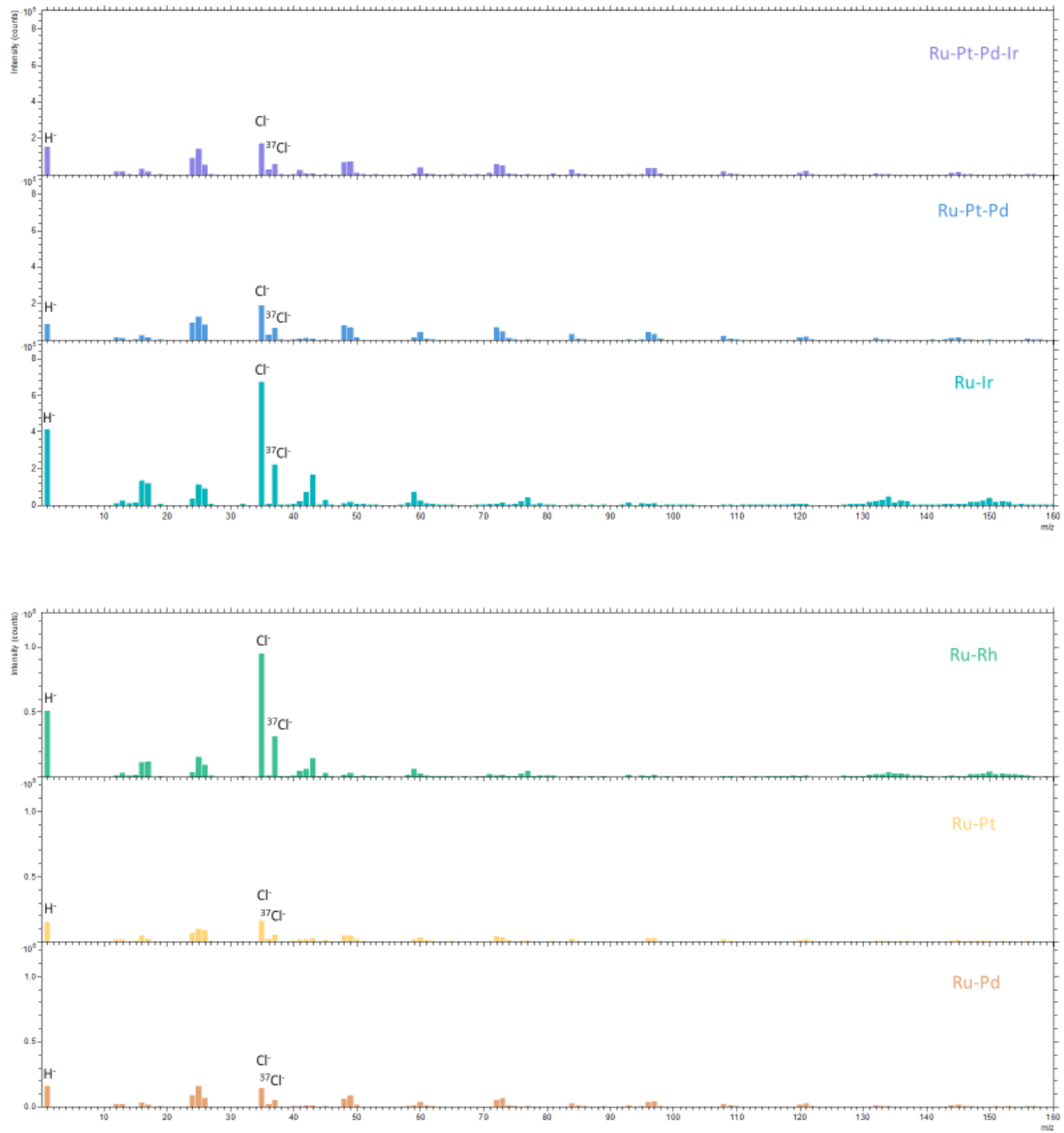
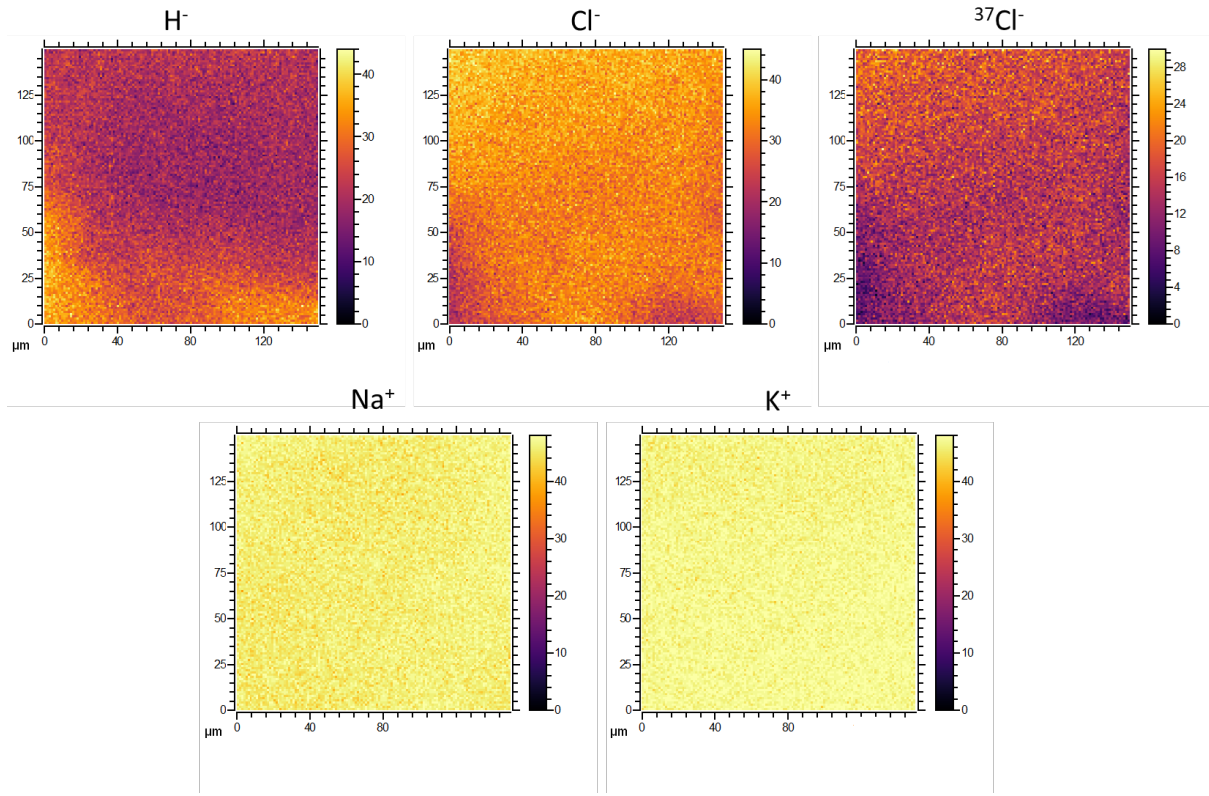
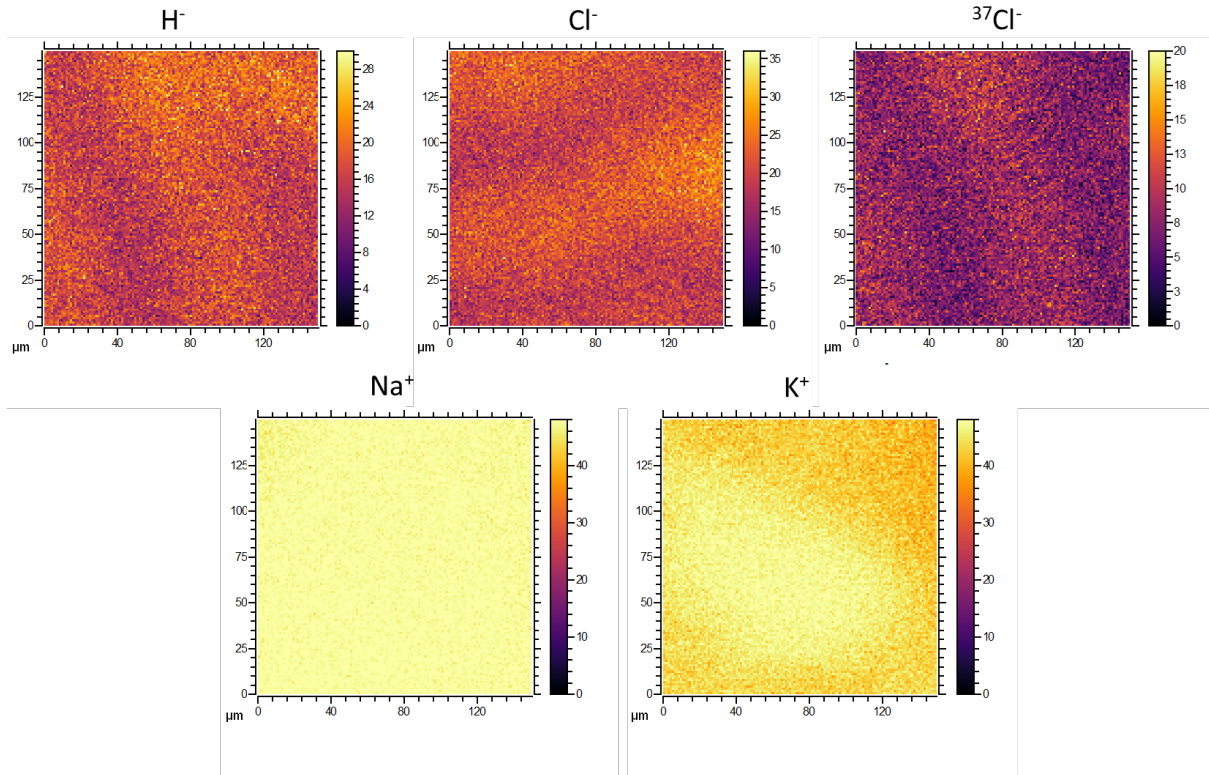


Figure A.2: Raw spectrum of the six sample analysed during this master thesis in negative mode with Bi_5^+ .



(a) Ru-Rh



(b) Ru-Ir

Figure A.3: Spatial distribution of the contaminant peaks for the Ru-Rh and Ru-Ir sample with Bi_5^+ .

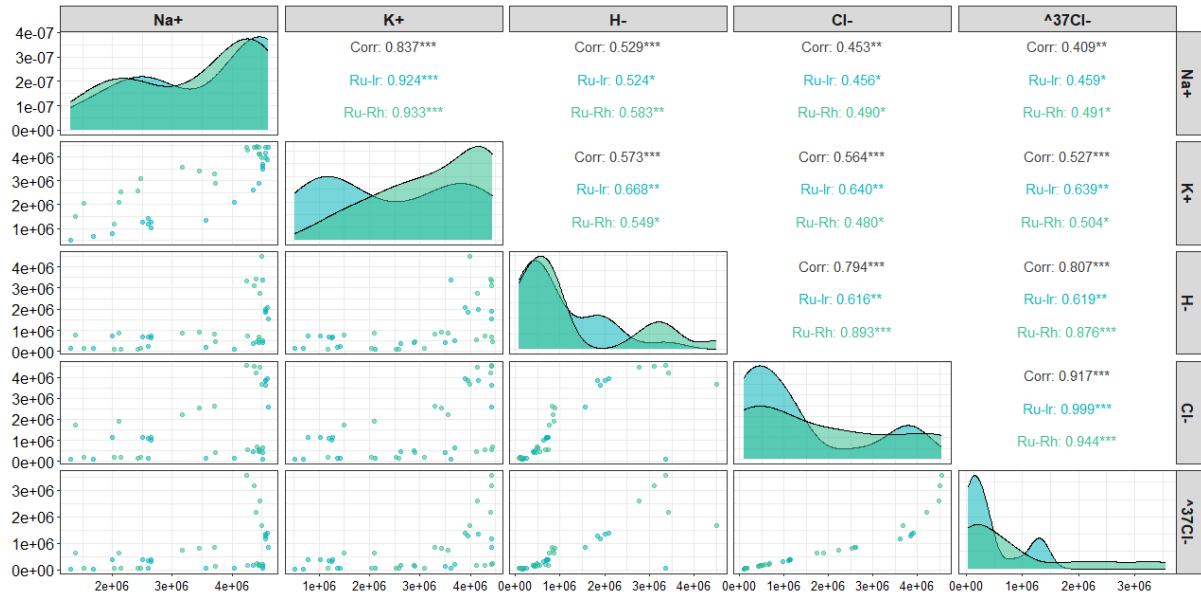
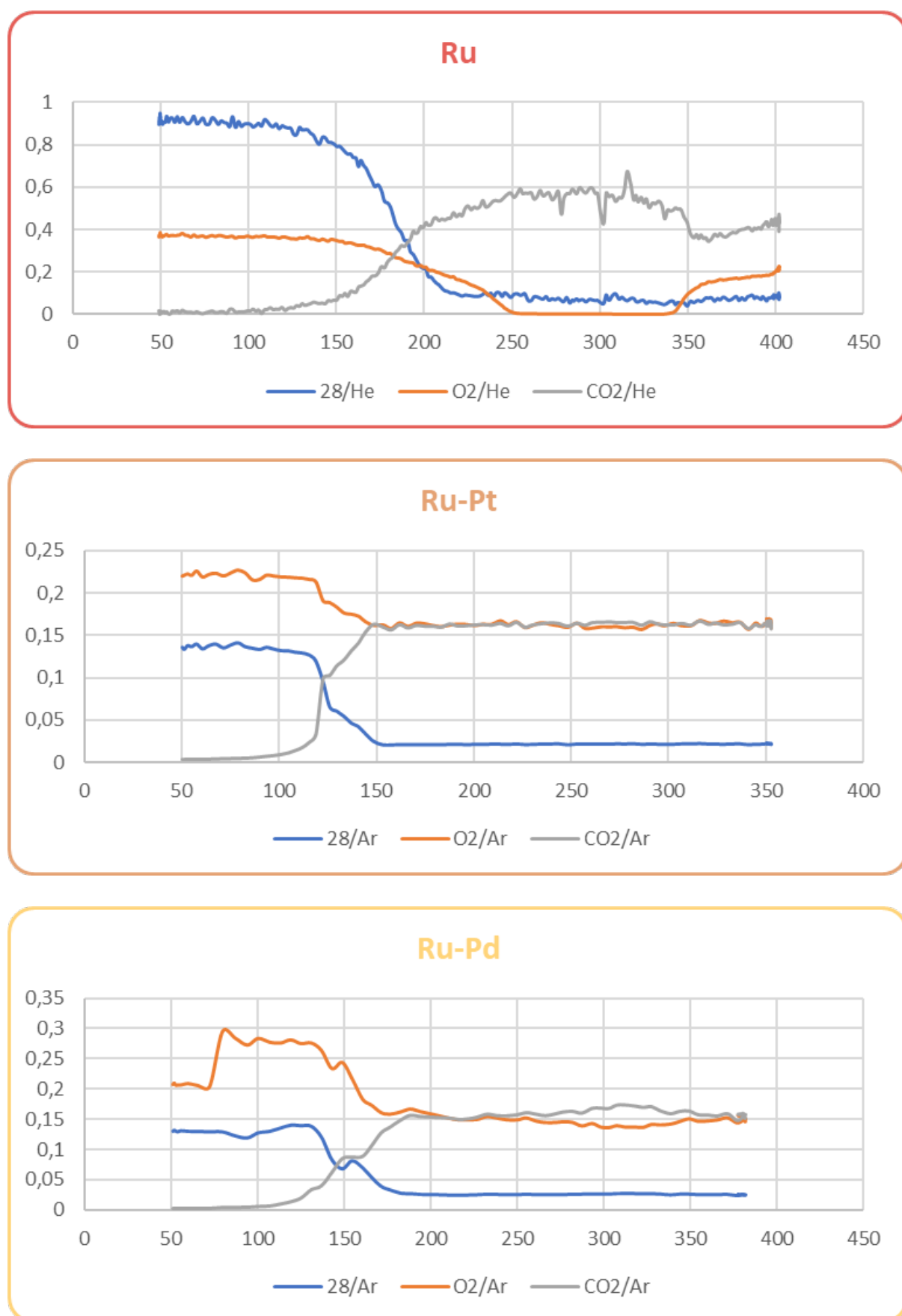
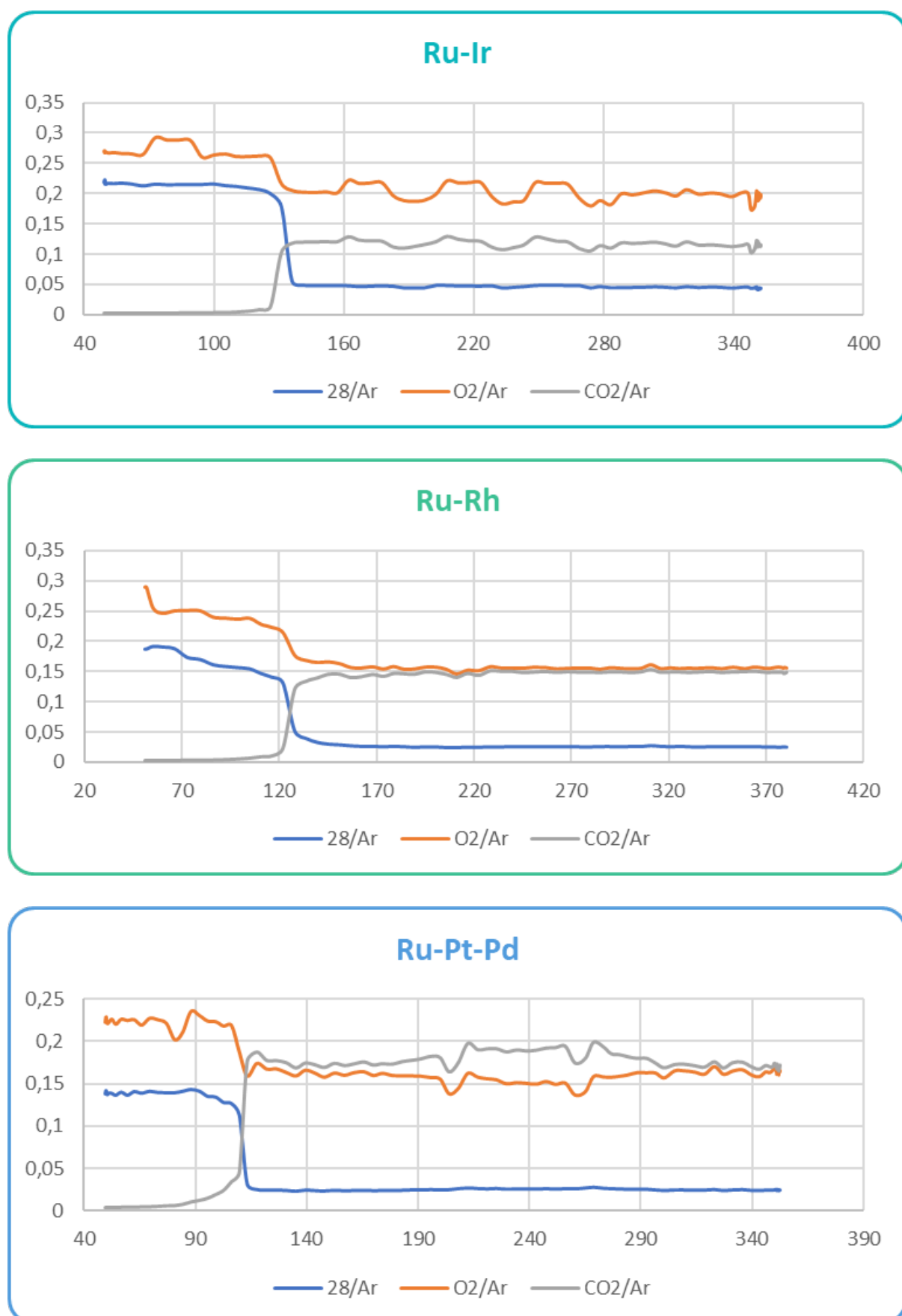


Figure A.4: Correlation plots of the Na^+ , K^+ , H^- , Cl^- , $^{37}\text{Cl}^-$ peaks for the Ru-Ir and Ru-Rh sample with all primary ions. Scatterplots of each pair of numeric variable are drawn on the left part of the figure. Pearson correlation is displayed on the right. Variable distribution is available on the diagonal.

A.3 CO Oxidation Capacities

Figure A.5: Normalised signal of O₂, CO₂ and CO+N₂ for the Ru, Ru-Pt and Ru-Pd samples.

Figure A.6: Normalised signal of O₂, CO₂ and CO+N₂ for the Ru-Rh, Ru-Ir and Ru-Pt-Pd samples.

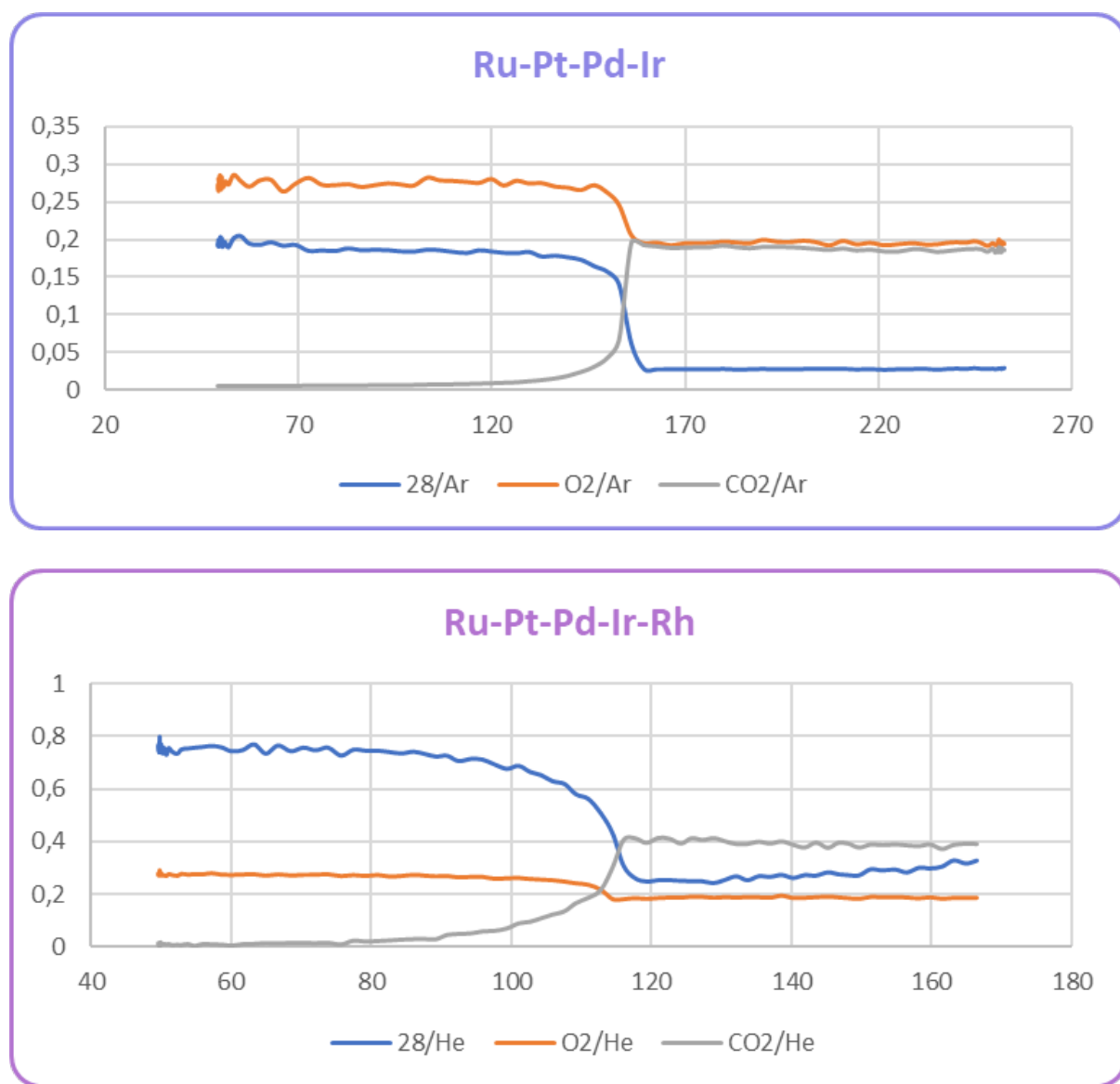


Figure A.7: Normalised signal of O₂, CO₂ and CO+N₂ for the Ru-Pt-Pd-Ir and Ru-Pt-Pd-Ir-Rh samples.

Characterisation of Nanostructured High Entropy Alloys by ToF-SIMS

Master's thesis submitted by Oscar Laurent

High entropy alloys (HEAs) are gaining attention due to their unique properties and potential as heterogeneous catalysts. However, their atomic-scale dynamics remains understudied.

In this work, a macroporous Ru-Pt-Pd-Ir-Rh HEA and seven simpler alloys were investigated using time-of-flight secondary ion mass spectroscopy (ToF-SIMS) and X-ray diffraction. Starting with pure Ru and its binary combinations, the research sequentially progressed through ternary and quaternary compositions, culminating with the HEA. The methodology was optimised through statistical analysis of ToF-SIMS conditions to improve the detection of large-mass clusters.

Initial insights from binary samples revealed unequal atomic mixing among them, ranking as Ru-Rh > Ru-Pd > Ru-Pt > Ru-Ir. Further investigations of alloys with three, four, and five components revealed a direct positive correlation between the number of alloy components and their degree of atomic mixing. With each additional component integrated into the alloys, ToF-SIMS analyses also demonstrated a notable decrease in the oxides present and a shift toward a more equitable distribution of oxide constituents within the samples.

In addition to these structural analyses, CO oxidation tests offered insight into the reactivity. The resulting hierarchy of catalytic activity, in decreasing order, was Ru-Pt-Pd > Ru-Pt-Pd-Ir-Rh > Ru-Pt $\simeq$ Ru-Pd $\simeq$ Ru-Rh > Ru > Ru-Ir > Ru-Pt-Pd-Ir.

In an attempt to decode these results, this work presents two primary hypotheses. First, it is suggested that the CO oxidation reaction predominantly takes place at sites containing Pt and Pd atoms. The close proximity of these two elements within the FCC phase of the ternary alloy is believed to significantly enhance the CO oxidation reaction. Secondly, the presence of Ir, especially in a relatively low-mixed alloy, might lead to the formation of "oxygen traps." This phenomenon could monopolise oxygen within the alloy, thus constraining its interaction with CO during oxidation.

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Faculté des bioingénieurs

Croix du sud, 2 bte L7.05.01, 1348 Louvain-la-Neuve, Belgique | www.uclouvain.be/agro