AMALGAM DENTAL FILLINGS AS THE SOURCE OF MERCURY EXPOSURE AND ALTERNATIVE SOLUTIONS

2022
MASTER THESIS
BIOMEDICAL ENGINEERING

YOUSEF ABDALALI ALASHHAB

Thesis Advisor
Prof. Dr. İdris KABALCI

AMALGAM DENTAL FILLINGS AS THE SOURCE OF MERCURY EXPOSURE AND ALTERNATIVE SOLUTIONS

Yousef Abdalali ALASHHAB

T.C.
Karabuk University
Institute of Graduate Programs
Department of Biomedical Engineering
Prepared as
Master Thesis

Thesis Advisor
Prof. Dr. İdris KABALCI

KARABUK
October 2022

I certify that in my opinion the thesis submitted by Yousef ALASHHAB titled "AMALGAM DENTAL FILLINGS AS THE SOURCE OF MERCURY EXPOSURE AND ALTERNATIVE SOLUTIONS" is fully adequate in scope and in quality as a thesis for the degree of Master of Science.

Prof. Dr. İdris KABALCI ....

Thesis Advisor, Department of Biomedical Engeineering

This thesis is accepted by the examining committee with a unanimous vote in the Department of Biomedical Engineering as a Master of Science thesis. 03.10.2022

Examining Committee Members (Institutions)	Signature
Chairman : Prof. Dr. İdris KABALCI (UÜ)	....
Member : Prof. Dr. Fatma KANDEMİRLİ (KÜ)	....
Member : Assoc. Dr. Mehmet Akif ERDEN (KBÜ)	....

The degree of Master of Science by the thesis submitted is approved by the Administrative Board of the Graduate Education Institute, Karabük University.

Doç. Dr. Müslüm KUZU

Director of the Institute of Graduate Programs ....

"I declare that all the information within this thesis has been gathered and presented in accordance with academic regulations and ethical principles and I have according to the requirements of these regulations and principles cited all those which do not originate in this work as well."

Yousef Abdalali ALASHHAB

ABSTRACT

M.Sc. Thesis

AMALGAM DENTAL FILLINGS AS THE SOURCE OF MERCURY EXPOSURE AND ALTERNATIVE SOLUTIONS

Yousef Abdalali ALASHHAB

Karabük University
Institute of Graduate Programs
Department of Biomedical Engineering

Thesis Advisors:
Prof. Dr. İdris KABALCI
October 2022, 43 pages

The amalgam filling plays a major role in restorative dentistry when applied and has additional strength due to its contents, such as mercury and other alloys that could be cooper, silver, tin, or zinc.

A concern has been raised that amalgam causes mercury toxicity and two primary organs are the kidney and the central nervous system that are affected by Hg poisoning.

The objective of the present study is to examine new dental amalgam fillings and old amalgam fillings removed from patıent's teeth in term of a potential cause of mercury exposure, in addition to the alternative dental fillings. The technique of this study is a metallographic evaluation by using the rapid analytical technique of X-ray diffraction (XRD).

Moreover, the specimens used have been obtained from a different set of amalgam fillings, to measure the mercury present in an unmixed sample, a mixed sample according to the manufacturer's recommendations, and dental amalgam fillings that had been in the patient's theeth after filling them for 15 and 20 years to analyze exposure to mercury by comparison.

Mercury unmixed sample contains on silver Tin 64% and copper zinc 36% While mixed samples contain of silver mercury 63% and copper Tin 37%, the sample after 15 years' dental amalgam filling induced when the silver mercury contain is increased to 84% and low copper Tin 16%, While the sample after 20 years' dental amalgam filling containing approximately silver mercury contain is 80% and copper Tin 20%.

Keywords: Amalgam, Mercury exposure, XRD, Alloys, Metallographic evaluation.
Science Code: 92503

ÖZET

Yüksek Lisans Tezi

CİVA MARUZİYETİNİN KAYNAĞI OLARAK AMALGAM DİŞ DOLGULARI VE ALTERNATİF ÇÖZÜMLER

Yousef Abdalali Ashour ALASHHAB

Karabük Üniversitesi
Lisansüstü Eğitim Enstitüsü
Biyomedikal Mühendisliği Anabilim Dalı

Tez Danışmanı:
Prof. Dr. İdris KABALCI
Ekim 2022, 43 sayfa

Amalgam dolgu uygulandığında restoratif diş hekimliğinde önemli bir rol oynar ve içeriğindeki cıva ve bakır, gümüş, kalay veya çinko olabilecek diğer alaşımlar gibi ek dayanıma sahiptir.

Amalgamın cıva toksisitesine neden olduğu ve Hg zehirlenmesinden etkilenen iki ana organın böbrek ve merkezi sinir sistemi olduğu konusunda bir endişe dile getirildi. Bu çalışmanın amacı, alternatif diş dolgularına ek olarak, yeni amalgam dolguları ve hastanın dişlerinden çıkarılan eski amalgam dolguları, potansiyel cıva maruziyeti nedeni açısından incelemektir. Bu çalışmanın tekniği, X-ışını kırınımının (XRD) hızlı analitik tekniği kullanılarak metalografik bir değerlendirmedir.

Ayrıca, kullanılan örnekler, karıştırılmamış bir numunede bulunan civayı ölçmek için farklı bir amalgam dolgu setinden elde edilmiştir, üreticinin tavsiyelerine göre karışık bir numune ve doldurulduktan sonra hastanın dişinde bulunan dental amalgam dolgular. Karşılaştırma yaparak cıvaya maruz kalmayı analiz etmek için 15 ve 20 yıl. Cıva karıştırılmamış numune üzerinde gümüş Kalay %64 ve bakır çinko %36 içerir Karışık numuneler %63 gümüş cıva ve %37 bakır Kalay içerirken, 15 yıllık diş amalgam dolgusu sonrası numune, gümüş cıva içeriği %84'e yükseltildiğinde indüklenir ve düşük bakır Kalay %16, yaklaşık olarak gümüş cıva içeren 20 yıllık dental amalgam dolgu sonrası numune %80 ve bakır Kalay %20'dir.

Anahtar Kelimeler: Amalgam, Cıva maruziyeti, XRD, Alaşımlar, Metalografik değerlendirme.

Bilim Kodu **:** 92503

ACKNOWLEDGMENT

First and foremost I am extremely grateful to my dear supervisor, Prof. Dr. İdris KABALCI for his invaluable advice, continuous support, and patience during my MSC study. His immense knowledge and plentiful experience have encouraged me in all the time of my academic research.

I would like to thank all the members in the Karabük University for their kind help and support that have made my study and life in Turkey a wonderful time. I would like to thank the all the members of Libyan Petroleum Institute – Labs department for their support. I would also to thank Dr. Asmaa ABDEEWI (Dentist) for her support. Finally, I would like to express my gratitude to my family and their encouragement in the past few years.

CONTENTS

Page

Page

Page

LIST OF FIGURES

Page

LIST OF TABLES

Page

SYMBOLS AND ABBREVITIONS INDEX

ADA : American Dental Association

FDA : Food and Drug Administration

XRD : X-ray powder diffraction

SEM : Scanning Electron Microscope

CDC : Single composition spherical

Ag : Silver

Sn : Tin

Cu : Cooper

Zn : Zinc

Hg : Mercury

ISO : The international organization for standardization.

WHO : World health organization.

PART 1

INTRODUCTION

Liquid mercury and an alloy are the two primary components of the vast majority of mercury-containing fillings, which is a metal powder. When the word alloy is used in physics, it describes a mixture of one or more elements, at least one of which is a metal. As a result, the term "amalgams" refers to mixes of mercury and one or more other metals (such as silver or copper), which may be dissolved into the mercury or which may just be metal particles that the mercury has bonded together. The maker of dental amalgam sets the alloy/mercury mixing ratio at a level where it is purported that the mercury is firmly linked to the alloy [1]. In developing nations, silver amalgam is still the material of choice for dental treatment because of its superior mechanical qualities, low cost, and eases of insertion. More than 100 million silver-amalgam fillings are reportedly inserted into American mouths each year, according to the American Dental Association (ADA) [2]. Conversely, according to Mason et al. [3], Inorganic mercury (in the form of mercury salts), metal mercury (also known as elemental mercury), and organic mercury are all naturally occurring forms of the hazardous metal mercury (Hg) in the environment (methyl mercury being the most common). Dental amalgam is a mercury-based filling composed primarily of silver (35%) and trace amounts of tin (9%), copper (6%) and zinc (3%); it has a metallic mercury content of about 50%. (Hg0). Although a little quantity of mercury in the form of Hg0 is continuously released from surface of an amalgam fillings into the mouth's saliva and mouth air, or grinding motions. The two primary organs are the kidney and the central nervous system that are affected by Hg poisoning [4]. Additionally, according to Lorscheider et al report.'s [5], Estimates of the typical amount of mercury emitted by dental amalgams varies from 3 to 17 mg/day depending on the total number of amalgam fillings. The majority of researches [1, 5] have demonstrated that amalgam fillings gradually leak mercury vapor, with the lungs being the primary route via wherein 80% of the Hg0 that is breathed in enters the blood. As a result, its use has dropped significantly in recent years, and we are starting to wonder if silver amalgam is nearing its end. As an illustration, the Ministry of Foreign Affairs of Norway of Environment passed this law banning the manufacture, import, export, sale, and use of substances containing mercury [2].The method dentists perform operative dentistry has significantly changed in recent years, and one such shift is the increased use of resin composites for the repair of posterior false teeth [8]. The improvement of resin composite materials, bonding methods, and processes, greater patient demand for more cosmetic restorations over silver amalgam, and increased predictability of resin composite performance in posterior teeth have all contributed to this [9–10]. The usage of resin composite in occlusal and occlusal proximal cavities as a direct restorative material is currently supported by data in the dental literature [10]. Posterior resin composite restorations put properly may be just as functional as those made with silver amalgams [9]. Resin composite offers a more aesthetic appearance than silver amalgam [11], eliminates the need to remove healthy dental tissue for retention, lowering the danger of eventual tooth fracture, and strengthens the remaining tooth material [12]. Resin composites have more technique sensitivity, take longer to place a posterior replacement, and are more expensive than silver amalgam amalgams [9,10,13]. Based on the previous show and because The prescribed limits for daily mercury intake are frequently reached or exceeded by the mercury released over time from a few amalgam fillings. Hence, mercury from corroding amalgam fillings offers a potential health hazard. So, the main goal of the current study was focused on this phenomenon, which is the emission of metallic mercury (Hg0) from the surface of the fillings due to the formation of droplets rich in mercury on the surface of the amalgam filling, as result of corrosion, grinding motions, chewing. Also, we can estimates released mercury amounts by measuring the depth and type of corrosion attack. In this study metallographic evaluation was done by using the Energy Dispersive X-Ray Technique. Moreover, the specimens used have been obtained from a different set of amalgam fillings used on technique was used to analyze exposure to mercury present in an unmixed sample, a mixed sample according to the manufacturer's recommendations, and dental amalgam fillings that had been in the patient's mouth after filling them for 15 and 20 years.

PART 2

THEORETICAL CONCEPTS AND BACKGROUND

2.1. MERCURY

At room temperature, mercury is at 20 degrees Celsius, liquid metal has a 0.16 Pascal vapor pressure. At normal body temperature, the vapor pressure is approximately five times higher. Mercury is a highly hazardous metal that can be found numerous chemical and physical forms in the environment. Hg°, Hg^{1+}, and Hg^{2+} are the three oxidation states of inorganic mercury. The solubility of elemental mercury in water is just 0.28 mol/*l* at 20°C, but it is much higher with body fluid (such as blood). Elemental mercury can easily combine with other metals to make alloys. Sulfhydryl and selenide amalgams have a strong affinity for inorganic mercury [14, 15]. Organic mercury, which is mercury that is covalently bonded to a carbon atom, comes in a variety of designs. Mercury methyl is the most common organic compound to which humans are exposed, and it is also the most poisonous. Although the covalent bond is powerful, methyl mercury may attach to a sulfhydryl group with ease found in proteins [14, 16, 17, 15].

2.2. BACKGROUND OF AMALGAM

Amalgam, sometimes known as silver A mixture of silver and pure mercury is called amalgam. That was first used as a dental filling material by the Chinese in the Nevertheless; it had a different composition than that of now in the 7th century. In Europe and North America, silver amalgam was originally utilized as a dental material. in the early nineteenth century [18]. The use of amalgam for dental fillings was a point of contention. Some dentists stated that amalgam was dangerous since they were aware of mercury's hazardous characteristics. The American Dental

Association, which was founded in 1859, deemed amalgam to be safe for use as a tooth filling material.

The risk of human poisoning was not raised again until the beginning of the twentieth century, when the great German doctor Alfred Stock [19] demonstrated that amalgam emitted mercury. When World War II broke out, he requested that amalgam be phased out, but the topic faded away and was forgotten. In 1950, in Sweden [20], The emission of mercury from amalgam has been the subject of some research. However, it wasn't until the end of 1970 that the discussion over mercury's safety was reignited, when the matter garnered widespread attention thanks to newspaper and television coverage [21,15]. New research [22,23] discovered that mercury was released from amalgam fillings on a constant basis, in addition to when fillings were first placed. As a result, it was found that amalgam was less stable than initially believed.

2.3. DENTAL AMALGAM

Dental amalgam now contains around 50 percent Silver, tin, and copper powder made about 50% of the weight of the metallic mercury [15]. This metallic powder is mixed with elemental mercury to make a plastic amalgam (alloy).just before being inserted into the tooth cavity, the amalgam is combined. This can be done with mercury automata or with amalgam capsules, which is more frequent. Amalgam capsules are created by separating the mercury and alloy with a thin plastic wall. During amalgam preparation, the capsule is quickly shaken, which breaks the plastic separator and mixes the components. Amalgam has the benefit of being an affordable material that is "convenient" for dental fillings. 1.7 tonnes or so of mercury were used in dentistry in Sweden in 1991[24]. However, the annual amount consumed is declining. In Sweden, over 2 million new amalgam fillings were installed in adults in 1991. A middle-aged individual typically has 30 amalgam fillings [24].

2.4. RETENTION OF MERCURY AND TISSUE UPTAKE

The blood is most likely the primary mode of transport for elemental mercury in the human body. Mercury ions move from the bloodstream into the brain and other tissues, where they are oxidized to Hg2+ in cells.

The sulfhydryl groups of protein molecules are then linked to mercury [25]. Inorganic mercury, such as mercuric mercury, is carried through blood cells, red attached to sulfhydryl- in hemoglobin groups or glutathione, or through the plasma cells that are attached to albumin or other proteins [25]. In the kidneys, divalent mercury builds up, where it accounts for over 90% of the total body load. This explains why mercury can damage the kidneys more severely than other organs poisoning. The emission of radioactive mercury from amalgam put in sheep's teeth, as well as its intake, has been studied by means of a full-body imaging scan [26]. According to the findings, there are three potential pathways for absorption: the lungs, the digestive tract, and the jaw or gum mucosa. The liver and kidneys were found to contain high levels of mercury, supporting the conclusions of human studies.

The biological half-times that prevent inorganic mercury from leaving the human body are a problem varies by tissue, as well as exposure period and concentration. Mercury has a lengthy half-life, and its concentration in the urine and blood eventually achieves a constant state, reflecting the balance between taking and removing. Mercury defecation half-time in blood is most likely based on a two-compartment model. The first half-time of excretion is brief, lasting between three and four days [27], 45 days later comes a slower half-time. The biological half-life of radioactively tagged mercury consumed by humans, whether it is protein-bound or free ionic inorganic mercury, has been demonstrated to be 42 days [28].

Following the end of exposure, Mercury excretion in urine normally has a half-life of 40 to 60 days [27,29]. The dead dentist's brain, which had not been exposed to mercury lately at work was found to contain a high amount of mercury [30]. This shows that the biological part-life mercury levels in brain tissue is very long. Similar findings have been obtained from investigations into mercury levels in primate brain tissue [31]. In two prior studies using human volunteers, the halftime in the brain was around 20 days old [32,33]. Mercury may be released an attempt was made to create a multi-compartment model using brain tissue in order to compute accumulation in the brain [15].

2.5. TOXICITY

For a long time, people have been aware of the harmful health effects of inorganic mercury exposure. Tremor, alterations in behavior and mental health such irritability, memory issues, sleeplessness, depressions, and other consequences such as gingivitis and protein urea are all common mercurialism symptoms [15]. For occupationally exposed persons, studies of low and long-term mercury exposure have been done [34]. However, there is very little research on the toxicity of mercury such as amalgam filling exposure, and the results of the few studies that have been done are generally contradictory. Hansson conducted a research. [35]. Non-occupationally exposed people with amalgam fillings experienced the same symptoms as those documented for those having a lot of mercury exposure at work. Another research revealed no appreciable link between symptoms and complaints and the amount of amalgam fillings, at least not at the population level [36, 37].

Mercury emitted from amalgam fillings has not been shown to have teratogenic consequences in epidemiological studies or animal trials [38]. individuals who had amalgam fillings exposed to inorganic mercury have been reported to have a little effect on their kidneys [39], however Herrström [40] was unable to demonstrate the observation was caused by mercury produced from amalgam fillings in renal impairment. Three investigations [34] have shown both allergy and immune consequences of Although a study by Langworth [41] revealed no connection between amalgam fillings and immunologic disturbance, amalgam fillings do contain mercury. There is a paucity of information on the cancer-causing properties of mercury and mercury compounds. There may be an elevated risk of brain cancer among dentists and nurses, and epidemiological studies point to a potential danger for lung and kidney malignancies [34].

2.6. MERCURY EXPOSURE FROM AMALGAM

The mercury is thought to be emitted in many forms from amalgam, including amalgam particles, oxidized mercury, and mercury vapor. Mercury vapor is easily absorbed by the lungs and can be breathed, with an absorption rate of about 80%. The brain system and the kidneys are the organs that are impacted the most by ongoing low-level exposure [34]. Mercury vapor, for example, can enter the body through the mouth's mucous membrane [42]. The vapor of mercury can also eat and absorbed through the gastrointestinal system after being dissolved in saliva. However, little is known regarding the amount of mercury ingested. Saliva can oxidize mercury vapor, which can then be eaten. Or amalgam may leak oxidized mercury as corrosion products. Only around Inorganic mercury salts are absorbed in the digestive tract between 5 and 10 percent of the time. The kidneys are primarily affected by oxidized mercury, and excessive levels of mercury exposure can cause renal impairment [34]. Mercury dust or particles can be ingested or breathed. The lungs and intestines are likely to have limited uptake.

2.6.1. Occupational Exposure

Dental clinic employees, such as Dental professionals, Hygienists, nurses, and others are all exposed to mercury vapor and dust. When preparing amalgam, Nurses and the dentist are made public. Even when capsules are utilized, throughout the working day, mercury levels in the air could occasionally surpass the threshold limit value (TLV). [43]. When placing new fillings, polishing old amalgam fillings, and drilling out old amalgam fillings, the exposure can be very high. When cleaning dental instruments, the staff is also exposed [34].

Employees in the dentistry business, who make dental materials, as well as dental technicians, may be exposed [24]. During the burning of bodies with amalgam fillings, Mercury vapor may be inhaled by crematory workers [24].

2.6.2. Non-Occupational Exposure

Characters with dental amalgam filling are exposed to mercury through the dental fillings, which relief mercury continually [34]. Dental amalgam fillings are put or bored out, the exposure can be very high, just as it is for the dentist. When people with amalgam restorations chew, bite, eat hot foods, or grind their teeth while sleeping or when they are anxious, their exposure is increased [34]. Characters are also exposed to mercury making from dental amalgam in the environment through inhaling contaminated air, intake contaminated water, and eating contaminated foodstuff. Mercury from amalgam is released into the environment at various points of its life cycle. Mercury is emitted, for example, in the flue gas emitted by crematories [24].

Mercury from dental operations is discharged into the sewage system even if amalgam separators are used [44]. Furthermore, mercury from dental amalgam is expelled in human excrement and makes its way into the sewage system, where it may eventually end up in the sea, where it might be deposited and methylated by microbes before being stored in fish. However, as compared to the exposure from personal amalgam fillings, indirect exposure from the environment is negligible.

2.7. MERCURY TOXICITY FROM AMALGAMS

Despite the fact that amalgam exposes exposure of dental patients to risky mercury vapor, the American Dental Association (ADA) commends that dentists respond to patients in the resulting custom when asked if mercury is poisonous: "When mercury is combined with other metals and used as amalgam, it is not harmful. It combines with them to create a physiologically inert material ".

Even if patients enquire, the American Dental Association advises dentists not to tell them that amalgam continues to produce mercury. Although no government organization has developed acceptable mercury intake criteria from dental amalgams, some experts feel that "there is nontoxic threshold of mercury exposure [45]."

n 1984, the American Dental Association researched the effects of amalgam fillings and informed the public that "despite the lack of proof of a healthiness concern, we will pursue the issue of care until the problem is resolved to the satisfaction of the American people."

Mercury is discharged from amalgam fillings, according to the 1984 Workshop on the Care and Biocompatibility of Metals in Dentistry. Nonetheless, the ADA claimed that such a little level of exposure could cause no health effects. Following research tying amalgam fillings to a variety of incurable diseases, the American Dental Association (ADA) disputed any assertions that amalgam was to blame, while assuring those concerned that it would "continue" to do everything in its ability to settle any concerns about its care [45].

In 1987, the (ADA) bluntly stated that such assertions are unfounded, "unsubstantiated, unrecorded, and unproven." Several research conducted since 1981, however, have found a link between dental amalgams and mercury levels in the human brain. Other countries have imposed restrictions or outright bans on the use of amalgam fillings. The Swedish government recommended that dentists stop using amalgam fillings in the teeth of pregnant women two years ago. Since then, Swedish authorities have advocated that all mercury usage, including amalgam fillings, be banned by 1991, have demanded that its usage in pregnant women be stopped right away. "We now see that we made a mistake," said Viking Falk, division chief of the Swedish Social Welfare and Health Administration. People have suffered unnecessarily as a result of this [45].

"Quickly, the ADA considered [this study] as fake," according to the ADA. The Swedish ban, on the other hand, was subjected to public hearings before being maintained. In reality, the Swedish government established a law in November 1990 allowing residents to have their amalgam fillings removed under the national dental plan. In Germany, legislation prohibiting the use of amalgam has also been introduced. Dentists in Japan have also been looking for alternatives to amalgam.

Current research revealing substantial evidence of long term mercury toxicity in patients with amalgam fillings has failed to persuade the (ADA) to reconsider its stance. Based on recent studies, some dentists have advised their patients to consider replacing their amalgam fillings with non-toxic alternatives. The (ADA) has called these dentists' acts unethical, claiming that they create "a question of fraud or quackery in all but an extremely narrow spectrum of circumstances." Recent research, however, has pushed organizations such as the Environmental Dental Association to take action (EDA), to demand that any use of mercury in dental materials be prohibited. According to the EDA, it is unethical to use amalgam without first telling the patient about the hazards and alternatives. A review of current scientific studies reveals that amalgam poses health risks in laboratory animals and, most likely, in humans [45].

2.8. SILVER AMALGAM

Dental amalgam filling is made up of "a mixture of metals that include mercury, silver, tin, and copper," according to the American Dental Association. It is made by "mixing elemental mercury (43-54 %) with an alloy powder (46-57 %), primarily consisting of silver, tin, and copper [46]." When compared to composite resins, this long-lasting filler is more cost effective because it takes less time to apply to a cavity and the material itself is less expensive [47]. Silver amalgam is also more durable, and it's commonly utilized in molars, which are subjected to the most pressure during mastication, or chewing. Because silver amalgam hardens faster than composite resin, it can be used in places where the dentist can't get to or where it's difficult to maintain dry during application, such as cavities beneath the gum line. Because of its rapid application, it is also a more effective filling for youngsters or adults with specific needs [47]. In most cases, a single visit to the dentist is all that is required to effectively install a silver amalgam filling; the material is self-sealing, and there is little to no shrinkage once it is in the tooth [46].

When a person speaks or laughs, the filling is closer to the front of the mouth; the further back the filling is the less probable, it is to be visible in the mouth [47]. The amalgam may darken over time as a result of erosion in the mouth, which can cause darkening of the sealed tooth over time [46]. Another disadvantage of silver amalgam is the extent of the area required to secure the filling around the cavity. Because it is necessary to thoroughly seal the afflicted area, this type of filling necessitates the removal of additional tooth structure around the cavity. The dentist must seal, rather than simply fill, the cavity with the silver amalgam filling, or remove the silver amalgam filling from the cavity and clean the region around it [47]. The underlying tooth can be weakened and possibly fractured as a result of this [46]. Furthermore, the metal component of the amalgam filling is less thermally insulating and can more easily conduct hot and cold temperatures. Hypersensitivity to hot or cold liquids or solids in the mouth may occur in a tooth having an amalgam filling. One distinct downside is that when exposed to other metals, such as those found in saliva, the metal may conduct electricity. Although the electrical flow is not particularly strong, it may produce discomfort in the patient or unexpected redox chemistry in the mouth [46].

One contentious issue with silver amalgam is the presence of mercury residues in the substance. When mercury reacts with saliva in the mouth, it can be released as a vapor [46]. The American Dental Association, on the other hand, claims that "it makes a safe, stable substance [47] when coupled with the other metals." Dental amalgam is also a safe and effective cavity restorative material, according to the US Centers for Disease Control and Prevention, the US Food and Drug Administration, and the World Health Organization [47]. Figure 1 shows a graphic representation of an amalgam filling.

Figure 2.1. A silver amalgam filling is depicted in this image. Take note of the material's size and invasiveness (serenitydentalcenter.com) [46].

2.9. COMPOSITE FILLINGS

In tiny and mid-size fillings, composite resins often referred to as tooth-colored fillings which are effective longevity and may tolerate moderate pressure from mastication stress [48]. These fillings can be utilized on the front and back of teeth, which appeals to those who don't want their dental fillings to be apparent. The color of the patient's teeth can be matched with composite fillings, giving them a more attractive option for individuals seeking a more aesthetic solution. They also help to maintain the most amount of tooth feasible because they are less intrusive than other actions [46].

Due to the fact that they are chemically bonded to the tooth and chemically inert, composite resins also resist corrosion. Once they've been cured. As a result, composite fillings are more likely to withstand degradation, requiring less regular maintenance [46]. The high expense of a composite filling is one downside. They are more expensive than silver amalgam fillings, and insurance policies may not usually cover them [48]. Furthermore, some research has concluded that a composite filling does not endure as long as an amalgam filling. Because of the chemical reactions required to Sealing a cavity with a composite filling involves bonding the filling to the tooth, hardening the composite, and keeping the tooth clean and dry during the application process. Takes longer. When the restoration is done before another dental restoration or implant, multiple visits may be required [46].

When the material hardens, it can shrink, causing deterioration and minor sensitivity. Another downside, or rather, a potential health hazard, is that "certain composite resins contain crystalline silica, which is on California's Proposition 65 list of chemicals known to cause cancer" [46]. However, no comprehensive research has been done to see if the levels of this chemical present in a composite filling can cause cancer, and any silica retained inside the cured composite can cause cancer. Figure 2 shows an example of a composite filling.

Figure 2.2. A composite filling in action. The lack of color contrast between the restorative material and the tooth is notable [46].

2.10. DENTAL AMALGAM COMPOSITION

Mercury is combined by another metals, amalgam is generated. Mercury is one of the few metals that can quickly solidify when combined with other metals and are liquid at normal temperature. Any time a dentist chooses a particular type of dental amalgam, he or she is only concerned with the metal(s) with which mercury is mixed. Although the chemical makeup of dental amalgam varies depending on the manufacturer, the typical alloy used in dental amalgams is made up of silver, tin, copper, zinc, and, in some cases, mercury. Table 1 shows a typical composition (Van Noort 2007) [48].

Silver and tin are the major constituents, as shown in this table, and together they form the intermetallic complex Ag_3Sn, also known as the -phase. This phase reacts quickly with liquid mercury to form a therapeutically acceptable alloy that solidifies in minutes and hardens in hours. Furthermore, the speeds of the amalgamation reaction as well as the qualities of the ensuing dental amalgam structure are controlled by the exact percentage of this phase (SCENIHR 2008; Van Noort 2007) [48].

Table 2.1. Typical composition of dental amalgam [48].

Constituent	% Composition
(Ag)	67-74
(Sn)	25-28
(Cu)	0-6
(Zn)	0-2
(Hg)	0-3

2.11. TYPES AND COMPOSITIONS OF DENTAL AMALGAM

Alternatives currently, a variety of alternative materials are being used as dental amalgam substitutes, including:

- Composite resins
- Glass ionomer cement
- Compomers
- Giomers

Strength, wear resistance, fluoride release, and aesthetics, simplicity of usage are all factors to consider while choosing a material. Composites are attractive, sturdy, and resistant to wear. They do, however, release little or no fluoride. Compomers are less wear-resistant, but they are more attractive and release fluoride. Resin-modified glass-ionomer cements release more fluoride than Compomers. However, they are less wear resistant and are not recommended for posterior restorations. The most fluoride is released by conventional glass ionomers, which are suitable applications for people at high risk of carries at low-stress conditions (Powers and Wataha 2008) [48].

2.11.1. Composite Resins

In the 1960s, composite dental fillings were first developed are a tooth-colored filling made from a mixture of glass or quartz filler in a polymer sable resin medium. They're sometimes referred to as resin fillers. They are the most common materials used in dentistry today and presently dominate the materials utilized for direct cosmetic restorations.

The makers classify the composites in a variety of ways based on particle size, distribution, and volume %. Dental composites are classified as macrofill (10-100 m), midifill (1-10 m), minifill (0.1-1 m), microfill (0.01-1 m; used for Class II and V fills), and nanofill (0.005-0.01 m; used for Class I through V fills) based on particle size. Additionally, there are hybrid composites that combine two filler particle size fractions, such as midi-hybrids made up of microfillers and midifillers; mini-hybrids or micro-hybrids made up of microfillers and minifillers; and nanohybrids made up of nanofillers and minifillers. Despite the fact that larger fillings have superior mechanical properties, and a lower coefficient of thermal expansion, tiny particle size fillers can take and maintain an excellent surface finish. Large particle size fillers, on the other hand, have a poor surface quality and a drab look [48].

2.11.2. Glass Ionomer (Glass Polyalkenoate) Cements

Wilson and Kent (1972) As a result of an acid-base reaction involving basic ion-leachable fluoro-alumino-silicate glass powder (proton acceptor) and water-soluble polycarboxylic acid (proton donor) in the presence of water, the first glass-ionomer cement was formed (Wilson and Kent 1988; Davidson and Mjör (1999)[48].

When you combine the acid with the base, you obtain a viscous paste that hardens into a solid mass (Combe and Grant 1992). Melting alumina (Al2O3), silica (SiO2), metal oxides, metal fluorides, and metal phosphates at 1,100° C-1,300° C, followed by quenching and grinding, produces the filler particles (i.e. glass powder).

Aluminum (Al), calcium (Ca), strontium (Sr), zinc (Zn), sodium (Na), potassium (K), and lanthanum (Ln) are the most commonly used metal ions (La). To make a radio paque cement, lanthanum oxide (La2O3) or strontium oxide (SrO) is substituted for Ca. Glass powder can also contain barium sulfate (BaSO4), lattice oxygen (La2O3), strontium oxide (SrO), and zinc oxide (ZnO), but not within the glass composition [48].

Aluminum oxide and silicon dioxide are the major constituents of the glass, and their ratio (Al_2O_3/ SiO_2) is crucial for proper reaction. Table 2 shows the typical composition of a glass-ionomer cement powder [48].

Table 2.2**.** Typical composition of a glass ionomer cement powder [48].

Constituent	**Mass Percentage**
SiO_2	**30.1**
Al_2O_3	**19.9**
AlF^3	**2.6**
CaF^2	**34.5**
NaF^2	**3.7**
$AlPO^4$	**10.0**

2.11.3. Resin-Modified Glass Ionomer Cement

In the early 1990s, resin modified cements were developed to increase functionality and address glass ionomer cements' poor mechanical qualities (bending and tensile strength, as well as fracture roughness). A three-phase acid-base reaction takes place when sodium-calcium-aluminum-fluorosilicic acid powder and liquid (polyacrylic acid and tartaric acid) are combined in their original forms. This reaction causes calcium and aluminum ions to leach as the acid attacks the glass powder particles, hydrogel to form as the polyacrylic acid molecules crosslink, and polyalkenoate salt to gel as the polyalkenoate reacts with the calcium and aluminum ions (SCENIHR, 2008) [48].

In order to give resin modified cements higher strength and water resistance, water-soluble resin monomers (such as 2-hydroxyethylmethacrylate or HEMA, which can undergo free radical polymerization) are added to the aqueous solution of polyacrylic acid. As a result, resin-modified glass ionomer cement goes through both the polymerization and acid-base reactions. In the settling reaction, which combines the powder and liquid, the H+ ion in the liquid strikes the glass surface. The metal ion released from the glass particles combines with polyacrylic acid while HEMA cures at the same time, forming a silica gel coating on the surface of the glass particle (Davidson and Mjör 1999)[48].

2.11.4. Compomers

They were first launched in 1995, and they combine the advantages of resin composites and traditional glass-ionomer cements. In an effort to find a new restorative material, a fluoroaluminum glass was used to facilitate the polymerization of an acid monomer. This led to the creation of a new fluoride-releasing chemical that releases fluoride slowly in the oral environment. A compomer, like a composite resin, is a single-paste formulation in compules and syringes that consists of fillers and a matrix.

The filler is typically made up of fluoro-alumino-silicate glass powder, which releases fluoride into the environment through a mechanism similar to that of conventional and resin-modified glass ionomers. Some materials also include metal fluoride for the same reason. To make the substance radio paque, the glass powder incorporates strontium or another metal. In the presence of saliva, when an acidic monomer (such as polymer sable dimethacrylate resins like urethane dimethacrylate and TCB, which is a reaction product of butane tetra carboxylic acid and hydroxyethyl methacrylate) reacts with an ion-leachable basic glass filler, an acid-base reaction takes place. Based on the polymerization reaction of the monomer components, which is started by UV polymerization, the compound's setting reaction occurs. [48].

In the first setup, to create an acidic polymer, or a polymer with an acidic group, an acidic monomer is polymerized with other monomer components of the matrix. HEMA is released during the setting reaction, while fluoride is released after setting. The amount of fluoride produced and its duration are smaller in Compomers than in glass- and hybrid-ionomers due to the lower amount of glass ionomer present [48].

2.11.5. Giomers

They have only lately been released, and they combine Composite resins with glass-ionomers. They can stick to tough tooth tissues because they have a bonding polymer catalyst and an adhesive-booster monomer. The chemical composition of various composite, glass ionomer, and compomer formulations was summarized from Material Safety Data Sheets (MSDSs) of various composite, glass ionomer, and compomer formulations, as well as preparation and application material formulations (etchants, primers, activators, coupling agents, adhesives, bonding agents) produced by various companies in the United States (e.g., 3M, Dentsply, Kerr Corp., Ivoclar [48].

In the process of being prepared/applied Dental Amalgam and Resin-Based Alternatives Contain Mercury: A Comparative Analysis of Health Risks in the Appendix, there are 19 materials, glass ionomers (see Table 2.2) [48].

2.12. ADVANTAGES AND DISADVANTAGES OF DENTAL FILLINGS

2.12.1. Advantages (Amalgam)

Patients and dentists alike choose Amalgam because of its ease of application, minimal technique sensitivity, and reduced cost when compared to composite. Amalgam has a great tensile strength, outstanding wear resistance, and a unique marginal sealing effect by corrosion products, all of which contribute to positive long-term clinical results [49].

2.12.2. Disadvantages (Amalgam)

It is a non-insulating material that necessitates deeper tooth preparation; it has the potential to cause heat injury to the pulp in deep cavities. The damage can be avoided with the use of a varnish, liner, or base. Tooth structure is weakened by extensive tooth preparations. When amalgam fails, it must be completely removed and reinserted; restoration is not recommended. Mercury leakage, as well as the health and environmental risks that come with it, are still a source of contention. Amalgam is not recommended for use in esthetic areas or during pregnancy [49].

2.12.3. Advantages of Composite Resin

The most significant benefit of composite resin is its aesthetic presentation. In aesthetics, composite is unavoidable. Zones due of its wide spread acceptance. Tooth structure is conserved with less sophisticated tooth preparation, leaving stronger remaining tooth structure to support the restoration. Good retention, low micro leakage, and minimum interfacial stains arise from the micromechanical bond with the tooth structure. It provides an insulating effect and is repairable [49].

2.12.4. Disadvantages of Composite Resin

Composite resin disadvantages include polymerization shrinkage, which reduces the clinical success of composites. Technique-sensitive, with a strong demand for isolation in order to develop a strong bond with the tooth structure. Because many procedures such as etching, bonding, and segmental insertion, curing, finishing, and polishing are undertaken, the insertion technique is more complex and time demanding for dentists. It can be challenging to make proximal and occlusal axial interactions. If used without bonding or self-etching, it may show more occlusal wear and have less longitivity [49].

2.13. BIOCOMPATIBILITY

The mercury toxicity of Dental amalgam is still a contentious issue. In 1998, the (ADA) Assembly on Scientific Affairs declared that amalgam is a safe and effective restorative material for adults and children, based on scientific evidence from the past and present [50]. In 2002, 2003, and 2009, the ADA reaffirmed this remark. Except for particular contraindications such as esthetics and pregnancy, the available research does not directly link amalgam to mercury toxicity, nor does it necessitate its termination. Allergic reactions do occur, although they are quite uncommon [51,52].

2.14. PROVIDES STUDIES

MotohiroUo et el. (2003)[53]According to estimates, the enhanced surface layer is only a few nanometers thick.This basically corresponds to the XPS study's depth. Furthermore, their being metallic components such as zinc and tin, which quickly create a surface oxide layer that is permanent, inhibits mercury release.

E. Talik et el. (2005) [54] Within high copper dental amalgams, the optimum quantities and ratios of fundamental elements Ag, Cu, and Sn play a vital influence in mercury release behaviors and chemical properties. The increase in mercury evaporation is influenced by a high Sn/Ag ratio (1) in some of the investigated amalgams. Copper and silver concentrations affect the oxygenation reactivity of metallic elements in dental amalgams. The findings of this study corroborate previous findings. The corrosion resistance of dental amalgams is affected by the relative quantities of phases. The presence of pure Hg in the amalgams may imply that, as previously mentioned, the triturating circumstances can impact the release of this element.

Mahmoud Bahari et al. (2016)[55] Reported the silver content of dental amalgam is inversely proportional to the amount of mercury released.

Ulf G. Bengtsson et al. (2017) [56] showed the non-ɣ2-amalgams are touted as being stronger and more corrosion resistant. A significant sub-optimization has happened when attempting to satisfy these development goals. These amalgams, which were developed in the 1970s, emit around ten times more mercury vapor in experimental setups than the ones previously employed. Ordinary dental staff, politicians, and other decision-makers are unaware of the instability of current non-ɣ2- amalgams.

PART 3

MARTIALS AND METHOD

3.1. INTRODUCTION

This work aims to study metallographic evaluation was done by using the Energy Dispersive X-Ray Technique. Moreover, the specimens used have been obtained from a different set of amalgam fillings used on technique was used to analyze exposure to mercury present in an unmixed sample, a mixed sample according to the manufacturer's recommendations, and dental amalgam fillings that had been in the patient's mouth after filling them for 15 and 20 years.

3.2. SCOPE OF WORK

Figure (3.1) shows the sequence flow chart of the work to be done to fulfill the experimental part of the study.

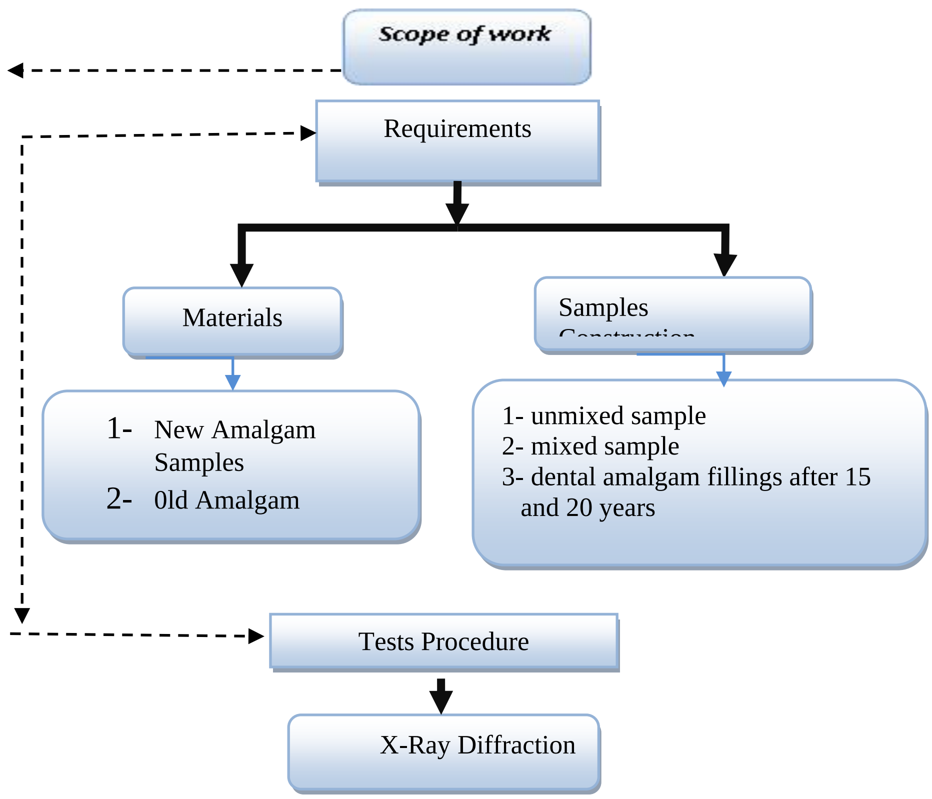

Figure 3.1. Show the Sequence Flow Chart of the Work to be Done to Fulfil the Experimental Part of the Study [Author design].

3.3. MATERIALS

Amalgam was selected in this study because it is used extensively for direct restoration that involves filling a cavity in the tooth structure in order to return the tooth's form and function to normal. To eliminate dental caries, this cavity is created inside the tooth.

Amalgam dental filling material manufactured by (Crown Alloy) Turkey, the material is provided in the form of Amalgam Sample mixed together by the amalgamator. The main constituent of Dental amalgam is an alloy created when mercury (Hg) and silver-tin combine (Ag-Sn). Additionally, there are fluctuating concentrations of copper (Cu) and trace levels of zinc (Zn). A combination of Ag, Sn, and Cu makes up the remaining portion of the final filling material after the mercury (Hg) and powder alloy react, as shown in Figure (3.2).

Figure 3.2. Amalgam dental filling material manufactured by (Crown Alloy) [Author image].

In this study other materials, instruments and equipment were used in different steps of the samples construction and testing.

The first step of the experimental work for samples preparation and testing for the amalgam dental filling was done in dental clinic and the other steps of measurements of x-ray diffraction were done in dental materials laboratory.

3.4. METHOD

3.4.1. Samples Preparation

These amalgam dental filling materials were the specimens used have been obtained from a different set of amalgam fillings used on technique was used to analyse exposure to mercury present in an unmixed sample, a mixed sample according to the manufacturer's recommendations, and dental amalgam fillings that had been in the patient's mouth after filling them for 15 and 20 years.

3.4.1.1. Unmixed Sample

Amalgam dental filling material manufactured by (Crown Alloy) Turkey, samples were fabricated as the following instructions:

- The plate is made of metal specifically according to the sample size that required by the XRD device. As shown in figure (3.3).
- Take a capsule of the amalgam manufactured by the company and open it on plate metal to prepare it for steps of measurements of x-ray diffraction.

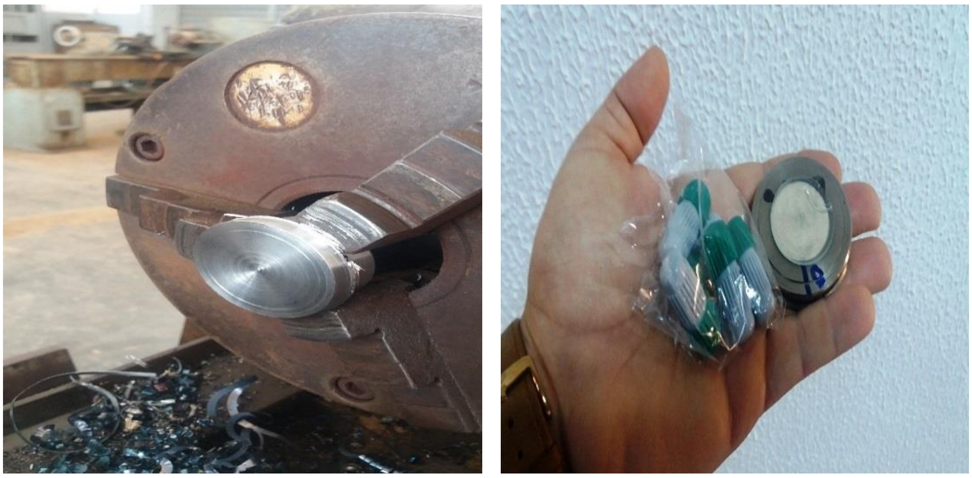

Figure 3.3. Plate Metal to Prepare it For Steps of Measurements of X-Ray Diffraction [Author image].

3.4.1.2. Mixed Sample

Amalgam dental filling material manufactured by (Crown Alloy) Turkey, samples were fabricated as the following instructions:

- 20 amalgam fillings mixed by the amalgamator device for 10 seconds and placed one by one in the sample metal form, smoothed and left Two hours to dry and firm. Then the sample is analyzed by XRD device according to manufactures' instructions and recommendations were had done in (EL Masah dental clinic, Tajoura, Libya) Figure (3.4).

Figure 3.4. Amalgam Fillings Mixed by The Amalgamator Device [Author image].

3.4.1.3. Old Samples 15 and 20 Years’

Dental amalgam fillings that had been in the patient's mouth after has been filled for 15 and 20 years.

- This step in the clinic, which included amalgam fillings, was for my patients in the clinic Thus, ethical approval was obtained from the patients from whom the amalgam fillings were taken after they were removed from the patient's mouth.
- Dental amalgam fillings that had been in the patient's mouth after filling for 15 and 20 years were ground and filled into a metal plate to prepare them for the steps of X-ray diffraction measurements.

3.5. X-RAY DIFFRACTION TEST

An analytical method based on the diffusion of x-ray radiation by a substance is called X-ray scattering. X-ray scattering can be utilized for crystalline or amorphous materials, whereas X-ray diffraction could only be employed with crystalline materials. The basis for X-ray scattering is the interaction of X-rays with atomic electrons. For materials with dimensions under one micrometer, such as big molecules (such as proteins and polymers) and nanoparticles (such as nanotubes), X-ray scattering can reveal their shape, size, and orientation. The substances that are evaluated can be foams, gels, liquids, solids, and more. Because this method is non-destructive, it can be applied to delicate materials. In figure (3.5), the XRD machine is displayed.

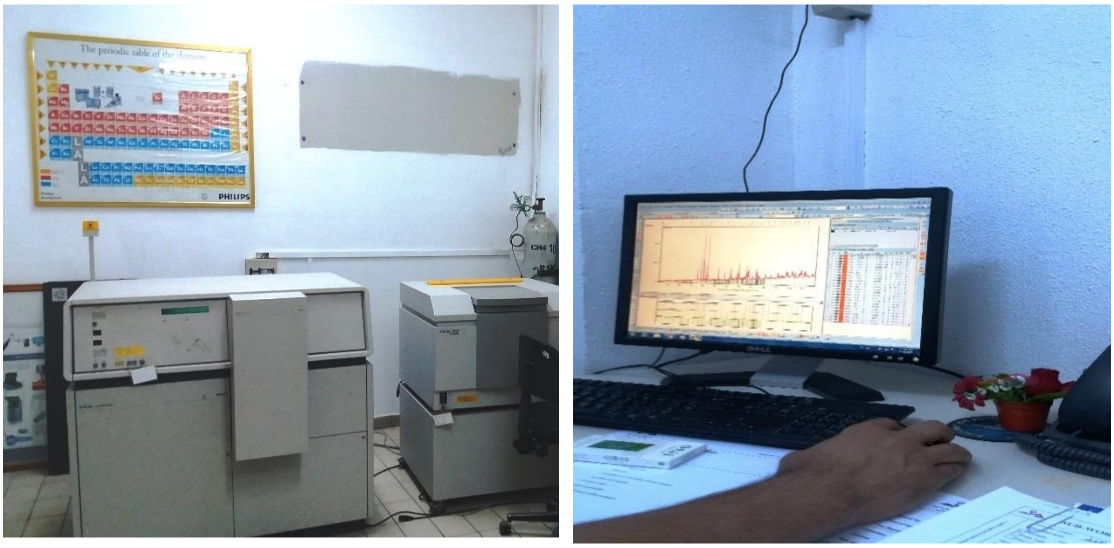

Figure 3.5. The XRD Machine. [Author image].

The XRD test was done (carried out at the laboratories of the Libyan petroleum institute, Tripoli, Libya).

The data collected and the mean of four amalgam dental filling samples for the all samples amalgam materials was measured, calculated and analyzed using

PART 4

RESULT AND DISCUSSION

4.1. X-RAY DIFFRACTION DATA AND RESULT

In this section the experimental result will discussion-ray diffraction data Analysis of amalgam fillings for mercury exposure was performed by the sol-gel method using X-ray diffraction (XRD). Amalgam dental fillings materials were analyzed with a PW 1800 X-ray Diffractometer, XRD patterns were recorded in the temperature range: 26.4 °C Relative humidity: 48%RH. The intensity of the obtained diffraction peak was determined by comparison with standard data having theta angle with higher intensity using JCPDS: 075-1687. The manufacturer of amalgam dental fillings, the peak intensity was mercury exposure. X-ray diffraction (XRD) technique was used to analyze exposure to mercury present in an unmixed sample, a mixed sample according to the manufacturer's recommendations, and dental amalgam fillings that had been in the patient's mouth after filling them for 15 and 20 years.

4.1.1. Unmixed Sample Dental Amalgam Filling

The results are shown unmixed sample in the Figure (1) revealed two main phases for the measured amalgams: $Ag3Sn$ and cu4zn in the XRD patterns were recorded from 2θ range of 26.4 °C.

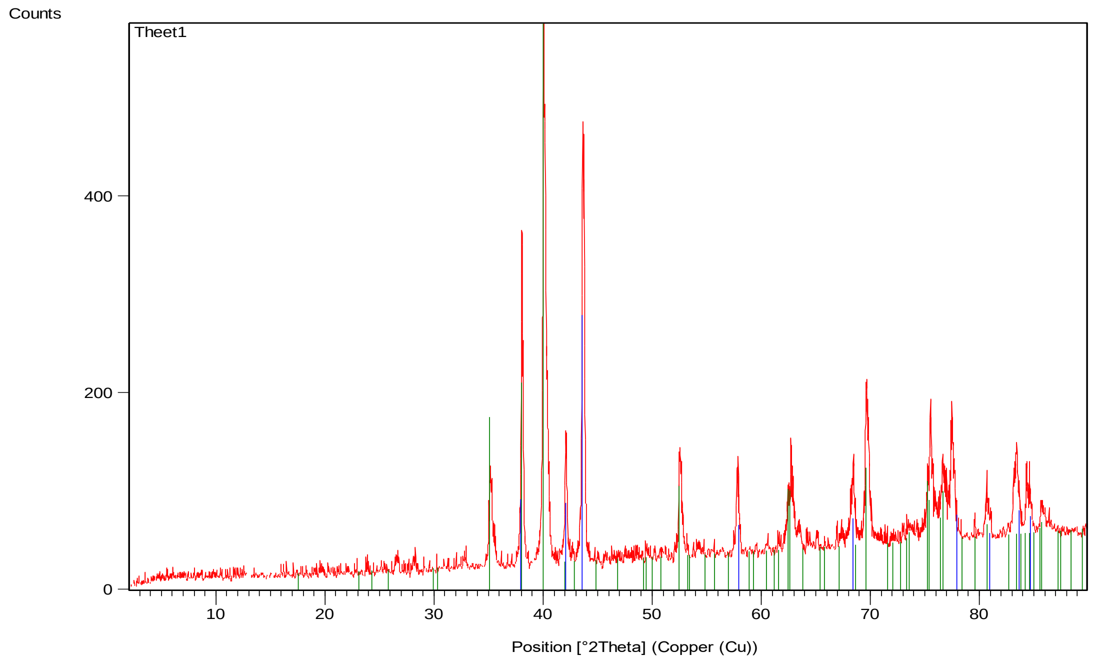

Figure 4.1. Analyze View of unmixed sample dental amalgam filling.

In Table 4.1. There is Analyze View of unmixed sample in the amount of mercury available in Pattern List & Semi Quantitative dental amalgam filling company unmixed was Ag3Sn 64 %, cu4zn 36%.

Table 4.1. Analyze view of unmixed sample dental amalgam filling.

	Ref. Code	Compound Name	Chemical Formula	Semi quantitative %
*	01-071-0530	Silver Tin	Ag3 Sn	64
*	03-065-6066	Copper Zinc	Cu4 Zn	36

Peak List of Unmixed Sample

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
26.58(2)	10(2)	0.24(7)	3.35098	2.44
26.65(2)	5(2)	0.24(7)	3.35098	1.22
35.183(6)	64(3)	0.33(2)	2.54872	16.27
35.273(6)	32(3)	0.33(2)	2.54872	8.13
38.046(2)	282(12) Ag3 Sn	0.133(9)	2.36324	71.42
38.145(2)	141(12) Cu4 Zn	0.133(9)	2.36324	35.71
40.102(2)	377(8) Ag3 Sn	0.271(9)	2.24672	95.48
40.206(2)	188(8)	0.271(9)	2.24672	47.74
42.071(4)	100(7)	0.17(2)	2.14601	25.44
42.180(4)	50(7)	0.17(2)	2.14601	12.72
43.654(2)	395(12)	0.170(7)	2.07178	100.00
43.768(2)	197(12) Cu4 Zn	0.170(7)	2.07178	50.00
52.546(5)	80(5)	0.27(2)	1.74022	20.25
52.686(5)	40(5)	0.27(2)	1.74022	10.13
57.796(6)	69(6)	0.22(3)	1.59399	17.38
57.953(6)	34(6)	0.22(3)	1.59399	8.69
62.68(1)	51(2)	0.64(4)	1.48092	12.80
62.86(1)	25(2)	0.64(4)	1.48092	6.40
68.34(1)	51(4)	0.40(4)	1.37145	12.93
68.54(1)	26(4)	0.40(4)	1.37145	6.47
69.654(4)	139(7) Ag3 Sn	0.27(2)	1.34880	35.23
69.852(4)	70(7)	0.27(2)	1.34880	17.61
75.46(1)	71(4)	0.52(5)	1.25879	18.10
75.68(1)	36(4)	0.52(5)	1.25879	9.05
76.68(2)	44(3)	0.60(6)	1.24183	11.27
76.90(2)	22(3)	0.60(6)	1.24183	5.64
77.482(7)	103(6)	0.26(2)	1.23090	26.19
77.711(7)	52(6)	0.26(2)	1.23090	13.10
80.69(1)	41(4)	0.24(3)	1.18991	10.43
80.93(1)	21(4)	0.24(3)	1.18991	5.22
83.32(1)	65(4)	0.41(4)	1.15888	16.36
83.57(1)	32(4)	0.41(4)	1.15888	8.18
84.37(1)	55(5)	0.26(3)	1.14708	13.99
84.63(1)	28(5)	0.26(3)	1.14708	6.99
85.78(3)	17(2)	0.6(1)	1.13180	4.21
86.05(3)	8(2)	0.6(1)	1.13180	2.11

4.1.2. Mixed Sample Dental Amalgam Filling

The results are shown mixed sample in the Figure (2) revealed two main phases for the measured amalgams: Cu10 Sn3 and Ag2 Hg3 in the XRD patterns were recorded from 2θ range of 26.4 °C.

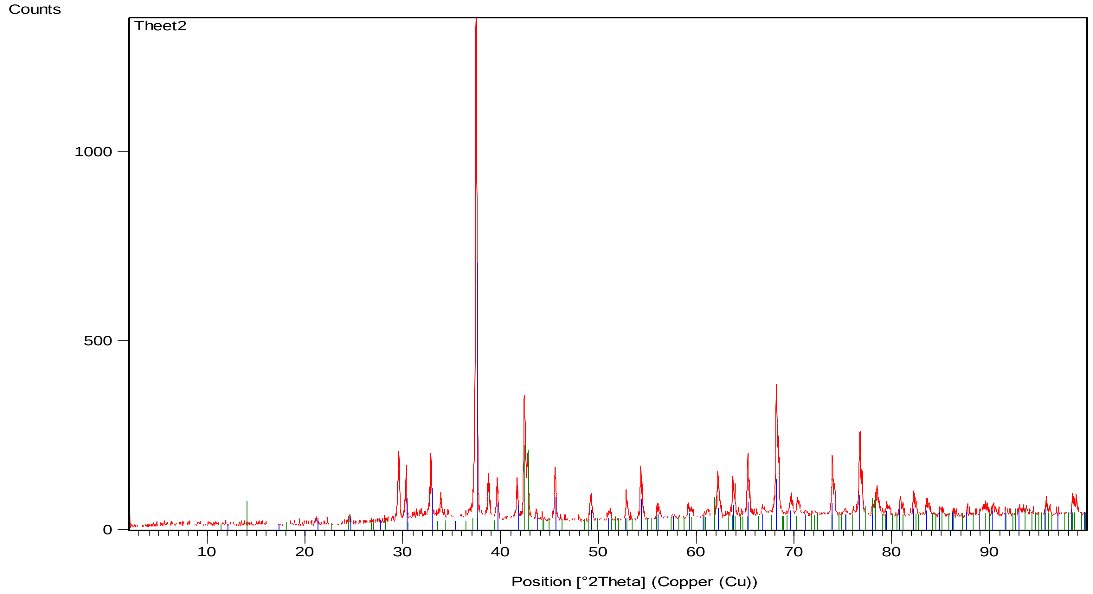

Figure 4.2. Analyze view of mixed sample dental amalgam filling.

In Table 4.2. There is Analyze View of unmixed sample in the amount of mercury available in Pattern List & Semi Quantitative dental amalgam filling company mixed was Cu10 Sn3 (37%), Ag2 Hg3(63%).

Table 4.2. Analyze view of mixed sample dental amalgam filling.

	Ref. Code	Compound Name	Chemical Formula	Semi Quantitative %
	03-065-3632	Copper Tin	Cu10 Sn3	37%
	03-065-6103	Silver Mercury	Ag2 Hg3	63%

Peak list of mixed sample

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
2.020878	0.001000	0.297659	43.68118	0.00
2.025900	0.000500	0.297659	43.68117	0.00
21.102600	8.137560	0.145690	4.20662	0.69
21.155640	4.068780	0.145690	4.20662	0.34
24.504270	17.105760	0.087852	3.62982	1.45
24.566100	8.552881	0.087852	3.62982	0.73
29.520040	130.437700	0.150110	3.02349	11.06
29.595070	65.218860	0.150110	3.02349	5.53
30.247470	73.967520	0.174889	2.95242	6.27
30.324430	36.983760	0.174889	2.95242	3.14
32.797020	125.014100	0.110788	2.72849	10.60
32.880830	62.507040	0.110788	2.72849	5.30
33.277240	15.118440	5.656797	2.69021	1.28
33.362340	7.559219	5.656797	2.69021	0.64
37.432680	1179.406000 Ag2 Hg3	0.115140	2.40056	100.00
37.529160	589.703000	0.115140	2.40056	50.00
38.714420	84.437040	0.161674	2.32398	7.16
38.814470	42.218520	0.161674	2.32398	3.58
39.579930	87.663830	0.144785	2.27513	7.43
39.682400	43.831910	0.144785	2.27513	3.72
41.631930	75.777570	0.153305	2.16761	6.43
41.740200	37.888790	0.153305	2.16761	3.21
42.393070	259.808200 Cu10 Sn3	0.175441	2.13044	22.03
42.503510	129.904100	0.175441	2.13044	11.01
42.697610	118.658900	0.158733	2.11595	10.06
42.808930	59.329440	0.158733	2.11595	5.03
43.597780	19.150960	0.163893	2.07432	1.62
43.711680	9.575479	0.163893	2.07432	0.81
45.523250	118.053600	0.139214	1.99096	10.01
45.642740	59.026780	0.139214	1.99096	5.00
49.163520	0.001000	0.198251	1.85172	0.00
49.293810	0.000500	0.198251	1.85172	0.00
49.301590	44.156210	0.001000	1.84686	3.74
49.432290	22.078100	0.001000	1.84686	1.87
52.812030	52.073970	0.156599	1.73206	4.42
52.953450	26.036980	0.156599	1.73206	2.21
54.304070	121.202700	0.138167	1.68794	10.28
54.450150	60.601370	0.138167	1.68794	5.14
56.041680	21.167480	0.280173	1.63966	1.79
56.193260	10.583740	0.280173	1.63966	0.90
59.243870	19.244760	0.381292	1.55844	1.63
59.405830	9.622382	0.381292	1.55844	0.82
61.100760	21.141290	0.163080	1.51545	1.79
61.268890	10.570650	0.163080	1.51545	0.90
62.175480	68.580890	0.268838	1.49182	5.81
62.347240	34.290450	0.268838	1.49182	2.91
63.734460	93.249610	0.147611	1.45903	7.91
63.911550	46.624810	0.147611	1.45903	3.95
65.235530	144.110200	0.139486	1.42904	12.22
65.417840	72.055100	0.139486	1.42904	6.11

4.1.3. Sample after 15 years' Dental Amalgam Filling

The results are shown after 15 years' dental amalgam filling in the Figure (3) revealed two main phases for the measured amalgams: CuZn and Ag_2Hg_3 in the XRD patterns were recorded from 2θ range of 26.4 °C.

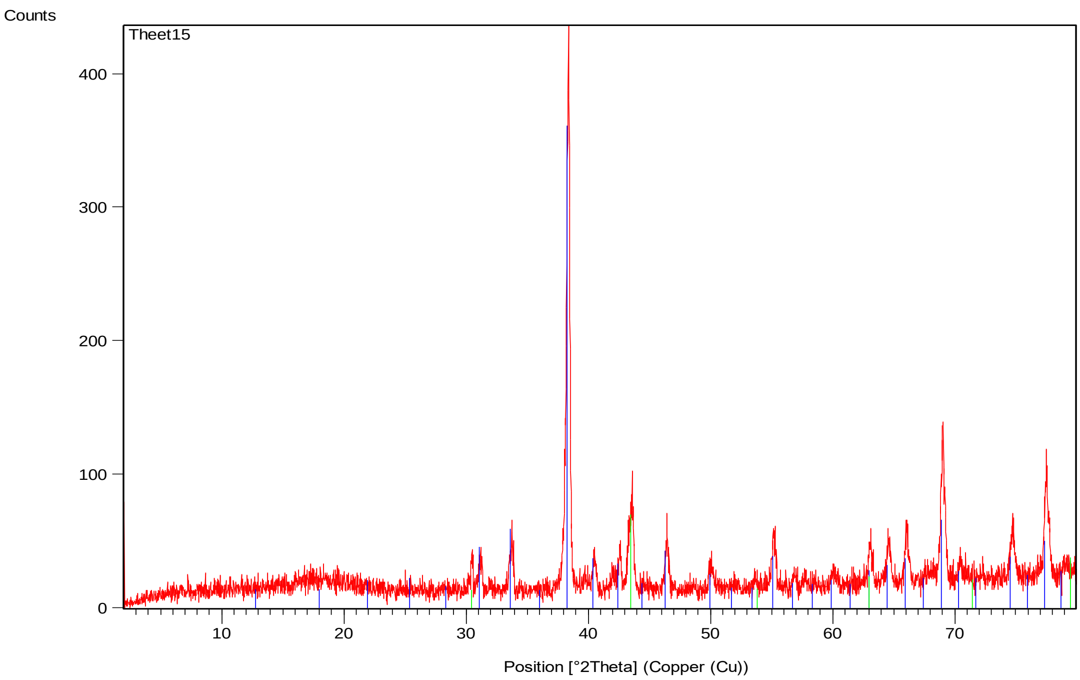

Figure 4.3. Analyze View of sample after 15 years' dental amalgam filling.

In table 4.3. There is Analyze View of samples after 15 years in the amount of mercury available in Pattern List & Semi Quantitative dental amalgam filling company mixed was CuZn (16%), Ag_2Hg_3(84%).

Table 4.3. Analyze view of sample after 15 years dental amalgam filling.

	Ref. Code	Compound Name	Chemical Formula	Semi quantitative %
(blue)	03-065-6103	Silver Mercury	Ag_2Hg_3	84
(green)	03-065-9061	Copper Zinc	CuZn	16

Peak List of sample# 15Y

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
30.457(8)	25(5)	0.11(3)	2.93263	6.85
30.534(8)	12(5)	0.11(3)	2.93263	3.42
31.15(1)	16(2)	0.27(3)	2.86879	4.59
31.23(1)	8(2)	0.27(3)	2.86879	2.30
33.671(9)	24(2)	0.31(2)	2.65962	6.70
33.758(9)	12(2)	0.31(2)	2.65962	3.35
38.326(2)	359(13) Ag_2Hg_3	0.17(1)	2.34663	100.00
38.425(2)	179(13)	0.17(1)	2.34663	50.00
40.47(1)	17(2)	0.32(4)	2.22712	4.71
40.58(1)	8(2)	0.32(4)	2.22712	2.36
42.53(1)	19(3)	0.31(7)	2.12374	5.30
42.64(1)	10(3)	0.31(7)	2.12374	2.65
43.472(7)	47(2) CuZn	0.41(2)	2.08005	12.98
43.585(7)	23(2)	0.41(2)	2.08005	6.49
46.395(8)	29(2)	0.28(2)	1.95558	8.02
46.517(8)	14(2)	0.28(2)	1.95558	4.01
50.04(2)	12(1)	0.37(5)	1.82116	3.35
50.18(2)	6(1)	0.37(5)	1.82116	1.68
55.147(9)	32(3)	0.29(4)	1.66413	8.93
55.296(9)	16(3)	0.29(4)	1.66413	4.46
60.05(3)	7(1)	0.4(1)	1.53941	2.07
60.22(3)	4(1)	0.4(1)	1.53941	1.04
63.04(1)	27(3)	0.24(5)	1.47351	7.54
63.21(1)	14(3)	0.24(5)	1.47351	3.77
64.56(1)	28(4)	0.23(5)	1.44238	7.85
64.74(1)	14(4)	0.23(5)	1.44238	3.93
66.03(1)	29(3)	0.31(4)	1.41369	8.02
66.22(1)	14(3)	0.31(4)	1.41369	4.01
68.975(5)	90(5) Ag_2Hg_3	0.27(2)	1.36040	25.06
69.171(5)	45(5)	0.27(2)	1.36040	12.53
74.68(1)	27(3)	0.34(4)	1.27003	7.43
74.89(1)	13(3)	0.34(4)	1.27003	3.72
77.460(6)	66(4)	0.28(2)	1.23120	18.39
77.688(6)	33(4)	0.28(2)	1.23120	9.20

4.1.4. Sample After 20 Years' Dental Amalgam Filling

The results are shown after 20 years' dental amalgam filling in the Figure (4) revealed two main phases for the measured amalgams: CuZn and Ag_2Hg_3 in the XRD patterns were recorded from 2θ range of 26.4 °C.

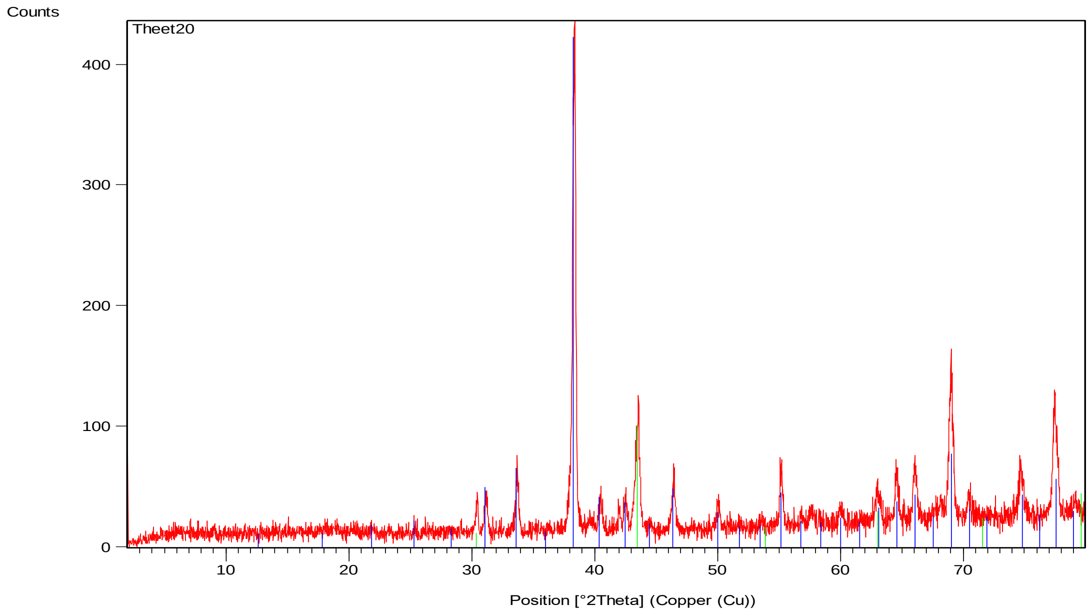

Figure 4.4. Analyze View of sample after 20 years' dental amalgam filling.

In Table 4. There is Analyze View of samples after 20 years in the amount of mercury available in Pattern List & Semi Quantitative dental amalgam filling company mixed was Cu Zn (20%), Ag2 Hg3(80%).

Table 4.4. Analyze View of sample after 20 years dental amalgam filling.

	Ref. Code	Compound Name	Chemical Formula	Semi quantitative %
	03-065-6103	Silver Mercury	Ag_2Hg_3	80
	03-065-9061	Copper Zinc	CuZn	20

Peak List of sample# 20 Y

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
30.408(9)	20(3)	0.18(3)	2.93723	5.44
30.485(9)	10(3)	0.18(3)	2.93723	2.72
31.146(9)	20(2)	0.28(3)	2.86922	5.52
31.226(9)	10(2)	0.28(3)	2.86922	2.76
33.686(7)	32(2)	0.26(2)	2.65851	8.68
33.772(7)	16(2)	0.26(2)	2.65851	4.34
38.311(2)	366(11) Ag_2Hg_3	0.184(9)	2.34752	100.00
38.410(2)	183(11)	0.184(9)	2.34752	50.00
40.46(1)	19(2)	0.27(5)	2.22753	5.31
40.57(1)	10(2)	0.27(5)	2.22753	2.66
42.48(2)	17(2)	0.32(8)	2.12637	4.60
42.59(2)	8(2)	0.32(8)	2.12637	2.30
43.467(6)	62(2) CuZn	0.39(2)	2.08026	16.95
43.581(6)	31(2)	0.39(2)	2.08026	8.48
46.382(9)	27(2)	0.31(3)	1.95607	7.35
46.504(9)	13(2)	0.31(3)	1.95607	3.67
50.04(1)	17(3)	0.23(4)	1.82148	4.73
50.17(1)	9(3)	0.23(4)	1.82148	2.36
55.158(7)	40(4)	0.22(3)	1.66382	11.01
55.307(7)	20(4)	0.22(3)	1.66382	5.50
60.01(2)	12(2)	0.28(7)	1.54043	3.15
60.17(2)	6(2)	0.28(7)	1.54043	1.58
63.01(1)	21(2)	0.35(6)	1.47414	5.70
63.18(1)	10(2)	0.35(6)	1.47414	2.85
64.552(8)	39(4)	0.21(3)	1.44250	10.56
64.732(8)	19(4)	0.21(3)	1.44250	5.28
66.034(9)	40(4)	0.26(4)	1.41369	10.85
66.219(9)	20(4)	0.26(4)	1.41369	5.43
68.959(5)	101(5) Ag_2Hg_3	0.28(2)	1.36069	27.55
69.154(5)	50(5)	0.28(2)	1.36069	13.77
70.42(2)	18(3)	0.20(4)	1.33602	4.85
70.62(2)	9(3)	0.20(4)	1.33602	2.42
74.66(1)	38(4)	0.22(3)	1.27023	10.39
74.88(1)	19(4)	0.22(3)	1.27023	5.19
77.423(6)	80(5) Ag_2Hg_3	0.29(2)	1.23169	21.85
77.651(6)	40(5)	0.29(2)	1.23169	10.93

4.2. DISCUSSION

This was an in vivo study which involves the use of remove dental amalgam filling human. Therefore, consent was obtained from the patients.

In the present study the amount of mercury released from dental amalgams with silver content unmixed sample, a mixed sample according to the manufacturer's recommendations, and dental amalgam fillings that had been in the patient's mouth after filling them for 15 and 20 years.

The results of this study showed There is no mercury unmixed sample This sample contains on silver Tin 64% and copper zinc 36% While mixed samples contain of silver mercury 63% and copper Tin 37%, the sample after 15 years' dental amalgam filling induced when the silver mercury contain is increased to 84% and low copper Tin 16%, While the sample after 20 years' dental amalgam filling containing approximately silver mercury contain is 80% and copper Tin 20%.

The silver-mercury phase (1) is the dental amalgam structure's matrix, and it has a significant impact on its mechanical behavior and interaction with the environment. In addition, amalgam restorations are the primary source of mercury emitted. 1 contains roughly 67-70 percent mercury as part of the dental amalgam composition.

The second approach, X-ray diffraction (XRD), takes advantage of the fact that atoms in alloys form crystal lattices, allowing for the identification of specific phases in materials.

The goal of the study was to use XPS and XRD techniques to analyze the general composition of seven distinct commercially available high copper dental amalgams (HCSS). We also looked into the chemical relationships between amalgam components and the oxygen reactivity of the key metallic elements in the amalgams under investigation.

The fractured samples' spectra revealed the presence of carbon. The relative concentrations of the various elements are critical for the XPS investigations. Using the peak area and peak height sensitivity factors, the Multipack Physical Electronics application can quantify XPS spectra. The typical atomic concentration computation yields a ratio of each component to the total number of other components in the data set. Only those elements were taken into account for which a distinct line can be seen in the spectrum. For those lines, the backdrop was removed, the line's region's limit was individually picked, and then integration was performed [57].

The association between the makeup and the mercury release rate of several type of dental amalgam was investigated. In the g1 phase, mercury emissions reduced as the tin level increased. Zinc, on the other hand, did not have the same effect as tin. The key predictor of mercury vapor release, according to this paper, is the tin level in the g1 phase. The creation of a surface oxide layer composed of tin and zinc, as well as its effect on mercury leakage, were validated in an ongoing work and this investigation by Berglund et al., which is consistent with Ferracane et. Indiloy, on the other hand, had a greater mercury release than the other indium-free amalgams because its surface was rapidly coated by indium with oxygen. As a result, indium's surface layer was shown to be less effective than tin and zinc at preventing mercury emission. Okabe et al., on the other hand [58].

PART 5

CONCLUSION AND FUTURE WORK

5.1. CONCLUSION

Within the limitations of the study, the following conclusions can be drawn:

- There are some changes that occurred in the unmixed sample dental amalgam filling in terms of compounds, as the silver Tin compound and another Copper Zinc compound appeared. As for the silver mercury element, it did not appear in the results.
- Dental amalgam filling mixed in terms of compounds, where the silver mercury compound appeared with a high value before it was filled inside the dental cavity and the other copper Zinc compound appeared.
- A sample after dental amalgam filling for 15 and 20years in terms of compounds, where the silver mercury compound appeared in a higher value than the filling of the mixed sample and the other copper compound appeared.
- Unmixed sample and mixed sample dental amalgam filling to new technological effect gives rise to decrease the mercury in the amalgam.
- A sample after dental amalgam filling for 15 and 20 years there was no like process might be leakage.

5.2. FUTURE WORK

I would recommend a future work following this study entitled microstructural treatment on Scanning Electron Microscope (SEM / EDAX) and X-ray fluorescence spectrometer (XRF) of the dental amalgam filling material.

REFERENCES

1. Bengtsson UG, Hylander LD. Increased mercury emissions from modern dental amalgams. ***Biometals.*** ;30(2):277–83 (2017).

2. Shenoy A. Is it the end of the road for dental amalgam? ***A critical review. J Conserv Dent JCD.*** ;11(3):99 (2008).

3. Mason HJ, Hindell P, Williams NR. Biological monitoring and exposure to mercury. ***Occup Med (Chic Ill).***;51(1):2–11 (2001).

4. Palkovicova L, Ursinyova M, Masanova V, Yu Z, Hertz-Picciotto I. Maternal amalgam dental fillings as the source of mercury exposure in developing fetus and newbor***n. J Expo Sci Environ Epidemiol***.;18(3):326–31 (2008).

5. Vimy MJ, Takahashi Y, Lorscheider FL. Maternal-fetal distribution of mercury (203Hg) released from dental amalgam fillings. ***Am J Physiol Integr Comp Physiol.***;258(4):R939–45 (1990).

6. Takahashi Y, Tsuruta S, Hasegawa J, Kameyama Y, Yoshida M. Release of mercury from dental amalgam fillings in pregnant rats and distribution of mercury in maternal and fetal tissues. ***Toxicology.*** ;163(2–3):115–26 (2001).

7. Pizzichini M, Fonzi M, Giannerini F, Mencarelli M, Gasparoni A, Rocchi G, et al. Influence of amalgam fillings on Hg levels and total antioxidant activity in plasma of healthy donors. ***Sci Total Environ.*** ;301(1–3):43–50 (2003).

8. Christensen GJ. Longevity of posterior tooth dental restorations. ***J Am Dent Assoc.*** ;136(2):201–3 (2005).

9. Roeters JJM, Shortall ACC, Opdam NJM. Can a single composite resin serve all purposes? ***Br Dent J***. ;199(2):73–9 (2005).

10. Burke FJT, Shortall ACC. Successful restoration of load-bearing cavities in posterior teeth with direct-replacement resin-based composite***. Dent Update.*** ;28(8):388–98 (2001).

11. Christensen GJ. Amalgam vs. composite resin: 1998. ***J Am Dent Assoc***. ;129(12):1757–9 (1998).

12. Lynch CD, McConnell RJ. The cracked tooth syndrome. ***Journal-Canadian Dent Assoc***. 2002;68(8):470–5 (2002).

13. Wilson NHF, Dunne SM, Gainsford ID. Current materials and techniques for direct restorations in posterior teeth: Part 2: resin composite systems. ***Int Dent J***. 47(4):185–93 (1997).

14. Index M. 9th edn., Merck and Co. Inc***(Rahway, NJ, USA***). 1976.

15. World Health Organization. Inorganic mercury. ***Who***, USA, (1991).

16. World Health Organization. Environmental health criteria. Environ Heal criteria 1 Mercury. ***Who***, USA , (1976).

17. World Health Organization. Environmental health criteria 101: methylmercury. Geneva, Switz ***Who***, USA.68–9 (1990).

18. Levason W, McAuliffe CA. The coordination chemistry of mercury. In: ***The chemistry of mercury springer***. p. 47–135 (1977).

19. Stock A, Cucuel F. Die Bestimmung des Quecksilber-Gehaltes der Luft. Vol. 67, ***Berichte der deutschen chemischen Gesellschaft*** (A and B Series). WILEY-VCH Verlag Berlin; (1934).

20. Frykholm KO. On Mercury from Dental Amalgam: Its Toxic and Allergic Effects, and Some Comments on Occupational Hygiene. ***Almqvist & Wiksells boktr***. (1957).

21. Abraham JE, Svare CW, Frank CW. The effect of dental amalgam restorations on blood mercury levels. ***J Dent Res***. 63(1):71–3.(1984).

22. Barregård L, Sällsten G, Järvholm B. People with high mercury uptake from their own dental amalgam fillings. ***Occup Environ Med.***;52(2):124–8.(1995).

23. Elinder CG, Gerhardsson L, Oberdoerster G. Bi-ological monitoring of toxic metals–Overview. In "Biological Monitoring of Toxic Metals"(TW Clarkson, I. Friberg, GF Nordberg, and PR Sager, Eds.). Plenum Press New York Erkkilä, J, Armstrong, R, Riihimäki, V, Chettle, DR, Paakkari, A, Scott, M, Somervaille, L, Starck, J, Kock, B, Aitio, A(1992) vivo ***Meas lead bone four Anat sites Long term Occup*** .;49:631–44 (1988).

24. Hahn LJ, Kloiber R, Vimy MJ, Takahashi Y, Lorscheider FL. Dental "silver" tooth fillings: A source of mercury exposure revealed by whole-body image scan and tissue analysis. ***FASEB J***. ;3(14):2641–6 (1989).

25. Sällsten G, Barregård L, Schütz A. Decrease in mercury concentration in blood after long term exposure: a kinetic study of chloralkali workers. ***Occup Environ Med***. ;50(9):814–21 (1993).

26. Rahola T, Hattula T, Korolainen A, Miettinen JK. Elimination of free and protein-bound ionic mercury (203 Hg 2+) in man. ***Ann Clin Res***.5(4):214–9 (1973).

27. Skare I, Engqvist A. Urinary mercury clearance of dental personnel after a longterm intermission in occupational exposure. ***Swed Dent J***, 14(6):255–9 (1990).

28. Nylander M, Friberg L, Eggleston D, Björkman L. Mercury accumulation in tissues from dental staff and controls in relation to exposure. ***Swed Dent J***, 13(6):235–43 (1989).

29. Lind B, Friberg L, Nylander M. Preliminary studies on methylmercury biotransformation and clearance in the brain of primates: II. Demethylation of mercury in brain. ***J Trace Elem Exp Med***, 1(1):49–56 (1988).

30. Hursh JB, Clarkson TW, Cherian MG, Vostal JJ, Mallie R Vander. Clearance of mercury (Hg-197, Hg-203) vapor inhaled by human subjects. ***Arch Environ Heal An Int J,*** 31(6):302–9 (1976).

31. Clarkson TW. Nickel.–Teoksessa Clarkson, TW, Friberg, L., Nordberg, GF, Sager, PR (toim.), Biological Monitoring of Toxic Metals, **Plenum Press**. New York, 265-282 (1988).
32. Engqvist A. Mercury ***exposure from amalgam fillings.*** 1998.

33. Hansson M. "Changes in health after removal of toxic dental filling materials". ***TF-BLADET***, 1:3–30 (1986).

34. Ahlqwist M, Bengtsson C, Furunes B, Hollender L, Lapidus L. Number of amalgam tooth fillings in relation to subjectively experienced symptoms in a study of Swedish women. ***Community Dent Oral Epidemiol,*** 16(4):227–31 (1988).

35. Berglund A, Molin M. Mercury vapor release from dental amalgam in patients with symptoms allegedly caused by amalgam fillings. ***Eur J Oral Sci,*** 104(1):56–63 (1996).

36. Larsson KS. Teratological aspects of dental amalgam. ***Adv Dent Res***. 6(1):114–9 (1992).

37. Eti S, Weisman R, Hoffman R, Reidenberg MM. Slight renal effect of mercury from amalgam fillings. ***Pharmacol Toxicol,*** 76(1):47–9 (1995).

38. Herrström P, Schütz A, Raihle G, Holthuis N, Högstedt B, Råstam L. Dental amalgam, low-dose exposure to mercury, and urinary proteins in young Swedish men. ***Arch Environ Heal An Int J,*** 50(2):103–7 (1995).

39. Langworth S, Elinder C-G, Sundqvist K-G. Minor effects of low exposure to inorganic mercury on the human immune system. ***Scand J Work Environ Health,*** 405–13 (1993).

40. Bolewska J, Holmstrup P, Møller-Madsen B, Kenrad B, Danscher G. Amalgam associated mercury accumulations in normal oral mucosa, oral mucosal lesions of lichen planus and contact lesions associated with amalgam. ***J Oral Pathol Med,*** 19(1):39–42 (1990).

41. Blitzer MH, Pollack B. Mercury leakage in commercially preloaded amalgam--mercury capsules. ***Gen Dent***, 29(2):144–5 (1981).

42. Rubin PG, Yu M-H. Mercury vapor in amalgam waste discharged from dental office vacuum units. ***Arch Environ Heal An Int J,*** 51(4):335–7 (1996).

43. Studebaker M. Review of: Life, Death, and In-Between on the US-Mexico Border (Martha Oehmke Loustaunau & Mary Sanchez-Bane, eds.). ***RISK Heal Saf Environ,***11(4):11(2000).

44. Internet : Dental Board of California. The Facts About Fillings. CALIFORNIA Department of consumer Affairs 2004. 4 p. Available from: **https://www.dbc.ca.gov/formspubs/pub_dmfs2004.pdf,** (2004).

45. Internet: A.D Association. silver-colored dental fillings 2019. Available from: **https://www.mouthhealty.org/en/az-topics/a/amalgam** (2019).

46. Internet: A.D Association. Composite Fillings 2019. Available from: **https://www.mouthhealthy.org/en/az-topics/c/composite-fillings** (2019).

47. Patki B. Direct permanent restoratives--amalgam vs composite. ***J Evol Med Dent Sci,*** 2(46):8912–9 (2013).

48. AFFAIRS ADACONS. Dental amalgam: Update on safety concerns. ***J Am Dent Assoc,*** 129(4):494–503 (1998).

49. Uo M, Berglund A, Cardenas J, Pohl L, Watari F, Bergman M, et al. Surface analysis of dental amalgams by X-ray photoelectron spectroscopy and X-ray diffraction. ***Dent Mater,*** *1*9(7):639–44 (2003).

50. Talik E, Babiarz-Zdyb R, Dziedzic A. Chemical characterization of selected high copper dental amalgams using XPS and XRD techniques. ***J Alloys Compd,*** 398(1–2):276–82 (2005).

51. Bahari M, Oskoee PA, Oskoee SS, Pouralibaba F, Ahari AM. Mercury release of amalgams with various silver contents after exposure to bleaching agent. ***J Dent Res Dent Clin Dent Prospects,*** 10(2):118 (2016).

52. Internet: Bengtsson, Ulf G LDH. springer.com. 2017; Available from: **www.springerlink.com** (2017).

RESUME

Yousef Abdalali ALASHHAB was born in Tripoli in 1983 and he graduated elementary, primary, high school education in this city. After that, he started undergraduate program in high institute – Tripoli, Department of Electrical Machines in 2005. Then in 2020, he started at Karabük University To complete M.Sc. education.