African Journal of Advanced Pure and Applied Sciences (AJAPAS)
Online ISSN: 2957-644X
Volume 3, Issue 3, July-September 2024, Page No: 149-154
Website: https://aaasjournals.com/index.php/ajapas/index
معامل التأثير العربي 2023: (1.55) SJIFactor 2023: 5.689 ISI 2023-2024: 0.877

Estimating the Percentage of Lead in Different Types of Pottery Dinnerware Used in Libyan Home

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تقدير نسبة الرصاص في أنواع مختلفة من بعض أواني الطعام الفخارية المستعملة في المنزل الليبي

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Received: June 12, 2024	Accepted: August 04, 2024	Published: August 28, 2024

Abstract:

Many people have long used ceramics to make dishes and utensils needed to prepare and cook food, and these colorful ceramic utensils used for eating are a source of lead poisoning. The current study aimed to disclose the amount of lead in the colors used to paint ceramic dinnerware in the Libyan home. In this study, dissolved lead was estimated from pottery utensils manufactured locally in Libya and imported from Tunisia and China for comparison, using a 4% acetic acid solution by volume. Through the results of the analysis of lead released in the acid solution from 18 samples of ceramic vessels, the results showed that the concentrations of total lead released in locally manufactured ceramic vessels ranged between (0.204 - 1.968) µg/ml. These results came within the range of values allowed by the US Food and Drug Administration as well as the International Evaluation Organization. The concentration of dissolved lead in ceramic utensils imported from Tunisia and China ranged between (0.223 - 2.160) µg/ml and (0.0124 - 3.597) µg/ml, respectively. These values are higher than those allowed internationally, which must not exceed 2.2 parts per million. The amount of lead dissolved in these utensils is directly proportional to the increase in its concentration. In the paints used, in addition to increasing the colors that contain it, which are red, green, white, and pink. In general, the concentration of lead released from locally manufactured ceramic utensils is lower than ceramic utensils imported from Tunisia and China, which must not exceed internationally permissible limits.

Keywords: Lead Poisoning, Ceramic Vessels, Food, Paint Colors.

الملخص

يستخدم الكثير من الناس منذ فترة طويلة السيراميك في صنع الأطباق والأواني اللازمة لإعداد وطهي الطعام، وتعتبر هذه الأواني الخزفية الملونة المستخدمة في تناول الطعام مصدرًا للتسمم بالرصاص. هدفت الدراسة الحالية إلى الكشف عن كمية الرصاص الموجودة في الألوان المستخدمة في طلاء أواني الطعام الخزفية في المنزل الليبي. في هذه الدراسة تم تقدير الرصاص المذاب من الأواني الفخارية المصنعة محليا في ليبيا والمستوردة من تونس والصين للمقارنة، وذلك باستخدام محلول حمض الخليك 4٪ من حيث الحجم. ومن خلال نتائج تحليل الرصاص المنطلق في المحلول الحمضي من 18 عينة من الأواني الخزفية أظهرت النتائج أن تراكيز الرصاص الكلي المنطلق في الأواني الخزفية المصنعة محلياً تراوحت بين (0.204-1.968) ميكروغرام/مل. وجاءت هذه النتائج ضمن نطاق القيم التي تسمح بها إدارة الغذاء والدواء الأمريكية وكذلك منظمة التقييم الدولية. تراوح تركيز الرصاص المذاب في الأواني الخزفية المستوردة من تونس والصين بين (0.223-2.160) ميكروغرام/مل و(0.0124-3.597) ميكروغرام/مل على التوالي. وهذه القيم أعلى من تلك المسموح بها دوليا، والتي يجب ألا تتجاوز 2.2 جزء في المليون. وتتناسب كمية الرصاص المذابة في هذه الأواني بشكل مباشر مع الزيادة في تركيزها. في الدهانات المستخدمة، بالإضافة إلى زيادة الألوان التي تحتوي عليه، وهي الأحمر، والأخضر، والأبيض، والوردي. وبشكل عام، فإن تركيز الرصاص المنطلق من الأواني الخزفية المصنعة محلياً أقل من الأواني الخزفية المستوردة من تونس والصين، والتي يجب ألا تتجاوز الحدود المسموح بها دولياً.

الكلمات المفتاحية: التسمم بالرصاص، الأواني الخزفية، الأغذية، ألوان الطلاء.

Introduction

Lead has unique physical and chemical properties that make it suitable for a large number of applications, the benefits of which humans have exploited since historical times. Due to its continuous use, its levels are rising in almost every country, especially developing countries, and it is characterized by a high degree of persistence in the environment until it has become a common environmental pollutant, which poses serious threats and impacts. On the functions of the human body [1]. The main sources of lead exposure are paints, water, food, dust, soil, kitchen utensils, and leaded gasoline. The majority of cases of lead poisoning are due to oral ingestion and absorption through the gut [2]. Lead affects all systems of the body, but it also affects the neurological, hematologcial, and renal systems most prominently. Iron deficiency appears to increase the risk of lead absorption, but anemia due to lead poisoning is uncommon. Although children with lead poisoning require appropriate medical and public health intervention, efforts should be directed at primary prevention of lead exposure [3].

Pottery making is among the traditional industries that carry an artistic character. It was known to man before the invention of writing and was given great importance by man. The pottery industry appeared since ancient times, when people formed many vessels of different shapes and sizes to satisfy their daily needs and desires. They shaped them by hand and decorated them either by scratching on the soft clay before burning it or by painting in colors that contrasted with the color of the pottery made [1]. Recently, the use of regular and colored ceramic vessels has spread, especially for preserving and serving Food, and it is manufactured in an attractive and colorful way, as engraving and drawing are done using its own-colored printing inks, which include organic dyes and some non-food dyes. Organic salts such as lead, chromium, copper, and cadmium are likely to be transported, the components of those inks are transferred to food [6]. Lead chromate (PbCrO4) is an inorganic pigment used in paints and inks, and most countries prepare it from the use of PbCrO4 in coating ceramic vessels that come into contact with food. Contamination of food with heavy metals may pose a threat to human health, even if a small amount of these metals accumulates in human organs and thus transform into large concentrations in the human body, leading to the appearance of biotoxic effects and many diseases [7].

Just as in 1897, Britain suffered approximately 423 cases of lead poisoning, and it became clear that the cause was the use of ceramic vessels painted with paints containing lead compounds. This problem prompted the British government to ban the use of this type of lead paint on ceramic utensils used for eating and drinking. Because the use of lead-containing paints in ceramic vessels leads to the release of a quantity of lead into the acid solution.

As health organizations in the United States of America and the European Union have emphasized the necessity of the safety of materials in contact with food; In order not to cause any harm to human health, and to be inert materials that do not interact with food, and do not cause any change in the components of the food item [8], nutrition scientists have also been interested in studying the transfer of mineral elements from the utensils used in preparing, preserving and serving food to the food item and studying Factors that affect the leakage of metals into food, such as heating and the period of contact of food with those utensils [9].

It is no secret that the high toxicity of heavy metals causes harm to human health if their concentration exceeds the permissible limits because they are capable of accumulating in the body's tissues and negatively affecting cell growth. Poisoning occurs when these metals enter the body in large quantities over a short period or when they enter in the form of a compound (Biochemical) or when it enters the body indirectly [10].

Several studies and research have indicated that lead accumulates in the lungs, brain tissue, and nervous system, causing damage to nerve cells and slow mental development, and causes problems in the liver, pancreas, kidneys, and reproductive system. It is deposited in the teeth and bones in the form of insoluble lead triphosphate, and leads to Lack of full benefit from vitamin D [11],[12]. Lead also affects the blood by affecting the main enzymes for the formation of hemoglobin [7]. Lead oxides and its compounds were used in the manufacture of pigments and inks used in painting ceramic vessels, because of its characteristics that make it one of the most widely used metals, including its cheap price, low melting point, and its ability to mix with other metals. Lead oxides and its compounds were used in the manufacture of different types of paint, such as the oxide compound. Red lead (Pb3O4) is used in the manufacture of red paints, basic lead carbonate (Pb (OH)2] and PbCO3] are used in the manufacture of white paints, and lead chromate (PbCrO4) is yellow in color, which is used in the manufacture of yellow pigments. All of these are used Pigments are widely used in coating ceramic utensils and equipment [13].

Lead is a heavy, bluish-gray metal with the chemical symbol Pb, which is an abbreviation of the Latin name for lead (Plum bum). Its atomic number is 82 and its atomic weight is 207.2. Lead is one of the heaviest common metals, as its density is 11.3 g/cm3 and its melting point is 327.46 degrees Celsius, according to the World Health Organization [16]. Raw lead makes up 0.005 of the Earth's crust. It is located at the bottom of the carbon group in the periodic table. Its electronic structure is [Xe] 6S2 4f14 5d10 6P2. It has a low melting point. It is malleable and ductile. It can be combined with other metals to form alloys. It has been widely used for thousands of years and is used in the manufacture of many products such as batteries. Paints, dyes, glass manufacturing, ammunition, cable covering and protective clothing. It is similar to the rest of the members of the family in that it has two valences (+2) and (+4). +2 is its distinctive valence, and the valence (+4) is common, and this requires raising the

electrons from the lower state to an excited state in which the orbitals hybridize according to the SP3 pattern, so the molecules corresponding to this valence have a quadrilateral shape and regular faces [16, 17].
In a study conducted by Moftah and Waldayek (2016) on ceramic glaze and lead poisoning. The results of the analysis of lead released into the acidic solution from the ceramic pots indicated that the total lead released from those pots was (0.706-1.963) µg/mL in the local pots, (1.724- 2.039) µg/mL in the Tunisian pots, and (1.908-3.591) µg/ml. Milliliters in Chinese utensils were higher than those allowed by domestic and international standards, which should not exceed 2 parts per million (ppm). [14]
And another study was conducted by Al-Mahmudi and Abu Boslou'a (2016) to measure the amount of molten lead from ceramic pots in the Libyan market and its suitability with international standards. Where the results of the sample analysis showed that the locally manufactured utensils contained a concentration of lead that ranged between (0.622-1.963) micrograms/milliliter, and these results were in the range of values allowed by the American Food and Drug Administration (FDA) as well as the International Organization for Standardization (ISO). As for the utensils Ceramic pots imported from Tunisia and China, the concentration of dissolved lead in them ranged between (2.039-5.421) micrograms/milliliter (2.089 - 5.421) micrograms/milliliter, respectively, and these values are higher than those allowed globally. [15, 16]
The importance of the research lies in the definition and awareness of the danger of oxides containing lead, which are used in coloring ceramic dinnerware, which is directly related to various diseases that affect the human body. The current study aimed to disclose the amount of lead in the colors used to paint ceramic dinnerware in the Libyan market, and introduce and raise awareness of the dangers of using ceramic dinnerware that contains a high percentage of lead.

Material and methods

This study included 18 samples of local and imported pottery food utensils in the Libyan market, painted with different paints from three different sources from Libya, Tunisia, and China. The amount of lead in all samples was measured using an atomic absorption device, following the method used by Richard et al., 1979, and Margham, et al. 2000. Materials used in this study Acetic acid 4%, distilled water, pipette, standard beaker, capacity 100 ml, beaker, utensils Food, crockery, plastic lid, soap bottle, dry wipes, soft cloth, analysis tubes. Lead oxides. Flame atomic absorption device, model type (spectra A.A 50. B.). Samples were prepared for analysis. The samples were immersed and washed well with soap and water. After completing the washing process, the samples were rinsed with sufficient amounts of water, done with ion-free distilled water, and the samples were left to dry in the laboratory environment free of dust and dirt. Prepare a standard solution of acetic acid with a concentration of 4% by taking 4 ml of acetic acid 100% using a pipette and put this amount in a standard beaker with a capacity of 100 ml, then add distilled water up to the mark and shake well. than tack 100ml of a standard solution of 4% acetic acid is poured into each sample. the samples are covered with a plastic cap immediately after the acetic acid standard solution is poured; To prevent the acid from evaporating, it was left for 24 hours in a dark place, at a laboratory temperature of about 25 degrees Celsius, then the solution was transferred to volumetric bottles, and the dissolved lead was estimated using a Varian atomic absorption device, model 52/55, at a wavelength of 217 nm. Using a flame burner of acetylene gas and air.

Results and Discussion

1. Lead released from locally manufactured painted ceramic samples:

The results of the analysis of dissolved lead from ceramic vessels showed a difference in the amount of lead released from one vessel to another. In the locally manufactured ceramic samples indicated in Table (1), the average concentration of dissolved lead reached (0.76) micrograms/ml, as the lead concentration ranged between this samples (0.204 to 1.968) micrograms/ml, and by examining these results we notice that there is a difference in the dissolved lead content of those samples, and the reason for this is the different colors of the paints with which the samples were coated. These results were consistent with the results of Rahima, [15]. Some paint colors contain low amounts of lead, and this results from the contamination of those paints with lead as a result of storing them next to other paints that contain high concentrations of it, and using the same tool to transfer the paint when using it to paint utensils, and this is represented by brown-colored paints. Blue, purple and black, while other paints in yellow, white, green, pink and red have been proven to contain high concentrations of lead, and these the quantities result from the presence of some lead compounds included in the composition of these paints, and the use of these lead-containing colors in pottery paint is reflected in the concentration of lead released from these vessels when they are filled with an acetic acid solution.

Table (1): The colors and concentrations of lead released from local utensils.

Sample No.	1	2	3	4	5	6
Sample color	white	Mixed*	black	Blue	Mixed**	Dark brown
Concentration, Ppm \ Lead	1.398	0.063	0.703	0.204	1.968	0.224

* Painted in pale brown with green, blue and black drawings. **Painted in orange, yellow and green.

Lead released from painted pottery samples imported from Tunisia:
As for the painted ceramic samples imported from Tunisia, which are described in Table (2) The average concentration of lead released from the surfaces of these samples reached (1.3357) micrograms per milliliter. With a concentration range between (0.223- 2.160) micrograms/ml, some concentrations of lead where the filtrate from these samples is higher than the values allowed by the US Food and Drug Administration,

Which stipulated that the concentration of dissolved lead from hollow and small-sized vessels should not exceed 2.0 ppm.

Table (2): The colors and concentrations of lead released from utensils imported from Tunisia.

Sample No.	**1**	**2**	**3**	**4**	**5**	**6**
Sample color	White	Mixed*	black	Blue	Mixed**	Dark brown
Concentration Ppm \ Lead	1.725	0.324	2.040	1.542	2.160	0.223

* Painted in white, red, yellow and orange. ** Painted in pale brown with yellow and green drawings.

Lead released from painted ceramic samples imported from China:
The results of the analysis showed that the concentration of dissolved lead from the ceramic samples imported from China and indicated in Figure No. 4, that the average concentration of dissolved lead from them into the acid solution reached (1.4407) micrograms per milliliter, with a concentration range ranging between.(3.597 - 0.0124) Micrograms per milliliter, and the concentration of lead leached from some of these samples exceeded the values allowed by the US Food and Drug Administration.

Table (3): The colors and concentrations of lead released from utensils imported from China.

Sample No.	**1**	**2**	**3**	**4**	**5**	**6**
Sample color	White	Mixed*	Black	Blue	Mixed**	Dark brown
Concentration Ppm \ Lead	0.422	1.906	2.061	3.597	0.9256	1.036

* Painted in blue, yellow and white ** Painted in pale brown with dark brown drawings

A test was conducted on 18 samples of popularly traded, locally manufactured, or imported ceramic pots. Figure No. 1 show the results obtained from the analysis process. We notice from the results table that the least amount of lead released was from local pots, as the smallest amount was in sample No.4 ,which is dark blue in color, while the largest amount was for sample No. 5, which was painted in orange, yellow, and green, as it nearly exceeded the value allowed by the American Food and Drug Administration, which stipulated that the concentration of dissolved lead from hollow and small-sized vessels should not exceed 2.0 parts per million, While this value exceeded both samples No. 3 and No. 5 the colors are white and contain red, orange, and red patterns, respectively, in the Tunisian samples. As for the Chinese samples, only one sample contained a small amount of lead, which is sample No. 1, which is blue.

In Figure (1), notice that the amount of lead released from local utensils is very small compared to imported Tunisian and Chinese utensils. By examining these results, we notice that there is a difference in the dissolved lead content of those samples, and the reason for this is due to the difference in colors. The samples were coated with paints, as indicated by the results of an analysis conducted by Rahima, [15]. Some paint colors contain low amounts of lead, and this results from contamination of these paints with lead as a result of storing them next to other paints that contain high concentrations of it, and using the same tool to transfer the paint when using it to paint utensils, and this is represented by brown-colored paints. Blue, violet and black, while the other paints are yellow, white, and green Pink and red have been proven to contain high concentrations of lead, and these quantities result from the presence of some lead compounds included in the composition of these paints. The use of these colors containing lead in painting pottery was reflected in the concentration of lead released from these utensils when filling them with an acetic acid solution.

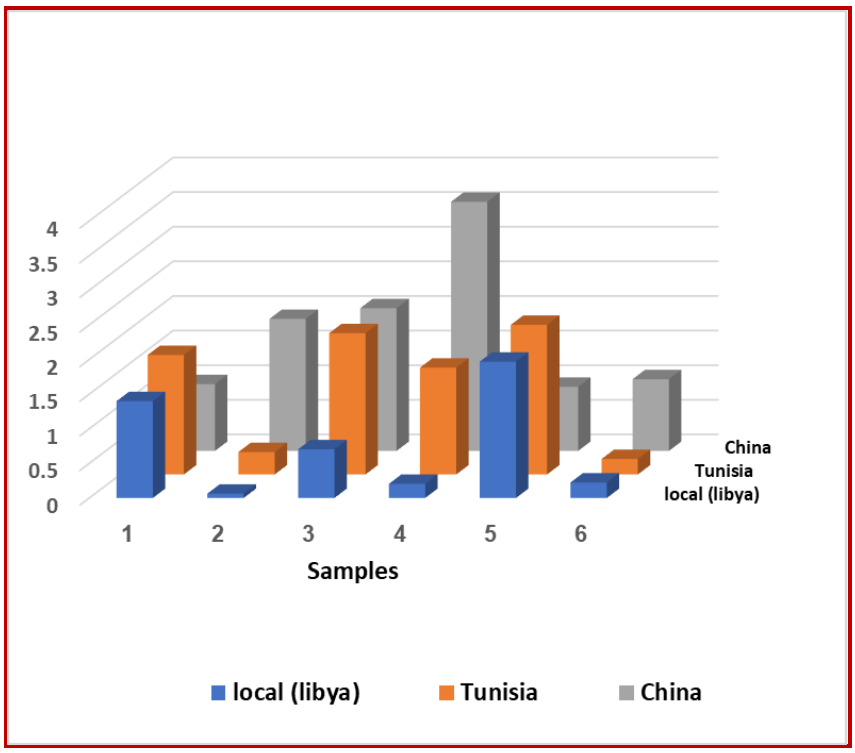

Figure (1): A graphical comparison of the concentration of lead released from the studied samples.

Conclusion:

It is concluded that the use of lead paint in painting ceramic vessels poses a threat to human life over the years, as lead accumulates in the body's tissues and causes serious diseases in humans. Local utensils recorded a small percentage of lead within the permissible limit compared to utensils imported from Tunisia and China. Colours play a major role in the percentage of lead in utensils, as brown, blue, and black colours recorded small amounts of lead compared to utensils in white, red, yellow, green, and pink. We recommend conducting periodic and continuous chemical analysis of ceramics sold in the Libyan market to monitor lead levels and activating the role of the media in directing and counseling citizens.

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