



Research on the release of harmful elements in simulation jewelry wear

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ABSTRACT

Migration of harmful elements during abrasion was researched. The dynamic abrasion model of jewelry wear was established. The release amount of harmful elements was analyzed by atomic absorption spectrometry. The results showed that the longer wear time, the more harmful elements released during the simulation jewelry wear. The release was essentially linear increase as the time of jewelry wear. About 80% of harmful elements would be ionized during the daily wear.

Keywords: Atomic absorption spectrometry; Harmful elements release; Precious metal ornaments; Wear; Abrasion simulation

INTRODUCTION

Precious metal jewelry products' consumption was growing with the improvement of people's living standard. Chromium, nickel, lead, zinc, copper, rhodium, silver, cadmium and other elements were added into precious metal jewelry in order to get the process requirements or to have good appearance effect^[1], especially in the simulation ornaments. The elements like chromium, nickel, lead, and cadmium are harmful to the environment. However, the metal will be the body's sweat erosion, slowly spread to the skin, resulting in harm to human health^[2].

Generally, the detection of harmful elements in ornaments was based on the standard of the EN1810:1998, EN1811:2011 and EN12472:2005^[3-4]. The above standards focused on the content for the harmful elements itself or the release amount of harmful elements with a coating layer object after abrasion treatment, but the release of harmful elements before abrasion treatment was never reported in literature.

The experiment of accelerated wear and corrosion was carried by EN12472:2005, to simulation the dynamic process of release for harmful elements in adornment. The sample was the lead sheet. It was placed in the wear test apparatus. The wear medium was removed in different time and immersed in artificial sweat. Lead element in wear medium was ionized. The concentration of lead ion in artificial sweat was determined by atomic absorption spectrometric (AAS). By comparing the theoretical and practical elements of lead leaching, we did two works: 1) Determine the proportion of harmful elements ionization. 2) Discuss the migration of harmful elements.

The paper studied on migration of harmful elements in the process of wearing adornment. The sample we used in this experiment was pure lead. Although the sample was different with the adornment actually this study provided a research foundation for the adornment of harmful element migration in the wear process.

EXPERIMENTAL SECTION

1.1 Materials

Except where indicated, all reagents shall be of recognized pro analysis, p.a., grade or better and shall be free of lead.

1.1.1 Deionized and aerated water

Fill a tall-form 2 L beaker with deionized water, specific conductivity max 1 $\mu\text{s}/\text{cm}$. Saturate with air by attaching a gas distribution tube (porosity 1) to a cork and positioning the lower end of the tube on the bottom of the beaker. Allow grease-free air to flow at a rate of 150 ml/min for 30 min.

1.1.2 Sodium chloride

1.1.3 3 DL-Lactic acid, $\rho = 1.21 \text{ g/ml}$, >88 % (m/m)

1.1.4 Urea

1.1.5 Ammonia solution, $\rho = 0.91 \text{ g/ml}$, 25% (m/m)

1.1.6 Dilute ammonia solution, 1 % (m/m)

Transfer 10 ml of ammonia solution (1.2.5) into a 250 ml beaker containing 100 ml of deionized water. Stir and cool to room temperature. Transfer the solution to a 250 ml volumetric flask and make up to volume with deionized water.

1.1.7 Nitric acid, $\rho = 1.40 \text{ g/ml}$, 65% (m/m)

1.1.8 Dilute nitric acid solution, approximately 5% (m/m),

Transfer 30 ml of nitric acid into a 500 ml beaker containing 350 ml of deionized water. Stir and cool to room temperature. Transfer the solution to a 500 ml volumetric flask and make up to volume with deionized water.

1.1.9 Degreasing solution

Dissolve 5 g of sodium dodecylbenzene sulfonate in 1000 ml water, aqueous solution of (5 g/mL).

1.1.10 Lead standard solution (1000 mg/L, GSB 04-1740-2004), National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials, China

1.1.11 Artificial sweat: prepared according with EN 1811-2011.

Transfer (1.00 \pm 0.01) g of urea, (5.00 \pm 0.05) g of Sodium chloride and (940 \pm 20) μl of lactic acid to a 1000 ml beaker. Add 900 ml of freshly prepared deionized water and aerated water and stir until the reagents were dissolved completely.

Immersed the pH electrode into the test solution and measured the pH. Slowly and gently, added drop by drop dilute ammonia solution until a stable value of (6.50 \pm 0.10) pH was reached. Transferred the solution to a 1000 ml volumetric flask and made up to volume with deionized and aerated water. Before use, ensure that the pH of the test solution is in the range of pH 6.50 \pm 0.10.

All the containers are non-metallic materials (nitric-acid resistant material) do not contain lead. Containers and abrasive were immersed into 5% dilute nitric acid solution for 4 hours in order to eliminate the influence of lead. After that, washing them to neutral and drying for the experiment.

1.2 Equipments

Wear test apparatus (meeting the requirements of EN 12472:2005),

AAS (ZEEnit 700P, Analytik Jena AG, Germany),

pH meter (accurate to $\pm 0.02\text{pH}$, Shanghai Precision Scientific Instrument Co., Ltd, China),

Constant temperature drying box(101-1BN, accurate to $\pm 1 \text{ }^\circ\text{C}$, North China Test Instrument Co. Ltd. China).

Working conditions of instrument of AAS:

Lead hollow cathode lamp; lamp current: 3 mA; flame: C2H2/ air; gas flow rate: 65 L/h; wavelength: 283.3 nm; slit: 1.2 nm; integral time: 3 s; measurement: 3 times.

Samples Preparation

99.99% lead sheet, 20mm \times 20mm \times 1mm, was polished by No. 600 followed by No.1200 sandpaper to surface silvery white.

Pretreatment

Gently swirled the sample for 2 min in degreasing solution at room temperature. Rinsed thoroughly with deionized water and dried using an absorbing cloth. After degreasing, articles shall be handled with plastic forceps or clean protective gloves.

Wear experiment

Wear medium and procedure were prepared by EN 12472:2005. Granules was outer shells of coconuts, walnuts, peanuts and almonds, mixed in a ratio 1:1:1:1 by weight, ground and sieved to give a mixture of particles having dimensions between 0.8 mm and 1.3 mm. The abrasive paste comprised: • 6% to 8% Ester wax of montanic acids-Wax E [CAS No. 73138-45-1], 3 % Octadecanoic acid (stearic acid) [CAS No. 57-11-4]; • 30 % to 35 % Petroleum distillates, hydrotreated light paraffinic [CAS No. 64742-55-8]; • 2 % Polyethylene glycol cetyl/oleyl ether [CAS No. 68920-66-1] or Triethanolamine [CAS No. 102-71-6]; • 48 % Silicon dioxide (quartz) 200 μm mesh size [CAS No. 14808-60-7]; 6 % to 9 % Deionized water. The ratio of wear medium and abrasive paste is 1000g: 7.5 g.

Wear procedure: filled the tumbling barrel to half its depth with abrasive (about 600 g), added the 4.5g of abrasive paste and homogenize by rotating in the barrel for 5h. Assemble the lead sample on a fixed support so that they can not collide with the barrel walls. Rotating the tumbling barrel at a speed of (30 ± 2) r/min. Reversed the direction of the rotation after 2.5h. Taken out and weighed the sample after a certain time, calculated the abrasion loss (Δm).

Immersion releasing

The same amount (10 g) abrasive was took out into containers with lid marked as 1#, 2#, 3#, 4#, 5# and 6#, when the wear time was 5, 10, 12.5, 15, 17.5 and 20 h, Then added 20 mL artificial sweat and placed into constant temperature drying box at $(30 \pm 2)^\circ\text{C}$ for 168 h. Filtered the abrasive soaked in the artificial sweat after 7 days, rinsed the abrasive and containers thoroughly with hot water and then poured 10 mL nitric acid solution. Transferred all the filtrate into the acid-washed volumetric flask.

The Pb element from the abrasive turned into lead ion in the artificial sweat. The lead ion concentration was analyzed by AAS, then found a curved relationship between wear time and the leaching lead.

Blank experiment

The blank experiment was conducted at the same time with the abrasive immersion releasing. All the containers, the amount of solution and experiment procedures were totally identical except that the blank test without abrasive.

Dissolved the lead standard solution in the artificial sweat, prepared the standard solution that the concentration is 0, 0.2, 0.3, 0.5, 1.0, 1.5, 2.0 mg/L, respectively. According to the working conditions of the instrument determine the lead standard solution. The equation of linear regression is: $A = -0.000472 + 0.03241C$, and $r = 0.9994$.

The theoretical leaching amount of harmful element Pb in the artificial sweat after a week during simulating the jewelry wear is calculated by the formula (1) according to the experiment procedure:

$$C = \frac{m' \cdot \Delta m}{M \cdot V} \times 1000 \quad (1)$$

In formula (1):

m' — the mass of the abrasive soaked in the artificial sweat, g;

M — total mass of the abrasive, g;

Δm — the variation mass after a certain wear time;

V — the volume, L.

The ionization ratio of the wear part of Pb sample in artificial sweat is calculated by the formula (2):

$$X = \frac{C_0}{C} \times 100 \% \quad (2)$$

In formula (2):

C_0 — the actual leaching amount, the actual concentration of the harmful element in the solution after a week, mg/L.

C — the theoretical leaching amount, mg/L.

RESULTS AND DISCUSSION**2.1 Relationships between the wear time and variation**

According to fig 1, when the wear time is 1 h and 2 h, the wear variation is 0.0019 g and 0.0013 g. After 3 h, wear variation is about 0.0009 g (0.0008~0.0010 g). During simulating the jewelry wear we can refer that the wear variation is obvious during the first year. And the wear variation gradually reduces in a certain range as the wear time is longer.

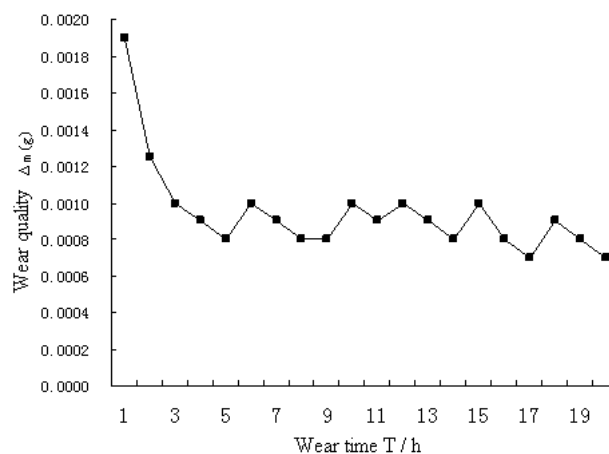


Fig.1 Relationship of the wear time and variation

2.2 Relationships between the wear time and lead leaching amount from abrasive

The data reflect the relationship between the wear time and lead leaching amount from abrasive are shown in table 1, the graph is shown in fig 1. Through calculating and test, the result that with the time increasing the lead leaching amount from abrasive increase is expressed. Then we can infer that during wearing jewelry as the time of jewelry wear, the release amount increases with time almost linear growth.

Table 1 Relationships between the wear time and lead leaching amount

Abrasion time/h	Simulation of wear time/year	Mass of Abrasive materials(Total) M/g	Mass of Abrasive materials(experiment) m/g	abrasion loss Δm /g	Constant volume V/L	Leaching amount(theory)/mg $\cdot L^{-1}$	Leaching amount(experiment)/mg $\cdot L^{-1}$	Ionization ratio X
5	2	600	10	0.0059	0.1	0.983	0.776	79%
10	4	600	10	0.0104	0.1	1.733	1.498	90%
12	5	600	10	0.0123	0.1	2.050	1.809	88%
15	6	600	10	0.0150	0.1	2.500	2.417	97%
18	7	600	10	0.0174	0.1	2.900	2.525	87%
20	8	600	10	0.0189	0.1	3.150	2.578	82%

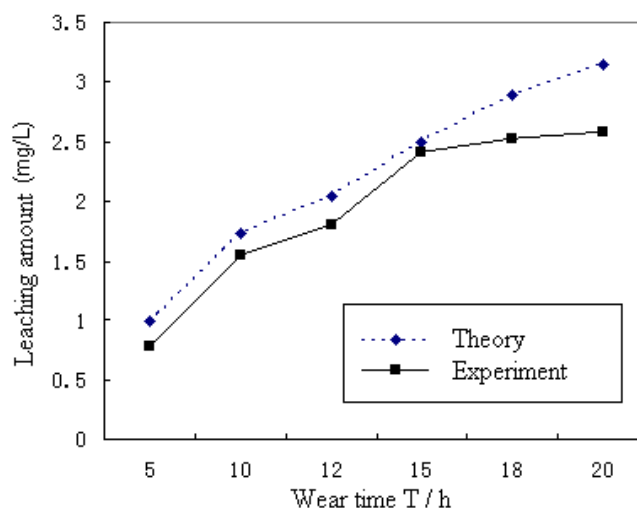


Fig.2 Relationships between the wear time and lead leaching amount, respectively.

2.3 Analysis of the lead ionization during wearing process

The data in table 1 show that the Pb ionization degree in synthetic sweat is no less than 79 %, the average is 87 %. It can be inferred that during wearing jewelry the lead harmful element ionization is about 80 % with the artificial of

sweat. And the harmful elements ion is bad to human health.

CONCLUSION

The author used an accelerated wear and corrosion method, which provided by EN12472, to simulate the migration of the harmful elements in adornment. Use the method provided by GB/T19719 to test the leaching amount from the abrasive. The experiment draws the following conclusions:

- (1) During simulation of the jewelry wear, the wear variation is obvious in the first year. With the extension of wear time the wear variation fluctuate in a certain range and gradually reduce.
- (2) During the simulation of the jewelry wear, at the same conditions the releasing amount of harmful element increase with the wear time extending, the release is essentially linear increase.
- (3) If the harmful element in jewelry is exceeding, 80 % of the harmful element would ionized during the daily wear process and that is bad to health.

The sample was pure lead in this experiment. It was different with the adornment actually; however, this study provided a research foundation for the adornment of harmful element migration in the wear process.

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