# Nickel release tests – How well do they work*

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**Abstract**
Nickel release testing has become a standard procedure in Europe for testing the products that come into direct and prolonged contact with the skin. Even though the Standard describes the test procedure in great detail, it has been reported that the test is hard to reproduce and the results on the same sample may vary between different laboratories significantly. Therefore, the same product may be failed by one laboratory and approved by another laboratory. To learn more about nickel release, and how the surface finish may affect it, we have conducted European test EN 1811:1998 on a number of samples of 14K Ni-containing and Ni-free alloys, an 18K reference alloy and pure nickel. To represent the most common surface condition of jewelry articles, we prepared the surface of the samples by hand polish, wet and dry finish. A correlation between the surface finish and the nickel release rate is discussed.

**Introduction**
Nickel-containing white golds have been widely used by jewelers for more than half a century as an alternative to platinum. The certain advantages of using these alloys, such as relatively low cost and high strength, are upset by the fact that nickel is reported to be one of the most common causes of allergic contact dermatitis (1).

In recent years, the issues of European legislation related to nickel allergy, and the metallurgical options for white golds have been addressed in the publications of *Gold Technology* and Santa Fe Symposium: (2), (3), (4) and (5). Following up on the developments in nickel related legal issues that originated in Europe around 1989, the MJSA published a special report on "Nickel Controversy in Europe" in 1992 (6).

It appears that until recently, the jewelry industry in the US did not fully recognize the nickel allergy problem, partially because the data on nickel allergy in the US was not readily available. It is known that, among the general population in Europe, 2% to 10% (depending on the country and gender) are allergic to nickel. Only one recent publication provides similar information for the US – 5.8% (7). Among US patients, 10% to 14% show allergic reaction to nickel according to North American Contact Dermatitis Group [8] – this is the highest percentage from 50 tested substances. There are no legal limitations on use of nickel in this country. The dermatologists have certain recommendations, however, for nickel sensitive patients on how to minimize the contact with nickel in a wide variety of products including jewelry (1).

The EU Directive 94/27/EC that restricts the use of nickel has become law in the European countries, and the supporting test on nickel release, EN 1811:1998, is now a Standard. Therefore, all jewelry products that reach the European market must satisfy the requirements of the Directive and pass the nickel test.

The European Directive establishes two basic nickel requirements for alloys:

- The first requirement deals with the post and earwire assemblies used for pierced ears and other body parts. The nickel content in these products must be below 0.05% by weight. This requirement, in fact, sets nickel as an impurity, and the alloys as nickel-free. Such a low level of nickel can be controlled during alloy manufacturing. It also can be measured reliably using standard spectroscopy methods such as AA (European Standard E1810:1998) or ICP Spectroscopy.
- The second requirement covers the products that come in 'direct and prolonged contact with the skin'. The test, using artificial sweat solution, (EN1811:1998) must show the nickel release rate below 0.5 micrograms per square centimeter per week (μg/week/$cm^2$). In 1999 at the Santa Fe Symposium, Roy Rushforth [4] pointed out the wide variation obtained in the results of this test. He showed that the same product may be failed by one laboratory and approved by another laboratory as a result of such an inconsistency.

We believe at this point that the relevance of the nickel release test remains to be proved. The nature of high variation of the results is not clear. We feel that more data on nickel release test for common nickel-white golds is needed, so that we may understand better both the results and their interpretation. We have carried out nickel release tests on a number of samples made with different alloys and with different surface textures strictly following the instructions of EN1811:1998 Standard.

*This paper is based on one presented at the Santa Fe Symposium, Albuquerque in May 2001

## Sample consideration and preparation

The selection of samples included:

- two common 14K white alloys containing 6.5% and 11% nickel respectively,
- two 14K "nickel-free" alloys – a yellow and a palladium-white – both containing less than 0.01% nickel,
- an 18K (76% gold) reference sample, as described in EN1811:1998, containing 6% nickel,
- pure nickel.

Thus, this selection covers nickel-white golds as well as "boundary" metals: pure nickel and nickel-free alloys.

The sample shape chosen was similar to that described for the reference sample in the European Standard: 0.5" diameter and 0.010" thick disk with the 1 mm center hole. The area of both sides of the disk is 2.52 cm$^2$. The described disk is shown in Figure 1.

Each alloy sample was prepared with four different surface textures, as shown in Figures 2a – 2d:

- 1200 grit sand paper. This is a surface condition of the reference sample. This texture is easy to reproduce consistently.
- Hand polished, dry finish and wet finish surfaces. Those are typical surface textures of finished jewelry. A common polishing compound was used for hand polishing. Dry finish was achieved by tumbling the samples in walnut shells for 24 hrs. Wet finish was done by tumbling the samples with steel shots in soap for 2 hrs.

## Test procedure

The preparation of artificial sweat solution and the test procedure are described in EN1811:1998 with great

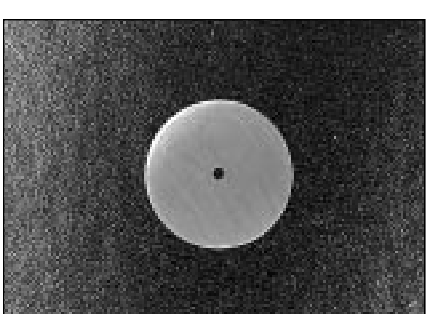

**Figure 1 -** Test sample

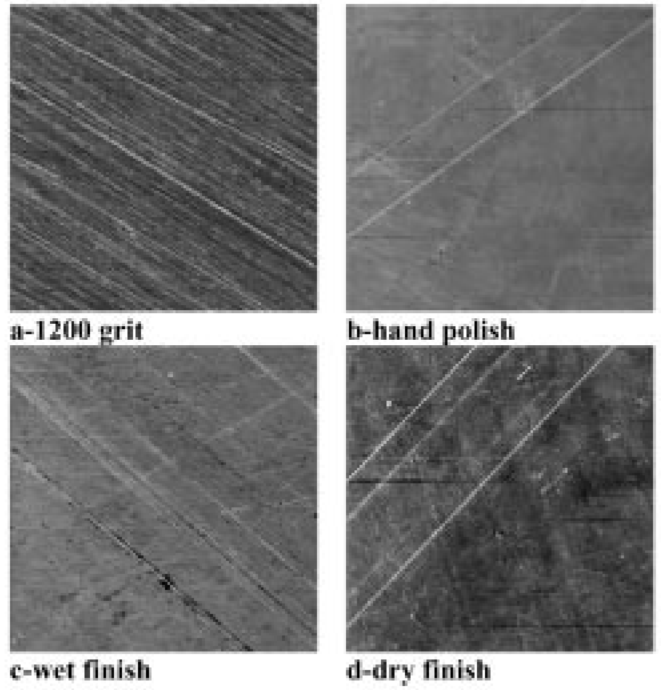


**Figure 2 -** Surface finish of tested samples: a-1200 grit, b-hand polish, c-wet finish (2 hrs in steel shots and soap), d-dry finish (24 hrs in walnut shells)

detail. Basically, the solution consists of deionized and aerated water containing 0.5% sodium chloride, 0.1% lactic acid, 0.1% urea. A 1% solution of ammonia is added to bring pH to 6.5 ±0.1. A fresh solution was prepared for each test session.

In each session we used three disk samples. The total sample surface area, therefore, was 7.56 cm$^2$. The disks were attached to a platinum wire through the center holes and placed inside the glass container with 10 ml of artificial sweat solution as shown in Figure 3.

One blank sample of 10 ml of solution and platinum wire accompanied each session. The containers were put in the oven and kept at 30 ±2 C for one week. In one session we kept the containers in the oven for 3 weeks.

When the samples were removed from the containers at the end of the session, they were rinsed with deionized water (the rinse was added to the container). Two ml of 5% nitric acid was added to prevent the redeposition of dissolved nickel as recommended by the Standard. Finally, deionized water was added to bring the total volume to 15 ml.

The nickel concentration was measured with a flame AA Perkin Elmer Analyst 300 machine in ml/L. The nickel release rate was calculated to the first decimal place in µg/week/cm$^2$ using 15 ml volume and 7.56 cm$^2$ surface area. Standard EN1811:1998 allows the adjustment of the calculated values of nickel release rate by the factor of 0.1. All reported experimental results in this work are unadjusted.

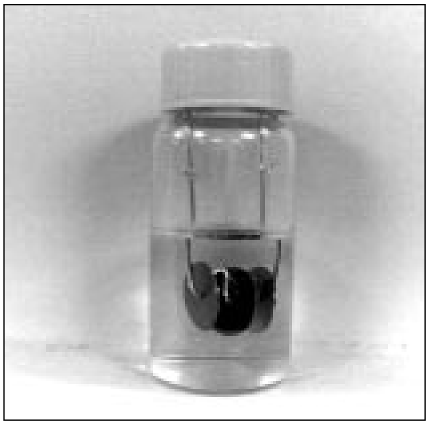

**Figure 3 -** A glass container with 10ml of artificial sweat solution. Three submersed disks are attached to platinum wire through center holes

**Table 1. Nickel release rate (μg/week/cm$^2$, unadjusted). Samples are finished with 1200 grit sand paper**

| Session # | 76%Au 6% Ni Reference | 14K 6.5% Ni | 14K 11% Ni | 100% Ni |
|---|---|---|---|---|
| 1 | 0.5 | | | |
| 2 | 0.5 | | | |
| 3 | 0.7 | 1.6 | 1.7 | 3.2 |
| 4 | 0.5 | 2.0 | 2.4 | 4.6 |
| 5 | 0.6 | 1.6 | 1.7 | 7.0 |
| 6 | 0.6 | 1.3 | 1.8 | 4.8 |
| av: | 0.6 | 1.6 | 1.9 | 4.9 |
| stdev: | 0.1 | 0.3 | 0.3 | 1.6 |

**Table 2. Three week test. Surface condition: 1200 grit sand paper. Nickel release rate (μg/cm$^2$, unadjusted)**

| | 76%Au 6% Ni Reference | 14K 6.5% Ni | 14K 11% Ni | 100% Ni |
|---|---|---|---|---|
| per week | 0.2 | 0.7 | 0.8 | 4.2 |
| 3 weeks total | 0.6 | 2.1 | 2.4 | 12.4 |
| Av. (Table 1) | 0.6 | 1.6 | 1.9 | 4.9 |

**Table 3. Ni release rate (μg/week/cm$^2$, unadjusted). Samples with different surface conditions**

| 76%Au6% Ni Reference | 14K 6.5% Ni | 14K 11% Ni | 100% Ni | Surface condition |
|---|---|---|---|---|
| 0.2 | 0.1 | 0.1 – 2.1 | 20.3 | Wet finish |
| 0.8 | 0.4 | 0.2 – 0.4 | 25.4 | Polished |
| 0.5 | 0.5 | 0.3 - 5.4 | 18.9 | Dry finish |
| 0.5 – 0.7 | 1.3 – 2.0 | 1.7 – 2.4 | 3.2 – 7.0 | 1200 grit |
| 0.0 – 0.9 | | | | Data [4] |

## Results and Discussion

Nickel-free samples consistently showed practically no nickel release over eight different sessions regardless of the surface finish. This actually proves that no surface contamination with nickel was introduced during our sample preparation. This also means that the nickel-free alloy samples can be used as blanks, and the nickel release rate in nickel-white golds can be measured against nickel-free alloys.

We have conducted a majority of our tests using samples finished with 1200 grit sand paper. The data is shown in Table 1:

The reference sample shows the variation of nickel release rate between 0.5 and 0.7 with the average 0.6 μg/week/cm$^2$. The expected value according to EN1811:1998 is 0.4 ±0.2. Rushforth reported values between 0.2 and 0.9 in one Test House, and between 0.02 and 0.2 in another three Test Houses [4]. For a somewhat similar alloy with similar surface conditions, Faccenda and Oriani reported values from 0.1 to 1.0 μg/week/cm$^2$ (5).

There is no significant difference between 14K nickel-white golds: 1.6 μg/week/cm$^2$ average for 6.5% nickel and 1.9 μg/week/cm$^2$ for 11% nickel alloys. For a 10% nickel 14K white alloy, Faccenda and Oriani reported 3.4 μg/week/cm$^2$ (5).

Surprisingly, the nickel release rate of pure nickel is not as high as one would expect – 4.9 μg/week/cm$^2$ average with the variation between 3.2 to 7.0 μg/week/cm$^2$.

The results obtained from the same samples after three weeks of test (as opposed to one week as recommended by the Standard) are shown in Table 2. The average release rate values (from Table 1) are listed in the last row for a comparison.

The three-week total accumulation of nickel released from a reference sample is the same as one-week average. The data shows, therefore, that nickel in the reference sample is most likely protected from being released by 76% gold. Practically all the nickel is released during the first week, and no further release took place during next two weeks.

14K golds provide less protection, and as a result, the release of nickel in these alloys continues after first week, but the rate apparently slows down. The total three-week accumulation of released nickel is greater than one-week average, but

**Table 4. Ni release rate (µg/week/cm², *adjusted*)**

| 76%Au 6%Ni Reference | 14K 6.5% Ni | 14K 11% Ni | 100% Ni | Surface condition |
|---|---|---|---|---|
| 0.02 Pass | 0.01 Pass | 0.01 Pass | ***2.03 Fail*** | Wet finish |
| | | 0.21 Pass | | Wet finish |
| 0.08 Pass | 0.04 Pass | 0.02 Pass | ***2.54 Fail*** | Polished |
| | | 0.04 Pass | | Polished |
| 0.05 Pass | 0.05 Pass | 0.03 Pass | ***1.89 Fail*** | Dry finish |
| | | ***0.54 Fail*** | | Dry finish |
| 0.05 Pass | | | | 1200 grit |
| 0.05 Pass | | | | 1200 grit |
| 0.05 Pass | 0.16 Pass | 0.17 Pass | 0.32 Pass | 1200 grit |
| 0.07 Pass | 0.20 Pass | 0.24 Pass | 0.46 Pass | 1200 grit |
| 0.06 Pass | 0.16 Pass | 0. 17 Pass | ***0.70 Fail*** | 1200 grit |
| 0.06 Pass | 0.13 Pass | 0.18 Pass | 0.48 Pass | 1200 grit |

not proportionally.

In case of pure nickel, the release rate appears practically constant during three weeks.

Table 3 summarizes our data obtained from the samples with different surface finish. For a comparison, we have also listed data published in (4) for a reference sample.

Our data shows that there is no common relationship between surface finish and nickel release rate in nickel containing white golds. There is practically no affect on the reference sample (especially when considering data published in (4)). Mass media finishing and hand polishing seem to reduce the nickel release rate in the 6.5% Ni alloy, but show inconsistent results for the 11% Ni alloy.

Pure nickel samples show that mass media finishing and hand polishing somehow activate the surface and increase the nickel release rate noticeably from 4.9 (1200 grit) to as high as about 25 (polished) µg/week/cm².

Overall, our data on nickel-containing alloys shows between 20 to 50 fold variation in the results obtained in the nickel release test EN1811:1998. It is shown in (4) that lab-to-lab variation can be even higher.

When we adjust our nickel release rate data by a factor of 0.1 as required in the Standard EN1811:1998, Table 4, we see that the test consistently passes all the white gold samples with one exception (highlighted). The test fails pure nickel, but not consistently. It appears therefore, that this adjustment cannot be justified.

The test would have failed our 14K white golds and, in most sessions, the 18K reference as well, if we had considered unadjusted values. The pure nickel would have also failed the test in all the sessions. We believe that in order to simplify the interpretation of the results, only *unadjusted* values should be reported and considered in this test.

**Summary and Conclusions**

The test results on the "nickel-free" alloy samples, with nickel levels below 0.01%, show practically no difference from the blank (which contains no sample at all). We believe that in these types of tests in general, including EN1811:1998, nickel-free alloy samples should be used as blanks and as indicators of nickel contamination during sample preparation procedure.

For the reference sample with 1200 grit surface finish, we have obtained an average nickel release rate of 0.6 µg/week/cm² which is slightly higher than that defined by the European Standard EN1811:1998 – 0.4 µg/week/cm². Our data variation seems to be in agreement with the Standard. Other laboratories, however, reported a much higher variation.

The gold content in the alloy affects the dynamics of nickel release rate in the test. The nickel release becomes saturated within one week in the 18K reference sample. It slows down within the second week in 14K samples. For pure nickel the rate seems to be constant at least within three weeks. We see the least variation in the test results when the samples have 1200 grit sand paper finish. This, however, does not represent the texture of the finished jewelry.

We do not find a general and consistent relationship between the surface finish and the nickel release rate in nickel-white golds. The results on finished jewelry, therefore, may be quite misleading.

Our results confirm the published data, showing that common 14K Ni-white alloys may pass the nickel release test, either with or even without 0.1 adjustment. This makes the use of the EN1811:1998 Standard and the interpretation of the results very difficult.

We believe that 0.1 adjustment required by the Standard EN1811:1998 is too strong and not justified.

Our conclusion is that the European Standard EN1811:1998 does not provide the industry with the reliable nickel release test method for high nickel containing alloys.

We believe that, in order to avoid a controversy, the only practical alternative is nickel-free white gold alloys. They pass the nickel release test, and are proved to be safe clinically.

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