# RELEASE OF NICKEL FROM SILVER COINS

# Niels Bang Pedersen, Sigfrid Fregert, Peter Brodelius and Birgitta Gruvberger

From the Section of Occupational Dermatology, Department of Dermatology, University of Lund, Lund, Sweden

Abstract. Nickel was found in the film-like coating on used Swedish one-crown coins containing 5% Ni in the alloy (0.17  $\mu$ g/coin) and in those containing 25% Ni (0.16 µg/coin). A film-coating containing nickel was not found on newly minted one-crown pieces. Nickel was also found in the film-coating of used 5-öre coins of copper, which have no addition of nickel in the alloy (0.18 µg/coin), as well as in the film of used bank-notes (0.29 µg/bank-note). The copper coins and the banknotes seem to be contaminated with nickel from other coins and from fingers. Nickel was released from cleaned "silver coins" by both distilled water and synthetic sweat. More nickel was released from coins than from nickelplated metal sheets which had been treated in the same way as the coins. Nickel could be found in varying amounts (5-122  $\mu$ g/person) on the hands of persons who had been in contact with coins in their profession or who had counted coins for 5 minutes. Nickel from coins probably does not elicit dermatitis on healthy hands in sensitized persons but does contribute to the maintenance of a pre-existing dermatitis of the hands. No cobalt could be detected in the analyses.

Hypersensitivity to nickel is relatively common, but its position in the ranking order of allergens varies in different studies (6, 8), and in different years (13). When the hands are affected by nickel-dermatitis, the course often becomes chronic (13, 17), probably due to unavoidable contact with nickel in everyday life, e.g. contact with coins. The purpose of the present study has been to investigate the release of nickel from coins and nickel-contamination of the hands.

# MATERIAL AND METHODS

Swedish currency of the following denominations was used in the study: 1 crown (coin), 5 öre (coin, 1 crown = 100 öre) and 10 crowns (bank-note).

One-crown pieces are "silver coins". They have been of the same size for many years, i.e. 25 mm in diameter. Coins from 1967 and earlier contain 5% nickel, while newer one-crown coins contain 25% nickel. Five-öre coins are made chiefly of copper without the addition of nickel, and have a diameter of 27 mm. According to the Royal Swedish Mint, no nickel is added to the copper alloy, but we found traces of nickel amounting to 150  $\mu$ g/g alloy.

#### Experiment 1

In order to remove the film-like coating from the money, it was soaked twice in about 50 ml of ethylic ether, which was then collected for analysis. The following sorts were examined:

1) 100 pieces of 1-crown coins (25% Ni) in portions of 10, obtained directly from the Royal Swedish Mint.

2) 250 pieces of used 1-crown coins (5 % Ni) in portions of 10.

3) 150 used 1-crown coins (25% Ni) in portions of 10.

4) 100 pieces of 1-crown coins (both 5% and 25% Ni). The ether was shaken with distilled water, which was later separated from the ether.

5) 200 used 5-öre coins in portions of 50.

6) 10 used bank-notes to the value of 10 crowns.

7) 10 new 10-crown bank-notes, obtained directly from the Royal Swedish Mint.

The ether from the series above, with the exception of Expt. 4, was collected in a glass container and then evaporated. Twenty ml of 5 N hydrochloric acid was introduced and brought to the boiling point, and then evaporated to a volume of 15 ml. The content of nickel and cobalt in these solutions, and in the water-phase of Expt. 4, was examined by direct suction into an atomic absorption spectrophotometer (Perkin-Elmer 303).

#### Experiment 11

The release of nickel in water and in synthetic sweat was determined in the following way: The film-coating on used 1-crown coins, both 5% - and 25% -nickel coins, was removed by ether.

After this:

1) Ten 1-crown coins (5% Ni) and ten 1-crown coins (25% Ni) were placed for 24 hours in distilled water, each coin in 10 ml of water.

2) The same number and sorts of coins were treated in the same way as above, but instead of water, synthetic sweat was used (0.5% NaCl, 0.1% lactic acid and urea 0.1% in water; pH adjusted to 6.5 by ammonium hydroxide).

Acta Dermatovener (Stockholm) 54

I-crown, new	1-crown, used	1-crown, used	5-öre, used	10-crown	10-crown,
(25% Ni)	(5 % Ni)	(25% Ni)	copper	bank-note, new	bank-note, used
0	0.17 (0.09-0.25)	0.15 (0.11-0.27)	0.18 (0.11–0.26)	0	0.29 (0.12-0.35)

Table I. Nickel-release in ethylic ether expressed as mean values of  $\mu g$  Ni/coin (bank-note) The figures in parentheses are range values

3) Five 1-crown coins were placed in 5 separate glasses with distilled water and 5 coins in 5 glasses with synthetic sweat for 15 minutes to see if any nickel was released during that short time.

4) Ten metal sheets, each  $2.9 \times 2.9$  cm in size, nickelplated on both sides, were placed in distilled water or synthetic sweat for 24 hours in the same way as the coins.

The water and synthetic sweat were then analysed for nickel- and cobalt-content by direct suction into the atomic absorption spectrophotometer.

### Experiment III

Nickel- and cobalt-contamination of hands in different groups of subjects was investigated. None of the subjects had any history of nickel-sensitivity or any skin-changes on their hands. Five persons washed their hands twice in tap-water and soap, counted coins for 5 minutes, and then washed their hands twice in distilled water and with soap containing no nickel. All 4 portions of water were analysed. Nickel was found only in portions 1 and 3, which means that a single wash was sufficient to remove nickel from the hands before the experiment and contaminating nickel after the experiment.

The subjects who were examined washed their hands thoroughly for 3 minutes with water and soap. At the conclusion of the experiment, they washed their hands in one litre of distilled water and soap containing no nickel or cobalt. This portion of water was concentrated 10 times by evaporation, after which it was analysed for nickel and cobalt by direct suction into the atomic absorption spectrophotometer.

The following groups were examined:

1) Thirteen persons who had counted 100 pieces of ether-washed 1-crown coins for 5 minutes.

2) Thirty persons doing the same experiment with 1crown coins that had been in circulation.

Table II. Nickel-release during 24 hours from etherwashed coins and metal sheets (n = 10) expressed as  $\mu g$  Ni/coin and for the plated metal calculated as nickel-release from an area (11.2 cm<sup>2</sup>) of the same size as the coins

	1-crown (5 % Ni)	1-crown (25 % Ni)	Nickel-plated metal sheets
Distilled water	49	15	5
Synthetic sweat	96	137	5

Acta Dermatovener (Stockholm) 54

3) Five employees in a department store were examined after 4 hours at work. One of the employees worked at the information desk, where she also had to count the coins coming from the bank to the cash-registers in the store. Two others sold cosmetics, one sold bicycles and toys, and the fifth sold clothes. The four last-mentioned persons took payment for the goods at their desks.

4) Ten patients at the Out-patient Department of Dermatology were examined at 10 a.m. The patients had no hand dermatitis and had no particular contact with nickel on the day they were investigated. None of the persons in this group washed their hands according to the schedule above before coming to the department.

## RESULTS

## Experiment I

The quantities of nickel found in the film-coating of different coins and bank-notes are given in Table I. When the ether used to wash 100 pieces of 1-crown coins was shaken with water, 30% of the nickel was transferred from the ether-phase to the water-phase.

### Experiment 11

The quantities of nickel released from 1-crown coins in distilled water and synthetic sweat during 24 hours are given in Table II. The amount of nickel released from plated metal sheets under the same conditions is also indicated in this table. The metal sheets have a surface area of 16.8 cm<sup>2</sup>. In order to compare the nickel-release with that of the coins, the release is expressed as  $\mu g \text{ Ni}/11.2 \text{ cm}^2$ , which is the surface area of 1-crown coins.

Water released more nickel from coins containing 5% nickel than from coins containing 25% nickel. Synthetic sweat released more nickel from both types of coins than did water. More nickel was released from both sorts of coins in water and synthetic sweat than from plated metal sheets. The nickel-release in each group, according to the Students *t*-test, was significantly different (P< 0.001) from that of all other groups, with two exceptions, i.e. there was no variation of the nickel-release from 5% Ni coins and 25% Ni coins into synthetic sweat—and no variation of the release from plated metal into water and synthetic sweat.

In the short-term experiment, nickel could be demonstrated both in distilled water and in synthetic sweat after only 15 minutes.

### Experiment III

The hands of different groups of subjects were found to be contaminated with nickel:

1. Thirteen persons who had counted etherwashed 1-crown coins for 5 minutes, 32  $\mu$ g Ni/person (range 5-70).

2. Thirty persons who had counted used 1-crown coins for 5 minutes, 37  $\mu$ g Ni/person (range 6-122).

3. Nickel could be determined on the hands of all the 5 employees in the department store in the range of 17  $\mu$ g (information desk) – 96  $\mu$ g (clothes). The mean value was 50  $\mu$ g/person.

4. Ten patients at the out-patient department of dermatology, 16  $\mu$ g Ni/person (range 10–18).

Cobalt was not found in any of the analyses. The minimum detectable amount with the atomic absorption spectrophotometer is less than 0.5  $\mu$ g.

## DISCUSSION

Ethylic ether could free nickel from used 1crown pieces, but not from newly minted coins. The nickel regained in the ether has probably been located in the film of dirt, fat, sweat and oxides on the surface of the coins. The mean value of nickel found on the surface of coins containing 5% and 25% nickel was the same, while the range of individual values was quite wide, probably depending on how worn the coins were. About 1/3 of the nickel found in the ether was water-soluble and thus probably ionized. The nonwater-soluble nickel remaining in the ether-phase may consist of metal and oxides. The non-watersoluble nickel in the film-coating could probably be dissolved on contact with skin and sweat.

The ether contained the same quantity of nickel per coin after having been used for washing copper coins (5 öre) as was found in the ether after washing silver coins. This is remarkable, as there are only traces of nickel in the alloy of these coins. The presence of nickel is interpreted as a contamination of the copper-coins from other coins containing nickel, and from hands. Used bank-notes were also contaminated with nickel.

In Experiment II there was some variation in the release of nickel from individual coins. Onecrown coins containing 5% Ni released more nickel in distilled water than coins containing 5 times more nickel; thus the 25%-nickel alloy seems to be more resistant to water.

It is noteworthy that the release of nickel from an alloy consisting partly of nickel, i.e. from coins, is much greater than that from metal sheets plated of 100% nickel, where it is intended to be resistant. The relief design on the coins increases their surface-area, but not to such an extent that it can explain this variation of nickel-release.

When two series of persons counted 1-crown coins for 5 minutes, the mean nickel-contamination of the hands from used coins and from ether-washed coins was almost the same. The film on the coins thus offers no protection. Only 5 minutes of intense handling of coins is sufficient to release nickel.

The range of individual nickel-contamination of hands was quite wide and was probably correlated to the degree of sweating. Collins has shown a positive correlation between metal-corrosion and palmar sweat-rate (4). All the 5 employees of the department store had nickel on their hands. The mean value of nickel-contamination after 4 hours at work was only slightly higher than that for persons who counted coins for 5 minutes. All the employees had contact with coins, but there may have been other nickel-sources in their environment. The group of 10 out-patients also had nickel-contamination of their hands.

The present study demonstrated nickel that could be washed off the hands, but the method does not exclude the possibility that some nickel might have been more firmly bound to the skin.

Under patch test conditions it has been shown that a 15-minute test produces equally strong skin reactions as does a 24-hour test (16).

The nickel-contamination of hands expressed in absolute amounts of nickel in the present study cannot be compared to eliciting threshold concentrations of nickel in a cup-test (12) or a patchtest (10).

Smaller amounts of nickel are required in a patch-test in order to elicit a skin reaction, if the skin barrier is injured (10, 15), as compared with

# 234 N. Bang Pedersen et al.

normal testing conditions. Nickel can accumulate in keratin and in sweat-ducts under patch-test conditions, and even in deeper layers of the epidermis, if the skin is injured (17).

Patients hypersensitive to nickel are often primarily sensitized in regions other than the hands, for instance the earlobe. Nickel does not seem to penetrate the skin of healthy hands in amounts sufficient to elicit a hand-dermatitis. The handdermatitis often starts several years after the sensitization, as an irritant dermatitis (3).

Calnan (3) found that 20% of female patients suffering from nickel-allergy had hand-dermatitis. while others (11, 18) found hand-dermatitis in more than 50% of patients who reacted positively to a nickel-test. In a health-survey of hand-dermatoses, Agrup (1) found nickel to be first in rank on the list of allergens causing hand-dermatitis. Cronin (5) finds the relevance of coins, household objects, cooking utensils, etc., undetermined as the cause of hand-eczema, since the eczema is only to a small extent localized to the palmar surface of the hands and fingers. We are of the contrary opinion, and find nickel to be the allergen most often causing allergic contact-dermatitis on the volar side of the hands. Occupational contact-dermatitis from coins has been reported in persons allergic to nickel (2, 14). Silver coins can be used in the testing to reveal nickel-hypersensitivity (6, 17), but it has not been shown that ordinary contact with coins can elicit dermatitis in allergic persons. There are many other nickelsources in our environment (9), and it is impossible to separate them from contact with coins in everyday life.

In the present study, much more nickel was released from coins in water and synthetic sweat than from nickel-plated metal. It indicates that silver coins are a more relevant source of allergen in everyday life than plated objects, apart from such objects as are in more or less permanent contact with the skin, such as zippers, ear-rings, etc. Contact with coins is almost unavoidable. It is thus possible that the contamination of the hands found in this study is sufficient to maintain an already established nickel-eczema.

It is surprising that no cobalt could be determined in the analyses. Patients are very often concomitantly sensitized to both nickel and cobalt (7), which have been thought to come from the same source.

#### REFERENCES

- Agrup, G.: Hand eczema and other hand dermatoses in south Sweden. Acta Dermatovener (Stockholm) 49: Suppl. 61, 1969.
- Bettley, F. R.: Nickel coin dermatitis. Contact Dermatitis Newsletter No. 9, p. 198, 1971.
- Calnan, C. D.: Nickel dermatitis. Br J Dermatol 68: 229, 1956.
- Collins, K. J.: The corrosion of metal by palmar sweat. Br J Ind Med 14: 191, 1957.
- Cronin, E.: Quarterly Review. Contact Dermatitis XIII: The significance of nickel sensitivity in women. Br J Dermatol 84: 96, 1971.
- Fisher, A. A. & Shapiro, A.: Allergic eczematous contact dermatitis due to metallic nickel. JAMA 161: 717, 1956.
- Fregert, S. & Rorsman, H.: Allergy to chromium, nickel and cobalt. Acta Dermatovener (Stockholm) 46: 144, 1966.
- Fregert, S., Hjorth, N., Magnusson, B., Bandmann, H.-J., Calnan, C. D., Cronin, E., Malten, K. E., Meneghini, C. L., Pirilä, V. & Wilkinson, D. S.: Epidemiology of contact dermatitis. Trans St John's Hosp Derm Soc 55: 17, 1969.
- Hjorth, N. & Fregert, S.: In Textbook of Dermatology (ed. A. Rock, D. S. Wilkinson and F. J. G. Ebling, p. 395, Blackwell, Oxford), 1972.
- Kvorning, S. A. & Svendsen, I. B.: A synthetic detergent as a provocative agent in patch test. J Invest Dermatol 26: 421, 1956.
- Magnusson, B., Fregert, S., Hjorth, N., Høvding, G., Pirilä, V. & Skog, E.: Routine patch testing V: Correlation of reactions to the site of dermatitis and the history of the patient. Acta Dermatovener (Stockholm) 49: 556, 1969.
- Malten, K. E. & Spruit, D.: The relative importance of various environmental exposures to nickel in causing contact hypersensitivity. Acta Dermatovener (Stockholm) 49: 14, 1969.
- Marcussen, P. V.: The rise in incidence of nickel sensitivity. Br J Dermatol 71: 97, 1959.
- Rothman, S.: Überempfindlichkeit gegen Hartgeld. Dermatol Wochensch 90: 98, 1930.
- Samitz, M. H. & Pomerantz, H.: Studies of the effects on the skin of nickel and chromium salts. AMA Arch Ind Health 18: 473, 1958.
- Schuppli, R.: Die Bedeutung der Hautaffinität von Metallen für die Entstehung von Zement- und Waschmittelekzemen. Dermatologica 135: 225, 1967.
- Wells, G. C.: Effects of nickel on the skin. Br J Dermatol 68: 237, 1956.
- Wilkinson, D. S., Bandmann, H.-J., Calnan, C. D., Cronin, E., Fregert, S., Hjorth, N., Magnusson, B., Maibach, H. I., Malten, K. E., Meneghini, C. L. & Pirilä, V.: The role of contact dermatitis in hand eczema. Trans St John's Hosp Derm Soc 56: 19, 1970.

Received August 17, 1973

S. Fregert, M.D. Section of Occupational Dermatology University Hospital S-221 85 Lund Sweden

Acta Dermatovener (Stockholm) 54