Int. J. Electrochem. Sci., 9 **(2014)** 5812 - 5819

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Assessment of the Nickel Ion Releases from the Broken Stainless Steel and Nickel Titanium Endodontic Instruments

İsmail UZUN[1,*], *Buğra GÜLER*[1], *Taha ÖZYÜREK*[1], *Okan UÇARLI*[2], *Emre BODRUMLU*[1], *Necati MENEK*[2,*]

[1] Ondokuz Mayıs University, Faculty of Dentistry, Department of Endodontics, 55139 Kurupelit, Samsun-TURKEY
[2] Ondokuz Mayıs University, Faculty of Sciences and Arts, Department of Chemistry, 55139 Kurupelit, Samsun-TURKEY
[*]E-mail: ismail.uzun@omu.edu.tr; nmenek@omu.edu.tr

Received: 12 May 2014 / *Accepted:* 18 June 2014 / *Published:* 16 July 2014

Purpose: The purpose of this study was to assess the nickel ion releases from the broken stainless steel and nickel titanium endodontic instruments in a phosphate buffer solution at different time periods.
Methods: Thirty-two extracted human mandibular premolars with mature apices, single canals and of similar lengths were selected for the study. #35.04 Mtwo and #35.02 K-files were used for this study. Thirty-two extracted human mandibular premolars were divided into two groups randomly (n: 16) according to material type of file (stainless steel or NiTi). These two groups were then divided into two subgroups: files located at the apical foramen level (n:8) or 3 mm beyond the apical foramen (n:8). The voltammetric experiments were carried out using a computer controlled electroanalysis system the Metrohm 757 VA Computrace Electrochemical Analyzer. Comparisons intragroup and intergroups were evaluated with Kruskal-Wallis H and Mann-Whitney U tests statistically.
Results: No ion release was detected in both file groups at the apical foramen level ($p>0.05$). In 3 mm beyond from apical foramen group, stainless steel showed no ion release; nevertheless, NiTi files presented ion release ($p<0.05$). Evaluation of nickel ion release of NiTi files showed statistical difference regarding time intervals ($p<0.05$).
Conclusion: It is concluded that removal of separated file in patients with history of nickel allergy, is important when separated file tip is 3 mm beyond the apical foramen because of possibility of nickel ion release.

Keywords: nickel titanium, endodontics, nickel release, voltammetry

1. INTRODUCTION

The success of root canal treatment is directly related to the cleaning, shaping and disinfection of the root canal [1]. All these procedures should be done throughout the lenght of the tooth. However,

complications can occur by the clinicians. In apical perforations and/or preparations extending beyond the apex, endodontic files may contact periapical tissues [2]. With the understanding that cyclic fatigue and torsional stress can cause file breakage due to careless usage of the files or be forced of the files, broken files may remain in root canals for years and release corrosion products that may lead to adverse biological effects [3].

The most common metals or alloys used in dentistry are nickel titanium and stainless steel for endodontic treatment. However, a major potential disadvantage of these materials is in vivo corrosion [4]. Even though the protective oxide film exists on the metal containing materials, the remnant file in closure tissue undergoes an electrochemical dissolution from the material [5-7].

There are different methods to detect ion releases from materials. The most common optical methods like spectrophotometry, AAS and ICP AES often do not have sufficient sensitivity, selectivity and freedom from matrix interferences. They also require relatively expensive instrumentation and are generally time consuming. In contrast, voltammetric techniques allow direct determinations without separate preconcentration steps and have the potential to be used on board ship, thereby permitting nearly real-time analysis [8, 9]. Voltammetric and stripping techniques have been used for quantitative determination of a variety of dissolved inorganic and organic substances. In recent years, modern electrochemical techniques, especially square wave voltammetry (SWV) and stripping voltammetry which improve sensitivity and selectivity have promoted the development of many electrochemical methods for ultra-traces measurements of a variety of organic and inorganic species. Especially adsorptive stripping voltammetry (AdSV) is a well-established electroanalytical technique for trace determination of aqueous Ni(II)) in the form of the dimethylglyoxime complex [$M(HDMG)_2$] [10–12].

The purpose of this study was to assess the nickel ion releases from the stainless steel and nickel titanium files of these broken instruments in a phosphate buffer solution at different time periods.

2. EXPERIMENTAL

Thirty-two extracted human mandibular premolars with mature apices, single canals and of similar lengths were selected for the study. The teeth were left in 5.25% sodium hypochlorite (NaOCl) (Caglayan Kimya, Konya, Turkey) solution for two hours to clean the periodontal tissue remnants from the root surfaces. The root surfaces were further scaled with a periodontal curette, and the teeth were stored in a saline solution. To create an easy reference point for working length, the teeth were decoronated from the cemento-enamel junction with a high-speed handpiece bur. The canals were controlled for apical patency with a size 15 K-file (Dentsply Maillefer, Ballaigues, Switzerland). Also, teeth were included in which a 10 K-file could barely be seen through the apex as well as a 15 K-file that fits tightly at the apical foramen.

#35.04 Mtwo (VDW, Munich, Germany) and #35.02 K-files (Dentsply Maillefer, Ballaigues, Switzerland) were used for this study. Samples were divided into two groups randomly (n: 16) according to material type of file (stainless steel or NiTi). These two groups were then divided into two subgroups: files located at the apical foramen level (n:8) or 3 mm beyond the apical foramen (n:8). The

handle tips of the files were removed by a carbon saw blade and the coronal portions of the roots were sealed with temporary filling material so that the file's coronal end would not be exposed.

Stainless steel and NiTi files were placed into root canals at the foramen apical level and 3 mm beyond the foramen apical. The handle tips of the files were removed by a carbon saw blade and the coronal portions of the roots were sealed with temporary filling material (Cavit G, Espe, Sefeld, Germany) so that the file tips would not be exposed. Samples were divided into two groups randomly (n: 16) according to material type of file (stainless steel/ NiTi). Those two groups were then divided into two subgroups: files located at the foramen apical level and files located 3 mm beyond the foramen apical.

All dilutions and samples were prepared using deionized water. An ammonia buffer (0.1 M, pH = 9.20) was prepared by mixing corresponding amounts of ammonium chloride (Merck S.p.A, Modugno, Italia), ammonia, and hydrochloric acid (Merck S.p.A, Modugno, Italia) solution. A dimethylglyoxime (DMG) solution (1%) was prepared by dissolving an appropriate amount in absolute ethanol. Sodium nitrite (5 M) was prepared by dissolving a corresponding amount of the salt in deionized water. DMG and sodium nitrite of analytical grade were obtained from Merck. A nickel standard stock solution (0.1 M) was prepared from the Merck product and diluted as required.

The voltammetric experiments were carried out using a computer controlled electroanalysis system which is the Metrohm 757 VA Computrace Electrochemical Analyzer. A three-electrode combination system was used; a Multi-Mode Electrode (DME, SMDE and HMDE), an Ag/AgCl /3 M KCl reference electrode and a Pt wire auxiliary electrode. All measurements were carried out at room temperature. Nickel determined by catalytic adsorptive stripping square-wave voltammetry was carried out under the following conditions: adsorption potential, -0.6 V *versus* Ag-AgCl-KCl (satd.); adsorption time 30 s; equilibrium time 5 s; potential step 4 mV; pulse height 50 mV, and scan rate 200 mV/s.

A Jenway 3040 model ion analyzer was used to monitor the pH of buffer solutions in the range of 2-12, standardized with a pH 7.00 stock buffer and a pH 10.00 stock buffer solution.

The solutions were purged with purified clean dry nitrogen for five minutes prior to the experiments to remove dissolved oxygen from the media and blanketed thereafter. An ammonia buffer solution at pH 9.20 was used as the supporting electrolyte at voltammetric studies, and 500 µl of sodium nitrite and 100 µl of the sample were added to 10 mL of supporting electrolyte. SW voltammograms were obtained following the passing of nitrogen for 300 s. Standard addition method has been used for the determination of the nickel.

First of all, the Kolmogorov-Smirnov test was used to assess whether the data fits normal distribution. Comparisons intragroup and intergroups were evaluated with Kruskal-Wallis H and Mann-Whitney U tests.

3. RESULTS AND DISCUSSION

Formation of the $Ni(HDMG)_2$ complex in acidic media is hindered due to protonation of the ligand. In alkaline solution, however, Ni(II) forms a stable complex with dimethylglyoxime, and the complex is slightly soluble in an aqueous alkaline buffer. It has been found, in close agreement with

many others, the optimum medium for analytical purposes to be a 0.1 M NH_3/0.1 M NH_4Cl buffer with pH 9.2. Under these conditions, the E_p for $Ni(DMG)_2$ appears at -1.0 V, and the polarographic and voltammetric peaks are well defined for $Ni(DMG)_2$ complex. These responses were compared to those obtained using the hanging mercury drop electrode (HMDE) (Fig. 1). The stripping voltammograms obtained using the HMDE are in agreement with what was published in previous literature for similar experimental conditions (pH= 9, ammonia buffer, DMG as complexing agent) [10-12]. A well-defined stripping peak is obtained at -1.0 V vs Ag/AgCl during the cathodic scan following the $Ni(DMG)_2$ complex adsorption onto the HMDE.

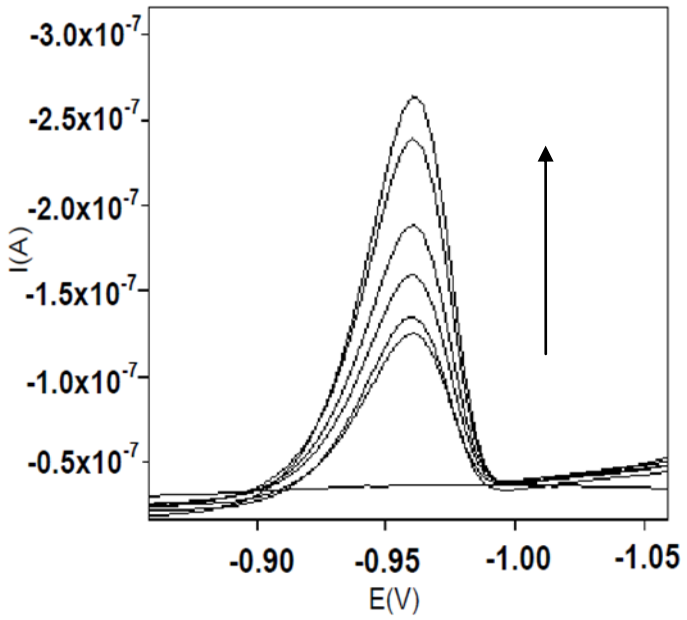

Figure 1. SWCAdSV voltammograms of the nickel-DMG at pH 9.2 for 21st day (sample, 0.02426, 0.04852 , 0.09704, 0.14556 , 0.19408 ppm respectively)

$Ni(HDMG)_2$ was adsorbed at controlled potential (-0.6 V) until equilibrium was reached [12]. To increase the sensitivity and to decrease the detection limit of the nickel determination adsorptive stripping voltammetry (AdSV) was examined and then the supporting electrolyte was modified by addition of $NaNO_2$ into the solution containing ammonia buffer and DMG. A linear calibration curve was obtained with good correlation coefficient in the 0 to 20 ppb concentration range (Fig. 2). Lower detection limits for Ni(II) can be achieved by SW cathodic adsorptive stripping voltammetry (SWCAdSV) [12], as illustrated in that demonstrates the effect of preconcentration time on the peak current of Ni(II). The metal ion is converted to a surface-active complex with dimethylglyoxime (H-DMG), then accumulated on the electrode surface and, finally, detected voltammetrically by reduction of the adsorbed complex:

$Ni^{2+} + 2H\text{-DMG} \rightarrow [Ni(DMG)_2]0 + 2H^+$

(complexation, stirring)

$[Ni(DMG)_2]_0 \rightarrow [Ni(E)_2]_0$ ads

(adsorption, accumulation at anodic potential, stirring)

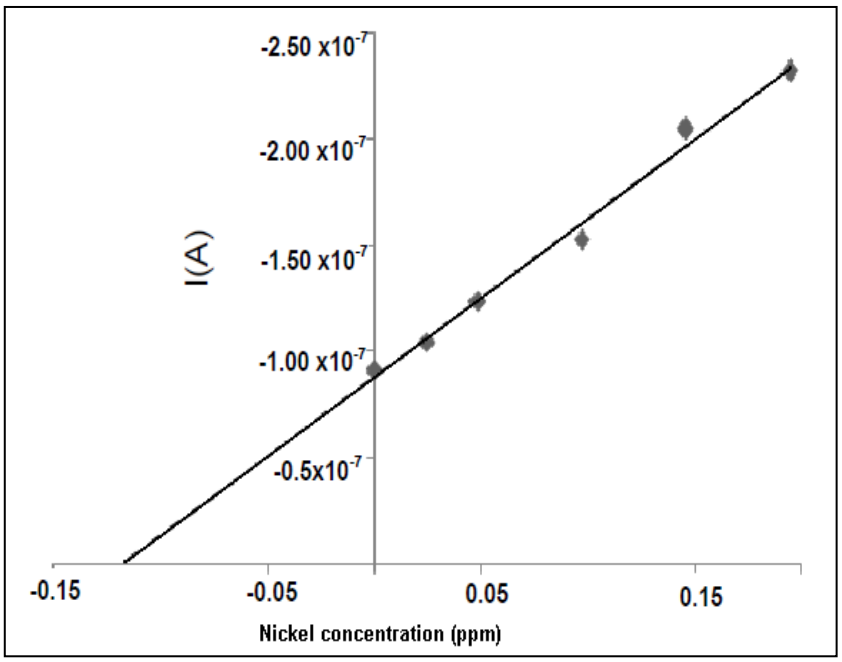

Figure 2. Peak current of the nickel dependent on the concentration for 21th day

Our studies have been planed as four step as Stainless steel at apical foramen NiTi at apical foramen, Stainless steel beyond 3 mm from apical foramen and NiTi beyond 3 mm from apical foramen all voltammetric parameters have been selected similar values all the samples. Determinations of the nickel ions release have been calculated by using standard addition methods from the voltammetric data. The results of the each of group at different days analyzed are given Table 1.

As shown Table 1, nickel ion release have not been detected for Stainless steel at apical foramen NiTi at apical foramen, Stainless steel beyond 3 mm from apical foramen at all days. But nickel ion release NiTi beyond 3 mm from apical foramen have observed all days.

Table 1 Shows the distribution mean and standard deviation (Std. Dev) of nickel release from stainless steel and Ni-Ti files.

		3. day	7. day	14. day	21. day	28. day
	N	Mean± Std. Dev	Mean± Std. Dev	Mean± Std. Dev	Mean± Std. Dev	Mean± Std. Dev
Stainless steel at apical foramen	8	0,00001±0.00000[b]	,00001±0.00000[b]	0,00001±0.00000[b]	0,00001±0.00000[b]	0,00001±0.00000[b]
NiTi at apical foramen	8	0.0001±0.00000[b]	0.0001±0.00000[b]	0.0001±0.00000[b]	0.0001±0.00000[b]	0.0001±0.00000[b]
Stainless steel beyond 3 mm from apical foramen	8	0.0001±0.00000[b]	0.0001±0.00000[b]	0.0001±0.00000[b]	0.0001±0.00000[b]	0.0001±0.00000[b]
NiTi beyond 3 mm from apical foramen	8	904,5000±5,71989[a]	3729,0313±1,27927[c]	6088,3438±5,98608[d]	13396,0312±5,88648[e]	33999,0313±14,27130[f]

* Significant differences between the different alphabetic characters

As shown from the statistical analysis of results, no ion release was detected in both file groups at the apical foramen level ($p>0.05$). In this group of files beyond 3 mm from apical foramen, stainless steel showed no ion release; nevertheless, NiTi files presented ion release ($p<0.05$).

Evaluation of nickel ion release of NiTi files showed statistical difference regarding time intervals ($p<0.05$).

Of all the complications that might occur during an endodontic procedure, one of the very worst is instrumentation breakage. Broken files can affect the clinician's success and can negatively affect the long-term prognosis of root canal treatment [13]. The remains of the endodontic files may release metal ions into the surroundings, which have been found to have toxic effects on the tissues [13].

Nickel is considered an essential trace element in humans and a component of some critical enzymatic systems with daily intake of 100–600μg [8]. The discharge of nickel ions, a strong immunologic sensitizer, can result in hypersensitivity, contact dermatitis, asthma, and cytotoxicity [1]. In addition to the allergen issue, cellular and genetic toxicity have been assigned to nickel and, to a lesser extent, chromium [14]. The epithelial stem cells play an important role in preserving the genetic information of the tissues, since the DNA is most vulnerable to damage during mitosis [15]. Many studies reported that unusual foreign body reactions may have originated from corrosion products from the remnant endodontic files that had contact with blood [16].

The present study showed that the NiTi broken file excess 3 mm from the apical foramen discharge nickel ions, although no nickel ion was determined in the broken files at apical foramen. This discrepancy might be due to the exposure of broken pieces to corrosive materials limitation. There was not any positive correlation between instrument time and nickel levels for the endodontic individuals. Shabalovskaya stated that the corrosion behavior of NiTi instruments may be influenced by body fluids consist of 0.9 % NaCl and other minor amounts of salts which aggravate corrosion of any metallic subject [17]. Saghiri *et al.* found blood caused more corrosion than deionized water and phosphate buffer saline [18]. It might be attributed to the different kinds of enzymes in blood and oxidative agents released from leucocytes, which may result in a powerful oxidative effect of blood on the surface of stainless steel files [18, 19]. However, the exposure of broken pieces to corrosive materials is limited due to their entrapment by obturation materials. Saghiri *et al.* reported that the amount of nickel can be increased in the urine of patients who have experienced broken endodontic instrument inside the dental canal. However, there is no positive correlation between the remaining pieces of instruments inside the canal and the elevation of nickel amount in urine. The findings of the current study are consistent with the Saghiri *et al.* studies. Since there are no studies comparing the releasing of nickel ions from the broken endodontic file, direct comparisons with the current study are not possible [18].

Nickel titanium endodontic files contain 55% nickel and 45% titanium; however stainless steel files contain less nickel alloy. Because of less nickel ratio stainless steel endodontic files showed less nickel ion releases compared to NiTi instruments [20].

The analytical advantages of the various voltammetric techniques used include excellent sensitivity with a very large useful linear concentration range for both inorganic and organic species (10^{-12} to 10^{-1} *M*); a large number of useful solvents and electrolytes; a wide range of temperatures;

rapid analysis times (seconds); simultaneous determination of several analytes; the ability to determine kinetic and mechanistic parameter; and a well-developed theory, which provided the ability to reasonably estimate the values of unknown parameters as well as ease in generating potential waveforms and measuring small currents [11].

It is concluded that removal of separated file in patients with history of nickel allergy, is important when separated file tip is 3 mm beyond foramen apical regarding possibility of nickel ion release.

Concentrations of Ni (II) dependent on different days are given in Figure 3. As shown in Figure 3, the nickel concentrations in the solutions media change with time periods.

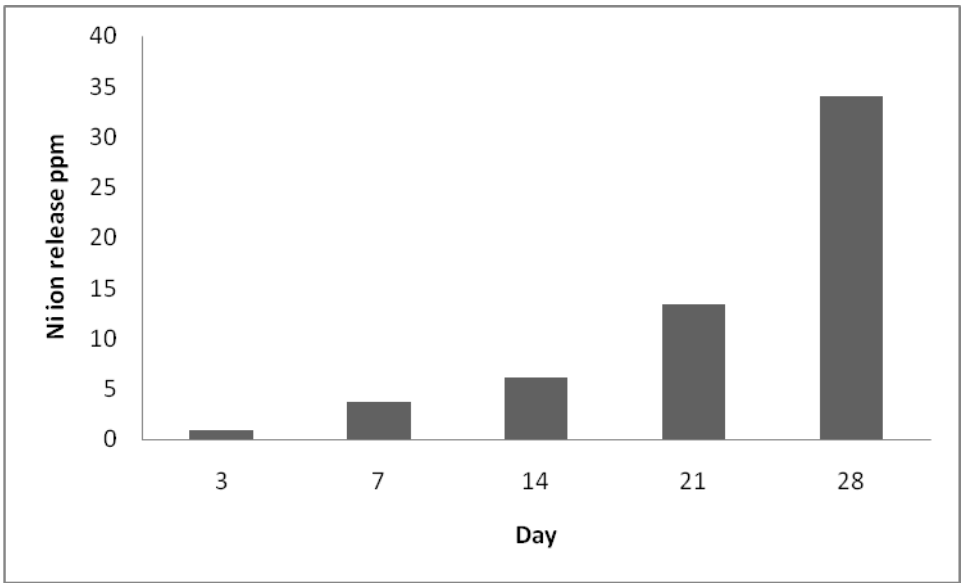

Figure 3. Concentration of the nickel in the solution dependent on different days

As reported in the studies, the critical concentration and daily dietary intake level of nickel ion gave different concentration range as 600-2500 μg [21] and 300-500 μg [22] respectively [10]. In the present study released nickel ion concentration level in NiTi beyond 3 mm from apical foramen was found below 30 μg/ml in all time periods (Fig. 3). Nickel ion release has not detected in other samples. Results showed that metal ions released in this experimental condition were well below the critical value to induce allergy and below daily dietary intake level. Therefore it is concluded that the quantities of metal ions released in the experimental conditions should not be the cause for concern.

4. CONCLUSIONS

In this present study nickel ion release from NiTi and stainless steel apical foramen which is used in dentistry at different days has been investigated. Totally16 stainless steel and 16 NiTi apical foramen were studied. Nickel in aqueous solutions was determined by square wave voltammetry, using

dimethylglyoxime as a complexion agent on mercury electrode. Results have showed that nickel ions released in this experimental condition are well below the critical value to induce allergy and below daily dietary intake level at only NiTi beyond 3 mm from apical foramen. It has not been observed nickel ions released at stainless steel at apical foramen, NiTi at apical foramen and stainless steel beyond 3 mm from apical foramen.

References

1. S. Shabahang, M. Pouresmail, M. Torabinejad, *J Endod*, 29 (2003) 450-452.
2. J. Siqueira, C.H. Silva, Md. Cerqueira, H.P. Lopes, Md. Uzeda, *Dental Traumatology* 14 (1998) 124-126.
3. A.C. Viana, B.M. Gonzalez, V.T. Buono, M.G. Bahia, *Int Endod* J 39 (2006) 709-715.
4. N. Staffolani, F. Damiani, C. Lilli, M. Guerra, N. Staffolani, S. Belcastro et al, *Journal of Dentistry* 27 (1999) 449-454.
5. T. Souier, M. Chiesa, *Journal of Materials Research* 27 (2012) 1580-1588.
6. G.T. Block, M. Yeung, *JAMA* 247 (1982) 1600-1602.
7. L. Peltonen, *International Journal ofDdermato*logy 20 (1981) 352-353.
8. P. Kapturski, A. Bobrowski, *Journal of Electroanalytical Chemistry* 617 (2008) 1-6.
9. J.R. Donat, K.W. Bruland. *Anal. Chem*. 60 (1988) 240-244.
10. N. Menek, S. Başaran, Y. Karaman, G. Ceylan, E.Ş. Tunç, *Int J Electrochem Sci* 7 (2012) 6465-6471.
11. O. Uçarlı, *The investıgatıon of polarographic and voltammetric of catalytiıc effect of nitrite on the cobalt and nickel dimethylglyoxime complexes*. Ondokuz Mayis University Scientific Institue;2010.
12. N. Menek, O. Uçarlı, S. Topçu, S. Zeyrekli, and Y. Karaman, *Int J Electrochem Sci* 9 (2014) 2445-2453.
13. A.A. Madarati, D.C. Watts, A.J. Qualtrough. *British Dental Journal* 204 (2008) 241-245.
14. D. Burrows, *International Dental Journal* 36 (1986) 30.
15. M. Natarajan, S. Padmanabhan, A. Chitharanjan, M. Narasimhan, *American Journal of Orthodontics and Dentofacial Orthopedics* 140 (2011) 383-388.
16. J.L. Saunders, P.D. Eleazer, P. Zhang, S. Michalek, *Effect J Endod* 30 (2004) 177-179.
17. S.A. Shabalovskaya, *Bio-medical Materials andEengineering* 12 (2002) 69-109.
18. M.A. Saghiri, A. Delvarani, P. Mehrvarzfar, G. Malganji, M. Lotfi, B. Dadresanfar, et al, *Oral Surgery, Oral Medicine, Oral Pathology*, 108 (2009) 29-34.
19. E. Zhang, H. Chen, F. Shen, *Journal of Materials Science: Materials in Medicine* 21 (2010) 2151-2163.
20. L. Bergmans, J. Van Cleynenbreugel, M. Wevers, P. Lambrechts. *Am J Dent* 14 (2001) 324-333.
21. K. Kaaber, N.K. Veien and J.C. Tjell, *British J. Dermatology*, 98 (1978) 197.
22. H.A. Schroeder, J.J. Balassa and I.H. Tıpton, *J. Chronic Disease*, 15 (1962) 941.