

IV. ENVIRONMENTAL DATA AND ENGINEERING CONTROLS

Sampling and Analytical Methods

During industrial operations, nickel and inorganic nickel compounds may escape into the environment as dusts from grinding, cutting, and melting operations [23,176], as fumes where high temperatures are involved, and as mists where nickel solutions are used [26]. Routine sampling and analytical methods do not permit the identification of individual nickel compounds present in the occupational environment. Therefore, only sampling and analytical methods for total nickel are discussed here. A direct readout method for analysis of airborne nickel dust, fume, or mist has not been found.

No air sampling methods specific for total nickel determinations have been found. A variety of methods suitable for general particulate sampling have been used [13,23,176], and samples collected by these methods often contain large amounts of other metals and metallic compounds. In a nickel smelter or refinery, other elemental components present in the ore, eg, copper, iron, lead, arsenic, and other trace materials, may be present [10]. Samples from the battery-making industry frequently contain cadmium [177]. Other metals, particularly chromium, are used with nickel in the electroplating industry [178]. Thus, since no sampling methods are nickel-specific and other metals are often present, the analytical method must be specific for nickel.

Tada [179], in 1968, recommended the use of a midjet impinger containing 5 ml of distilled water to sample water-soluble nickel compounds. A sample volume of 10 liters, collected at the rate

of 3 liters/minute, was recommended; the resulting sensitivity for nickel was reported as 0.1-3 mg/cu m. However, the use of impingers is not preferable to collection on a filter because of the inconvenience to the worker during sample collection and because of the unknown collection efficiency of an impinger with water for insoluble nickel dusts and fumes.

When gravimetric determinations of total dusts are performed concurrently with nickel analysis, filters are the preferred method of sample collection. However, when very low concentrations of nickel in the environment are being determined, the background concentration of nickel in the filter must be considered [180]. In 1972, Hwang [181] reported the following nickel concentrations in common filters: glass fiber filter, less than 0.08 μg nickel/sq cm; silver membrane filter, 0.1 μg nickel/sq cm; and organic membrane filter, 0.001 μg nickel/sq cm. Pate and Tabor [182], in 1962, reported 0.33 μg of nickel/37-mm glass-fiber filter. Because of their high nickel content, glass-fiber filters are not recommended for nickel sampling.

Membrane filters of many types have been used to collect particulate nickel [23,180,183]. Cellulose-ester membrane filters have been shown to contain very low amounts of nickel. Birks et al [184] reported 0.001 μg nickel/sq cm based on emission spectrographic analysis; Dams et al [185], using neutron activation analysis, reported the nickel content of these filters to be less than 50 ng/sq cm. Polycarbonate-membrane filters have also been used in sampling for airborne nickel [183], and a filter manufacturer [186] reports nickel concentrations of 0.007 μg /sq cm of filter. Polycarbonate-membrane filters, however, may cause digestion residue problems.

NIOSH's currently accepted sampling method for airborne metals uses a cellulose-membrane filter [187]. Although the cellulose-membrane filter may contain some contaminant nickel, the use of a blank filter for estimating background levels and a sufficiently large sample volume can overcome this potential problem. A sampling rate of 2.0 liters/minute and a filter pore size of 0.8 μm are recommended. The recommended sampling procedure is detailed in Appendix I.

To collect sufficient nickel for analysis by personal monitoring methods, a large sample volume must be used, generally requiring a sampling period approaching 6 hours. Because some operations may emit variable amounts of nickel into the workplace air, short-term sampling may be necessary to determine the need for engineering controls in particular cycles of an operation; high-volume samples may then be required to collect sufficient nickel for these determinations.

For many metals including nickel, particles collected on a filter can be analyzed by one of several methods. Nickel, if not already in solution, is dissolved and concentrated, this solution can be extracted and is finally analyzed. Lewis and Ott [188] have published a thorough review of the analytical chemistry of nickel. The analytical methods reviewed here are discussed in terms of their suitability for analysis of samples of airborne nickel.

Chromatographic methods of analysis for nickel have been developed. Circular, thin-layer chromatography was found to be semiquantitative for nickel, with a sensitivity of 0.03 $\mu\text{g}/\text{drop}$ of test solution when extracted from a mixture of other cations [189]. Paper chromatography has been used in the analysis of nickel-chromium aerosols with a limit of detection of

0.5 $\mu\text{g}/\text{sample}$ [190,191]. However, these determinations were based on visual comparisons with color standards.

The ring oven technique, initially a qualitative method but adaptable to semiquantitative analysis [192], is especially useful in area monitoring with a sequential tape sampler [3]. The method is inexpensive and has a limit of detection of 0.075 μg of nickel [193]. Its application to personal breathing-zone samples, however, is less practical.

Gas-liquid chromatography (GLC) has also been used for nickel analyses [194,195], eg, Barratt et al [194] measured nickel concentrations down to 0.1 $\mu\text{g}/\text{ml}$. Rodriguez-Vazquez [195] reviewed the applications of GLC to inorganic chemical analysis and mentioned three necessary conditions for the analysis of metals: the metal must be convertible to a volatile form; the volatile complex must be thermally stable; and the conversion must be quantitative. Thus, GLC requires the measurement of a secondary nickel complex, the formation of which may introduce error into the analysis.

Investigators have also used activation analysis for the determination of nickel [196-198]. Although these methods are sensitive and do not destroy the sample, the requirements for elaborate equipment, the safety precautions necessary for use of an irradiating beam and radioactive sources, and the relatively small thermal neutron cross section of nickel make activation analysis undesirable for routine use. Activation analysis is primarily useful as a research method.

Polarographic methods have also been used to analyze nickel [199,200]. Polarography possesses the required sensitivity ($2\mu\text{g}/\text{sample}$ [200]) and specificity for a variety of heavy metals; however, when this

method is used for mixtures of metals, such as nickel and cobalt, as is common with air samples, quantitation becomes difficult [200]. Polarographic methods, therefore, depend on prior knowledge of the components of the samples.

Colorimetric methods of analysis for nickel have also been widely used [179,201]. Following the formation of a colored nickel complex, the complex is extracted, and the color intensity is determined with a spectrophotometer. Dimethylglyoxime and ammonium pyrrolidine dithiocarbamate have often been used as complexing agents. Sunderman [201] has reported the limit of detection as 0.04 $\mu\text{g}/\text{sample}$. For repetitive analyses, however, a less time-consuming procedure is desirable.

X-ray fluorescence spectrography has also been used for nickel analyses [184,202]. The method is sensitive and nondestructive. Detection limits of 0.037-0.18 μg nickel/sq cm have been reported [184]. Analysis is accurate and linear in the range from one to several hundred micrograms [202].

The use of the emission spectrograph is a widely reported and extremely accurate method of nickel analysis [176,180,203-205]. Sugimae [180] reported the working range of emission spectroscopy as 10-1,000 μg of nickel/g of sample; the relative standard deviation was determined to be 13.2% at a nickel concentration of 180 $\mu\text{g}/\text{g}$. A sample was analyzed by atomic absorption in 12 laboratories and found to contain 209-293 μg nickel/g (mean 264); Sugimae, using emission spectroscopy, reported 230 $\mu\text{g}/\text{g}$ for the same sample. The use of this method has usually been restricted to high-volume samples [203,204].

Atomic absorption spectrometry (AAS), both flame and flameless, has been used to analyze metals in environmental samples [23,183]. Nickel, as well as other metals in the air, can be identified quickly and simply [206]. Advantages of AAS include minimal sample preparation, good selectivity, and relatively simple operating procedures. It is readily adaptable to the measurement of nickel in biologic media and combines good sensitivity with relatively low cost [207].

Begnoche and Risby [183] have reported the use of flameless AAS for the determination of metals, including nickel, in atmospheric particles. However, the authors reported that, because of the use of aqua regia, the graphite tube in their furnace became unreliable after four or five determinations without major modifications. Mitchell et al [208], in 1975, suggested that flameless methods should be used only to exploit their unique characteristic, excellent sensitivity with a small sample size. Otherwise, flameless methods were reported to be slow and interference prone and to require precise operator skills. These problems can be overcome and flameless methods may eventually be sufficiently well characterized for routine nickel determinations. ●

Flame AAS has been used extensively for the analysis of nickel in samples of airborne particulate matter [23,205,206]. Kneip et al [205] have proposed a tentative method for analysis of nickel. NIOSH has also proposed a similar method [187]. The reported working range of this method was 0.1-20.0 μg of nickel/ml of solution [205]. Hwang and Feldman [206] reported 101-108% recovery using flame AAS. This method was cited as having good selectivity, being simple to operate, requiring minimal sample preparation, and having high sensitivity [206]. Hwang [181] later reported

a sensitivity of 0.05 $\mu\text{g}/\text{ml}$ which gave a 1% absorption at the 232.0-nm line. Moreover, flame AAS is relatively free from sample carryover and memory effects; samples are easily nebulized; and a wide range of operating conditions is available [207].

This method has also been studied for interferences. Silica, beryllium, and antimony were noted to interfere when present in excess [205]. Sundberg [209] recommended an oxidizing flame to minimize the interferences found with hundredfold excesses of zinc, iron, copper, cobalt, and manganese. In unusual situations, therefore, other methods, such as the use of different reagents or centrifugation prior to analysis, may have to be used to overcome specific interferences.

In 1974, NIOSH reported a flame AAS method for the analysis of nickel [187], for which the range was specified as 0.2-20 $\mu\text{g}/\text{ml}$ of solution. Further evaluation of this method has resulted in a revision of the lower end of this range, so that the NIOSH Division of Physical Sciences and Engineering now estimates that the lowest reliably detectable concentration of nickel with this method is about 1 $\mu\text{g}/\text{ml}$. This estimate was partially based on consideration of matrix effects and the requirement that the relative standard deviation be 10% or less. This method, as described in Appendix II, is recommended for determining compliance with the recommended TWA concentration limit. In almost all cases, complete dissolution of the residue after acid digestion can be attained if the sample is brought up to a total volume of 10 ml. Therefore, assuming the lowest limit of detection as 1 $\mu\text{g}/\text{ml}$, 10 μg of nickel must be collected for analysis. Since the longest sampling period readily attainable in a single work shift is about 6 hours and a sample flow rate of 2.0 liters/minute is recommended, a

sample volume of 700 liters is the maximum volume readily collected. The lowest air concentration of nickel which will result in the collection of 10 μg of nickel in a 700-liter sample volume is 15 $\mu\text{g}/\text{cu m}$. As an additional condition for analysis, the total signal for the sample must be at least double that of the blank. Use of a filter with a low nickel content and digestion in a minimum amount of acid should eliminate the potential problem of high nickel concentrations in blanks. Any other method used for the detection of nickel in order to determine compliance with the recommended TWA concentration limit must meet or exceed the requirements specified above.

Biologic Monitoring

Urinary nickel monitoring is suggested as a medical surveillance procedure, but a standard for nickel in urine has not been recommended because available data represent an assessment of populations rather than of individuals. The following discussion and the method of analysis outlined in Appendix III may be useful in those situations where biologic monitoring is being considered.

The flame AAS method recommended in Appendix III has been sufficiently tested to ensure its reliability [155,210]. The instrumentation is compatible with that of the recommended environmental monitoring method. Sunderman [207] has reviewed the uses of both flame and flameless AAS in clinical pathology, citing disadvantages and advantages of each method. Nickel concentrations in urine are extremely low and methods are rapidly being developed to adapt flameless AAS to the measurement of nickel in urine.

At a subcommittee meeting of the International Union of Pure and Applied Chemistry [211], Mikac-Devic et al have recently reported an extremely sensitive and simple method for the determination of nickel in biologic fluids. Urine, serum, or whole blood were wet-digested, the pH adjusted, and a nickel-furil-dioxime complex extracted into an organic phase. The organic-phase nickel was analyzed in a flameless atomic absorption spectrophotometer. The method is extremely sensitive (0.2 $\mu\text{g/liter}$), sample preparation is not elaborate, and interferences should be minimal. The method is currently undergoing interlaboratory testing. Other direct flameless AAS methods were also reported by Anderson and Zachariasen and Bozic and Etier at that meeting [211]. These also are reported to be simple and sensitive methods for measuring nickel concentrations in biologic samples.

Normal values for nickel concentrations in a variety of biologic tissues have been reported. Nomoto and Sunderman [155] reported the results of AAS analysis of urine collected from 26 healthy subjects in central Connecticut. The mean concentration of nickel found in urine was 0.23 $\mu\text{g}/100\text{ ml}$ (SD=0.14). Urinary nickel concentrations in men and women did not differ significantly. The mean urinary excretion of nickel was 2.4 $\mu\text{g/day}$ (SD=1.1; range 1.0-5.6).

The results of Nomoto and Sunderman [155] were verified in 1972 by McNeely et al [212]. The mean concentration of nickel found in the urine of 20 healthy Hartford, Connecticut, subjects, not exposed to nickel in their workplace, was 2.0 $\mu\text{g/liter}$ (SD=0.9; range 0.7-4.0). The mean daily urinary excretion of nickel was found to be 2.5 $\mu\text{g/day}$ (SD=1.4; range 0.5-6.0). McNeely et al [212] were also able to correlate environmental and

urinary levels of nickel in this study. The average atmospheric concentration of nickel in Hartford was 36 $\mu\text{g}/1,000$ cu m. During the same period, the average atmospheric concentration in Sudbury, Ontario, was 533 $\mu\text{g}/1,000$ cu m. The mean concentration of nickel in the urine of 19 healthy Sudbury residents who did not work with nickel was 7.2 $\mu\text{g}/\text{liter}$ (SD=3.9; range 2.1-16.5). The average daily urinary excretion of nickel was determined to be 7.9 $\mu\text{g}/\text{day}$ (SD=3.7; range 2.3-15.7). The authors concluded that the significantly higher urinary nickel concentrations in Sudbury residents resulted from their exposure to much higher environmental levels of nickel.

Zachariasen et al [213] reported an average urine nickel concentration of 24 $\mu\text{g}/\text{liter}$ (SD=4; range 16-35) in 8 healthy residents of Kristiansand, Norway, who were not exposed to nickel in the workplace.

Horak and Sunderman [214] reported that nickel in feces collected from 10 healthy Hartford, Connecticut, subjects, not exposed to nickel in their work, averaged 3.3 $\mu\text{g}/\text{g}$ wet weight (SD=0.8; range 2.1-4.4) and 14.2 $\mu\text{g}/\text{g}$ dry weight (SD=2.7; range 10.8-18.7). Fecal excretion of nickel averaged 258 $\mu\text{g}/\text{day}$ (SD=126; range 80-540).

Nodiya [215] reported similar results in an investigation of nickel excretion in 10 healthy Russian vocational students. Total daily nickel ingestion was estimated at 280-300 μg . Fecal excretion of nickel averaged 257.85 $\mu\text{g}/\text{day}$ (range 219-278) and urinary excretion averaged 29.07 $\mu\text{g}/\text{day}$ (range 27.6-31.3).

Hohnadel et al [216] reported that sweating is a significant route of nickel excretion. An analysis of sweat collected during sauna baths from 48 healthy adults who did not work with nickel showed a mean concentration

of 52 μg of nickel/liter (SD=36) for arm sweat of men and 131 μg /liter (SD=65) of women. The total volume of arm sweat excreted averaged 23 ml (SD=12) in men and 7 ml (SD=3) in women.

Catalanatto et al [217] have reported the concentration of nickel in the parotid saliva from 38 healthy adults, who were employees of the University of Connecticut Health Center, and in Naval recruits in Chicago. None of the subjects worked with nickel and all subjects abstained from eating and smoking for at least 1 hour prior to sample collection. A flameless AAS technique was used to analyze the samples for nickel. The concentration of nickel in the saliva averaged 1.9 μg /liter (SD=1.0; range 0.8-4.5). No differences in the salivary nickel concentrations were found between men and women, health center employees and naval recruits, caries-free subjects and caries-prone subjects, and smokers and nonsmokers.

Schroeder et al [175] reviewed data from several sources on nickel in human tissue. He noted that nickel was reported as normally present in the tissues of most human infants. In addition, the lungs, liver, kidneys, and intestines of most stillborn fetuses usually contained nickel.

Concentrations of nickel in urine and plasma following workplace exposure to nickel also have been reported. Kemka [218] reported the results of spectrophotometric analysis of nickel in the atmosphere of a smelting plant and in the urine of the employees. The highest average concentration of airborne nickel, 0.349 $\mu\text{g}/\text{cu m}$, was found in the electrolysis section of the plant; the highest urinary nickel concentration found in electrolysis workers was 240.0 μg /liter (24.0 $\mu\text{g}/100 \text{ ml}$). Urinary nickel concentrations of 10 randomly selected nonexposed subjects averaged 27.0 μg /liter (2.7 $\mu\text{g}/100 \text{ ml}$).

In 1967, Klucik and Kemka [219] reported the concentration and the elimination rate of nickel in the urine of six electrolysis workers exposed to aerosols of nickel sulfate and nickel carbonate. Environmental nickel concentrations were reported to have ranged from 0.086 to 1.265 mg/cu m. The six workers were isolated in a hospital after a work shift, and the nickel concentration in 24-hour urine samples was determined by polarography. The control value, obtained from persons with no exposure to nickel in their work, was 9.8 $\mu\text{g}/100\text{ ml}$. First-day nickel concentrations averaged 26.4 $\mu\text{g}/100\text{ ml}$; in all workers but one, the concentration returned to the normal within 7 days. This worker showed increasing urinary nickel concentrations (12.5-22.5 $\mu\text{g}/100\text{ ml}$) over the 7 days. The authors suggested that the increasing elimination of nickel may have resulted from nickel retention in that worker.

Morgan [220] used a colorimetric method of nickel analysis to determine the concentration of nickel in the urine of workers in various departments of a nickel refinery. In the carbonyl process department, nickel concentrations in the urine ranged from 0.008-0.15 ppm (about 0.8-15 $\mu\text{g}/100\text{ ml}$). In those departments where workers were exposed only to raw materials and not to nickel carbonyl the following urine-nickel values were reported: furnaces--0.01-0.043 ppm (1-4.3 $\mu\text{g}/100\text{ ml}$); chemical precipitation plants--0.005-0.06 ppm (0.5-6 $\mu\text{g}/100\text{ ml}$); and calcination plant--0.002-0.05 ppm (0.2-5 $\mu\text{g}/100\text{ ml}$). Morgan [220] compared these data to those of control applicants for employment in the nickel plant aged 18-48 years, whose average urinary nickel concentration was 0.04 ppm (SD=0.02) (4 $\mu\text{g}/100\text{ ml}$).

Hogetveit and Barton [221], in 1975, presented plasma and urinary nickel data collected from workers at a nickel refinery in Kristiansand, Norway. Plasma nickel concentrations averaged $0.74 \mu\text{g}/100 \text{ ml}$ in "tank house" electrolysis workers exposed to soluble nickel compounds and $0.6 \mu\text{g}/100 \text{ ml}$ for 126 roasting and smelting department workers. These values were compared to those obtained from university students, which averaged $0.42 \mu\text{g}/100 \text{ ml}$. Four persons (anode-cleaning worker, smelting department worker, metal shop employee, and university volunteer) were monitored serially. Plasma and urinary nickel analyses were made every 10 days for 6 months. The nickel values dropped to nearly normal during a 2-week off-work period and increased during periods of overtime and increased production. The metalworker's plasma and urinary nickel values were lower than those of the two nickel refinery workers but were still above those of the university student. The authors [221] concluded that workers exposed to soluble nickel compounds (electrolysis workers) had higher biologic nickel values, and that nickel concentrations decreased rapidly when an employee went on furlough or retired.

In 1975, Noreseth [222] compared worker exposures to airborne nickel, as measured by personal samplers, with the preshift and postshift urinary nickel concentrations of the same workers. The study included workers from the roasting, smelting, and electrolysis departments of a nickel refinery, and welders. Roasting and smelting department workers were potentially exposed to nickel concentrations of $1.3 \text{ mg}/\text{cu m}$ ($\text{SD}=0.3$) as determined from 32 mean weekly determinations, but these workers wore respiratory protection; their urinary nickel concentrations averaged $6.6 \mu\text{g}/100 \text{ ml}$ ($\text{SD}=0.4$) for 189 determinations. The electrolysis department workers were

exposed to 0.4 mg nickel/cu m (SD=0.3) (26 mean weekly values) and showed 13.2 μ g nickel/100 ml (SD=0.85) of urine in 180 determinations. Six of 19 welders were exposed to nickel concentrations greater than 1 mg/cu m and 1 welder was exposed to as much as 5.4 mg nickel/cu m; 4 of 19 welders had urinary nickel concentrations exceeding 10.0 μ g/100 ml and the other 15 were below 10.0 μ g/100 ml. Noreseth [222] also observed that welders had urine excretion ratios similar to those of roasters and smelters; he attributed this to exposure to similar chemical forms of nickel. Electrolysis workers, although exposed at lower nickel concentrations, had elevated excretion levels because their exposure was to soluble forms of nickel such as nickel chloride or nickel sulfate. Although the exposure-to-excretion ratios of welders were fairly well correlated (correlation coefficient 0.85), this may have been due to a more uniform exposure than that of other groups; the author stated that, on the whole, urinary excretion of nickel was poorly correlated with an individual's exposure and, therefore, of limited use in assessing the exposure of the individual.

Environmental Data

Nickel is ubiquitous in the environment. Varying amounts of nickel are found in food, in the air, and in most soils. Schroeder et al [175] analyzed several diets for nickel content, concluding that, based on the various foods consumed, a 2,300 calorie diet with 100 g fat, 100 g protein, and 250 g carbohydrate could have a nickel content varying from 3-10 to 700-900 μ g. They also concluded that a rough estimate of the daily average intake of nickel was 300-600 μ g. The diets of four laboratory workers contained 305, 340, 360, and 480 μ g of nickel. A vegetarian diet would be

higher in nickel, since plants generally have a higher nickel content than do edible animal tissues.

It was estimated in a review of the health effects of nickel [3] that the average adult consumed 10 μg of nickel/day in drinking water. McNeely et al [212] reported that nickel in the municipal tapwater in Hartford, Connecticut, averaged 1.1 $\mu\text{g}/\text{liter}$. Tapwater in Sudbury, Ontario, had an average nickel concentration of 200 $\mu\text{g}/\text{liter}$ [212].

Nickel concentrations in ambient air have also been reported [223-225]. Nickel concentrations in suspended particulate matter varied between urban and nonurban air [225]. Urban areas (217 stations) had an average nickel concentration of 0.017 $\mu\text{g}/\text{cu m}$; proximate nonurban areas (5 stations), 0.008 $\mu\text{g}/\text{cu m}$; intermediate nonurban areas (15 stations), 0.004 $\mu\text{g}/\text{cu m}$; and remote nonurban areas (10 stations), 0.002 $\mu\text{g}/\text{cu m}$. In 1968, the ambient air concentration of nickel in the Ironton, Ohio-Ashland, Kentucky-Huntington, West Virginia, area was reported [223]. Huntington, the site of a large nickel mill, had an ambient air nickel concentration of 1.2 $\mu\text{g}/\text{cu m}$, while the concentration at six sampling stations in other areas of the study averaged about 0.04 $\mu\text{g}/\text{cu m}$.

Environmental data for workplace exposures have been reported for several processes:

(a) Smelting and Refining Operations

Recent environmental data have been reported for Sudbury and Port Colborne, Ontario, nickel smelting and refining plants [41]. Nickel concentrations of 0.006-0.04 $\text{mg}/\text{cu m}$ were reported from an unstated number of respirable dust samples from underground mining operations. High-volume samples taken in the milling and ore-separating areas showed nickel

concentrations of 0.0-2.8 mg/cu m. In processing departments, the following nickel concentrations were reported: reverberatory furnaces, 0.08-1.4 mg/cu m; roasters, 0.03-3.3 mg/cu m; converters, 0.03-0.2 mg/cu m; and matte separation, 0.17-15.3 mg/cu m. The number of samples was not reported.

In the Port Colborne electrolysis plant, high-volume sampling was done in 14 areas [41]. Nickel concentrations averaging 0.11 mg/cu m (SD=0.14, range 0.002-0.254) were reported. Personal samples were also taken. An average nickel exposure of 0.19 mg/cu m (range 0.11-0.27) was reported for three cementation operators. Other nickel exposures were reported for two cobalt precipitation operators (0.08 and 0.28 mg/cu m), one pressman (0.16 mg/cu m), one anode scrap washer (8.13 mg/cu m), and two tank cleaners (both less than 0.029 mg/cu m).

Klucik and Kemka [219] reported the concentration of nickel in the air over electrolysis tanks where nickel carbonate and nickel sulfate solutions were used. The mean environmental nickel concentration was 0.6 mg/cu m with a range of 0.086-1.265 mg/cu m.

In 1972, Sushchenko and Rafikova [26] reported concentrations of airborne nickel in an electrochemical refining plant. Electrolyte solutions contained 75-85% nickel in the anolyte and 74-79% nickel in the catholyte. For the years 1966-1970, the concentrations of hydro-aerosols of nickel salts were reported to have ranged from 0.035 to 1.65 mg/cu m. Highest concentrations of airborne nickel were found in the overhead-crane cabs and in the areas where the refined nickel was filtered from the solution.

(b) Nickel Alloy Production

Information supplied to NIOSH indicated the concentrations of airborne nickel found in several nickel alloy casting and forming operations [23,176]. In one plant, where the percentage of nickel found in high-volume samples was used to estimate the percentage of nickel in nearby total-dust breathing-zone samples, the nickel concentrations in atmospheric pressure-melting operations were estimated to range from less than 0.1 mg/cu m to 0.6 mg/cu m. Vacuum melting produced nickel concentrations ranging from less than 0.1 to 0.2 mg/cu m. In another plant, the concentrations of airborne nickel in 60 samples from the melting and casting area ranged from 0.006 to 1.210 mg/cu m, with an average of 0.152 mg/cu m. For other areas, the number of personal samples, average concentration of nickel, and range were reported as: annealing, shearing, and shot-blasting, 8 samples, 0.253 mg/cu m average (range 0.005-0.830); cold rolling, grinding, annealing, and pickling, 9 samples, 0.098 mg/cu m average (0.0005-0.244); and grinding and chipping, 6 samples, 1.103 mg/cu m average (0.259-3.148). Four samples were taken for operators in the hot rolling, sawing, and flame cutting departments; nickel concentrations determined were 0.233, 0.630, 0.654, and 1.851 mg/cu m, respectively.

Grinding operations at these nickel-alloy production plants have also been monitored [23,176]. In one plant, for 16 samples taken from 1972 through 1976, the nickel concentrations averaged 0.610 mg/cu m. In the other plant, less than 0.1 mg for total particulate matter/cu m, with an assumed nickel percentage of 1.4%, was reported in the grinding and cutting department in 1970.

(c) Welding, Grinding, and Flame Spraying

Nickel-metallizing or flame-spraying is a common industrial process for rebuilding worn nickel parts [13 (pp 491-493)]. In samples from the breathing zones of metallizing workers, which were collected on a filter and analyzed by AAS, 103 μg of nickel /cu m (range 9-230) has been reported [226].

The welding of nickel-containing metals or the use of nickel-based welding electrodes can result in employee exposure to nickel. Where alloys with low nickel content were welded, air samples all contained less than 100 μg nickel/cu m [227]. However, the welding of steel with more than 10% nickel resulted in breathing-zone samples with nickel concentrations of 3.80 mg/cu m [228].

Environmental measurements from steel grinding and cutting operations have also been reported [228,229]. The grinding of steel containing more than 10% nickel produced an airborne nickel concentration of 240 μg /cu m [228]. Eleven samples taken in another grinding shop were all less than 100 μg /cu m [229]. Cutting stainless steel ingots resulted in a total dust concentration averaging 70.8 (range 11.3-167.9) mg/cu m; the dust was reported to contain 11.5% nickel [55].

(d) Other Operations

Donaldson [230] reported sampling results from a plant where water-soluble nickel compounds were manufactured. Samples were collected on a 0.8- μm , 37-mm Millipore filter at a sampling rate of 2 liters/minute and a sample volume of over 800 liters. The results were analyzed by AAS. The average nickel concentration for 29 employees was 0.244 mg/cu m (range 0.009-2.780).

In 1974, Cohen et al [231] reported the results of environmental sampling near an automated nickel-chrome plating operation. The mean concentration of nickel in 14 samples was 27.1 $\mu\text{g}/\text{cu m}$ (range 8.9-71.2).

Battery production areas have also been sampled for nickel [177]. Area samples in a nickel-cadmium battery plant averaged 0.36 mg nickel/cu m (range 0.05-0.851) for 8 samples. Twenty-eight personal breathing-zone samples in the same plant had an average nickel concentration of 0.415 mg/cu m (range 0.06-2.42). Two additional samples contained nickel concentrations of 18.3 and 53.3 mg/cu m.

Tubich et al [232] reported the results of an environmental survey in an investment-casting operation. Nickel concentrations of 8-110 $\mu\text{g}/\text{cu m}$, with an average of 40 $\mu\text{g}/\text{cu m}$, were reported in the melting department. The concentrations of nickel in the grinding and welding areas of the investment castings operation were reported as 6-150 $\mu\text{g}/\text{cu m}$, with an average of 95 $\mu\text{g}/\text{cu m}$.

Nickel is also used to produce a catalyst used in the hydrogenation of fats and oils [233]. Environmental monitoring was conducted in one such catalyst plant. In 1974, seven area samples contained an average total nickel concentration of 0.15 mg/cu m (range 0.01-0.60) and five personal samples contained an average nickel concentration of 0.37 mg/cu m (range 0.19-0.53). In 1975, soluble and insoluble nickel fractions were determined separately. Two-hour area samples (approximately 60 cu m of air sampled) contained an average of 0.003 mg of soluble nickel/cu m (range 0.001-0.007) and an average of 0.288 mg of insoluble nickel/cu m (range 0.013-1.24). Breathing-zone samples were reported to contain average nickel concentrations of 0.003 mg/cu m (range 0.002-0.009) and 0.052

mg/cu m (range 0.012-0.159) for soluble and insoluble nickel compounds, respectively.

Engineering Controls

Prevention of cancer and dermatitis resulting from exposure to inorganic nickel requires the protection of employees from the inhalation of, or skin contact with, nickel dusts and fumes. The use of well-maintained closed systems and the prevention of dust generation, when compatible with the operation involved, are the best methods of preventing exposure. In areas where the escape of inorganic nickel into the environment of the worker is likely, the use of a properly designed and maintained ventilation system will prevent the accumulation of airborne nickel dusts and fumes in excess of the recommended environmental limit. Good ventilation practices, such as those outlined in the current edition of Industrial Ventilation--A Manual of Recommended Practice [178], published by the American Conference of Governmental Industrial Hygienists, should be followed. Where exhaust ventilation is required, adequate makeup air, conditioned as needed for worker comfort, must be provided.

Local exhaust ventilation systems should be designed and operated in conformance with the American National Standard Institute's Fundamentals Governing the Design and Operation of Local Exhaust Systems (Z9.2-1971) [234]. Enclosures, exhaust hoods, and ductwork must be kept in good repair so that design airflows are maintained. Airflow should be measured at each hood at least twice a year, and preferably more often. Continuous airflow indicators (such as water or oil manometers) are recommended and should be properly mounted at the juncture of the fume hood and duct throat or in the

ventilation duct and marked to indicate the desired airflow. Employers are encouraged to establish a schedule of preventive maintenance and servicing for all equipment necessary to keep the environmental levels of inorganic nickel at or below the recommended TWA concentration limit.

The use of bag burners and slurry-handling techniques can minimize employee exposure to powders and fine dusts [13 (pp 528-571)]. Fluid-bed roasters have been installed to minimize employee exposure during the refining of nickel ore [23]. Vacuum dust collection systems are efficient where a dusty nickel product is produced or where nickel dust is generated [235]. Enclosures over conveyors, the minimizing of free-fall vertical drops, and the use of vacuum packers for dusty operations should also be considered.

Electroplating operations and other operations involving open-surface tanks containing nickel in solution involve the potential release of nickel mists into the environment. Floating baffles of plastic chips or balls have been used to reduce environmental contamination from many open surface tanks [236] and might be considered where nickel solutions are used.