Speciation of Airborne Nickel in Occupational Exposures

John L. Wong* and Ting-Guo Wu[†]

Department of Chemistry, University of Louisville, Louisville, Kentucky 40292

■ Speciation from airborne nickel is important because total nickel in air has not shown a dose–response relationship in occupational hazards. A preliminary monitoring of nickel process equipment showed varying Ni^0: NiO_x ratios in the range of 0.01–0.17. Further study involved air sampling on three levels of a trilevel nickel manufacturing building by two filter types: one group of three area stations and another group of three personal-type monitors, at each site. One sample of each filter group was analyzed by atomic absorption for total nickel, and the other two were analyzed for speciation of nickel as metallic Ni^0, soluble salt Ni^{2+}, and the insoluble oxides NiO_x, by adsorptive stripping voltammetry. These results and the analysis of variance performed have shown for the first time significant heterogeneity in airborne nickel concentrations and nickel species, which are important variables in occupational dose–response studies.

Introduction

Inhalation of nickel products in a nickel refinery has been found to increase cancer incidences in the respiratory epithelium, nasal pharynx, and lungs (*1*). However, it is not known which nickel compounds are the culprits of these occupational cancers. Such structure–activity correlation is complicated by the fact that the cell-transforming capacity of nickel depends on phagocytosis, which is influenced by properties such as reactivity, solubility, surface charge, and crystallinity of the nickel sample (*2*). In an epidemiological study of nickel (*3*), the amounts of nickel in workroom air, nasal mucosa, blood plasma, and urine of exposed workers were determined and compared with the risk ratio of respiratory cancer. The smelting department, which had the highest concentrations of nickel in air, and the electrolysis department, which were lower, showed results as follows: 1.3 vs 0.4 (mg of Ni/m^3 air), 467 vs 178 (μg of Ni/100 g of mucosa), 5.2 vs 8.1 (μg of Ni/L of plasma), and 34 vs 73 (μg of Ni/L of urine). The nickel in air and mucosa are directly related, but they are inversely proportional to the nickel found in blood and urine. Yet both departments have $\sim$7 times the cancer risk. Thus, the total nickel in air does not yield a dose–response relationship. Since only total nickel was determined, a species-specific effect may not be apparent. We are involved with a health surveillance program for a nickel manufacturing plant, which handles mainly nickel oxides and nickel metal powders. We intended to rectify the lack of species information in the previous studies of nickel exposure by determining the concentrations of nickel species in air. Subsequently, we will correlate them with the worker's body burden and excretion of nickel species as well as with the health status of the exposed worker. In a previous paper (*4*), we described a practical speciation method for a solid mixture of nickel species: metallic Ni^0, soluble salt Ni^{2+}, and the insoluble oxides NiO_x. Here we report the speciation of airborne nickel sampled at different locations with two filter types inside a nickel manufacturing facility. Our results point to significant heterogeneity in airborne nickel concentrations and nickel species.

[†] Visiting scholar from Shanghai Medical Instrumentation College.

Experimental Section

Air Sampling. The collection process for air particulates was designed to meet or exceed the air sampling standards promulgated by the National Institute for Occupational Safety and the Occupational Safety and Health Administration pertaining to nickel (*5*). Two types of air monitoring systems were used to determine short-term and time-weighted average values. One was an area station outfitted with a pulsation-free, air-sampling pump, a rotameter style flow meter, and a filter assembly containing a preweighed, Gelman glass fiber membrane, type AE, 50-mm diameter, and 0.3-μm pore size, $\sim$5 ft from standing level. The air flow was regulated at 0.0708 m^3/min, and air was sampled for 1 h. Hereafter this system is referred as filter type G. The other was a personal monitor type, $\sim$5 ft from standing level, employing a SKC 224-30 constant-flow air sample pump attached to a filter cassette, in which was placed a preweighed cellulose ester membrane, 37-mm diameter, 0.8-μm pore size, with air flow at a rate of 0.002 m^3/min for 8 h (referred as filter type C). The dust weight on the filter membrane was obtained gravimetrically. The filter membrane after use was enclosed in a plastic bag, properly labeled, and stored in a desiccator.

Nickel Speciation in Air Samples. The building in which the nickel manufacturing processes took place contained various kinds of nickel oxides (NiO_x) and miscellaneous nickel agents (Ni^0, Ni^{2+}) but no sulfides or arsenides. The air particulates in this building were collected on a filter membrane and sonicated into 25 mL of deionized water in a beaker. The suspension was filtered and the filtrate saved in a volumetric flask for determination of water-soluble nickel salt Ni^{2+} by adsorptive stripping voltammetry (AdSV). The residue including the air filter membrane was resuspended in 25 mL of deionized water and extracted three times with the electromagnet rod as reported (*4*). The Ni^0 metal adhered to the rod was transferred to a quartz cell, where it was digested in 1 mL of boiling 18.5% HCl, evaporated, and analyzed by AdSV to give Ni^0. The remaining dust suspension was filtered and the residue digested in 4.5 mL of boiling 18.5% HCl to extract the water-insoluble nickel oxides. The acid solution was filtered, evaporated, and diluted with deionized water to a known volume, and AdSV determination gave NiO_x concentrations. Total nickel was also determined by atomic absorption spectrometry (AAS). The results are tabulated in Tables I–IV. The apparatus and reagents for electromagnetic extraction and AdSV are as described previously (*4*).

Statistical Analysis. The variability of data in the tables far exceeds those of the established analytical methods (*4*). Therefore, analysis of variance (ANOVA) by two-way classification (*6*) was attempted in order to determine the statistical significance of filter type (FT), location (LO), and their interaction (FT × LO). ANOVA was performed by the general linear model procedure (*7*), and the observed *P* values are reported in Table V.

Results and Discussion

Preliminary Air Monitoring of Nickel Process. A preliminary assessment of the need for speciation of airborne nickel was undertaken. Six area monitors with

Table I. Airborne Ni⁰ and NiOₓ at Nickel Process Equipment Sites

air monitor sites[a]	Ni⁰,[b] mg/m³ air	NiOₓ,[c] mg of Ni/m³ air	Ni⁰/NiOₓ
storage tank A	9.5×10^{-4}	5.6×10^{-3}	0.17
calciner discharge	1.9×10^{-3}	3.3×10^{-2}	0.06
storage tank B	4.9×10^{-3}	4.9×10^{-1}	0.01
furnace discharge	4.9×10^{-4}	1.7×10^{-2}	0.03
flaker discharge	4.2×10^{-3}	3.9×10^{-2}	0.11
rotoform discharge	6.4×10^{-3}	6.7×10^{-2}	0.09
mean	3.1×10^{-3}	1.1×10^{-1}	0.08
CV,[d] %	76	173	75

[a] Equipment spread out on first level within 100 ft of each other. [b] Determined by magnetic extraction and AdSV method (see ref 4), with coefficient of variation (CV) from 5.7% to 13.1%. [c] Determined by AdSV method (see ref 4), which has a coefficient of variation from 0.5% to 2.0%. [d] Six air monitors treated as one population, CV = (SD/mean) × 100%.

Table II. Nickel Speciation of Air Particulates Retained on Filter Type G[a]

sample[b] filter type G	Ni²⁺,[c] wt %	Ni⁰,[c] wt %	NiOₓ,[c] wt % Ni	Ni²⁺/NiOₓ	Ni⁰/NiOₓ
BA-1	0.8	0.3	37.6	0.02	0.01
BA-2	0.1	1.5	43.2	0.00 (2)	0.03
mean	0.45	0.9	40.4	0.01	0.02
CV, %	110	94	10	114	89
PL-1	0.2	0.6	26.6	0.01	0.02
PL-2	0.3	1.0	24.9	0.01	0.04
mean	0.25	0.8	25.75	0.01	0.03
CV, %	28	35	5	33	40
DC-1	0.5	0.3	15.4	0.03	0.02
DC-2	0.7	0.7	9.7	0.07	0.07
mean	0.6	0.5	12.55	0.05	0.05
CV, %	24	57	32	54	81

[a] Glass fiber membrane 0.3 μm, 0.0708 m³/min air, 1 h. [b] BA bagging area, level 1; PL Pulvacron loading, level 2; DC dust collector area, level 3, of a trilevel building with large central open space from ground to roof. [c] AdSV analysis given as percentage of filter dust weight.

Table III. Nickel Speciation of Air Particulates Retained on Filter Type C[a]

sample[b] filter type C	Ni²⁺,[c] wt %	Ni⁰,[c] wt %	NiOₓ,[c] wt % Ni	Ni²⁺/NiOₓ	Ni⁰/NiOₓ
BA-4	3.3	0.1	28.9	0.11	0.00
BA-5	1.1	2.5	5.0	0.22	0.50
mean	2.2	1.3	16.95	0.17	0.25
CV, %	71	131	100	45	140
PL-4	1.2	0.6	11.2	0.11	0.05
PL-5	1.3	0.9	22.9	0.06	0.04
mean	1.25	0.75	17.05	0.08	0.05
CV, %	6	28	49	43	22
DC-4	0.8	0.6	19.2	0.04	0.03
DC-5	0.5	1.3	3.8	0.13	0.34
mean	0.65	0.95	11.5	0.09	0.19
CV, %	33	52	95	73	118

[a] Cellulose fiber membrane 0.8 μm, 0.002 m³/min air, 8 h. [b] See footnote b, Table II. [c] See footnote c, Table II.

Table IV. Airborne Total Nickel and Dust Concentrations from Two Filter Types

sample[a]	filter dust,[b] mg/m³ air	Ni_total,[c] mg/m³ air	Ni_tot/dust, wt %
Filter Type G			
Ba-1	0.81	0.31	38
BA-2	0.98	0.44	45
BA-3	1.20	0.61	51
mean	1.00	0.45	45
CV, %	20	33	14
PL-1	0.55	0.15	27
PL-2	0.52	0.13	25
PL-3	0.42	0.11	26
mean	0.50	0.13	26
CV, %	14	15	4
DC-1	0.29	0.05	17
DC-2	0.33	0.04	12
DC-3	0.37	0.04	11
mean	0.33	0.04	13
CV, %	12	13	25
Filter Type C			
BA-4	0.98	0.32	33
BA-5	0.70	0.06	1
BA-6	0.81	0.26	32
mean	0.83	0.21	24
CV, %	17	64	56
PL-4	0.87	0.11	13
PL-5	1.01	0.25	25
PL-6	0.90	0.29	32
mean	0.93	0.22	23
CV, %	8	44	43
DC-4	0.82	0.17	21
DC-5	0.78	0.04	5
DC-6	0.50	0.05	10
mean	0.70	0.09	12
CV, %	25	83	67

[a] See footnote b, Table II. Samples 1–3 are air particulates retained on filter type G and samples 4–6 are air particulates retained on filter type C. [b] Gravimetric analysis. [c] Results for samples numbered 1, 2, 4, and 5 are from AdSV analysis and Ni_total is the sum of the Ni species; those numbered 3 and 6 are from AAS analysis.

0.3-μm pore size membrane were placed by the nickel process equipment as indicated in Table I. The air concentrations of Ni⁰ and NiOₓ reported in the table have significant variations, e.g., the Ni⁰ to NiOₓ ratios range from 0.17 to 0.01, with a coefficient of variation (CV) of 75%. The latter is ~6 times the largest CV for the AdSV method in Ni speciation. Such variations of Ni species and concentration by sampling sites have not been considered in previous environmental monitoring. Hence, a more extensive investigation of the airborne nickel species in the

nickel manufacturing building was performed.

Nickel Species Retained by Filter Type G. The air particulates were sampled at three locations inside a trilevel building used exclusively for the manufacture of nickel products. Three potentially dusty sites were chosen, one on each level: the bagging area on level 1 (BA L-1), the Pulvacron loading area on level 2 (PL L-2), and an area adjacent to a dust collector on level 3 (DC L-3). A large central open space from ground to roof allowed unimpeded air flow between levels. The air was sampled with three filter type G monitors clustered 1 ft apart at each site: one to provide sample for AAS analysis of total nickel, and two for nickel speciation by AdSV. Shown in Table II are the weight percentages of three nickel species in the dust collected. Not only do they vary between levels, which is not unexpected, but it is surprising to find that they give such a divergence of CV (5–110%) from presumably replicative samples of the same site. This cannot be dismissed as analytical error since the same AdSV routine applied to simulated samples gave a maximum CV of 13% only (4). Despite the wide data spread, it appears that the weight percents of NiOₓ and Ni⁰ decrease with increasing elevations inside the building, while the opposite holds for the ratios of Ni²⁺ to NiOₓ and Ni⁰ to NiOₓ.

Nickel Species Retained by Filter Type C. The filter type C personal monitor, recommended by NIOSH for personal monitoring of airborne nickel (5), was used to obtain time-weighted averages of nickel species. Three

Table V. ANOVA of Eight Air Particulate Variables[a]

source of variation	DF	Ni^{2+}	Ni^0	NiO$_x$	Ni^{2+}/NiO$_x$	Ni^0/NiO$_x$	Ni$_{total}$	dust	Ni$_{total}$/dust
						observed p value			
FT	1	0.05	0.59	0.08	0.01	0.24	0.45	0.01	0.17
LO	2	0.36	0.79	0.11	0.43	0.71	0.01	0.00 (1)	0.00 (4)
FT × LO	2	0.28	0.90	0.29	0.22	0.68	0.05	0.00 (4)	0.24

[a] FT, filter type, two levels; LO, location, three levels; FT × LO is their interaction term. ANOVA of each variable was run as in ref 7. Data set for Ni species includes 12 observations from AdSV. Data set for Ni$_{total}$ and dust includes 18 points (plus 6 from AAS analysis).
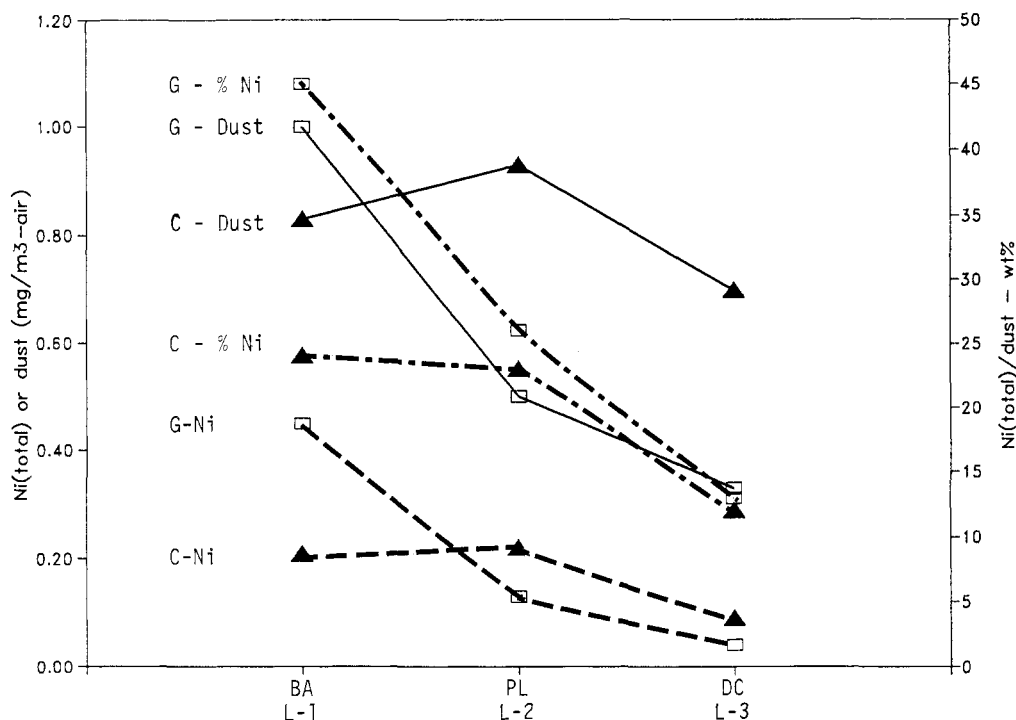
Figure 1. Relationship for air particulate concentrations with locations and filter types. X axis: three locations designated as bagging area level 1 (BA L-1), pulvacron loading level 2 (PL L-2), and dust collector level 3 (DC L-3). Y axis: mean values of Ni$_{total}$ and dust by locations and filter types G and C. Y' axis: weight percent of Ni$_{total}$ in dust. See data and footnotes in Table IV.

such filters were strapped to a pole within inches of one another at the same three locations listed above. The analytical data are tabulated in Table III. The variations among the three identical filters of the same site and between locations of these time-weighted averages are even more pronounced. For example, the CV of NiO$_x$ from filter type G are 10%, 5%, and 32% for levels 1, 2, and 3, respectively. They are 100%, 49%, and 95% from filter type C. Also the trends observed with type G, decreasing NiO$_x$ and increasing Ni^{2+} and Ni^0 ratios with elevation, are not evident. Indeed, NiO$_x$ remained the same between level 1 and level 2. However, the ratios of Ni^{2+} and Ni^0 to NiO$_x$ are considerably larger from filter type C than G. Consider the Ni^{2+} to NiO$_x$ ratios for the level 1 BA and level 2 PL samples. The ratios from filter type C are increased by an order of magnitude due to a 5-fold increase in Ni^{2+} and a 2-fold decrease in the NiO$_x$ trapped. The 8-h operation of type C favors trapping the more dilute Ni^{2+} than the 1-h operation of type G. Also, these results point to smaller NiO$_x$ particulates, hence, less retained on type C (0.8-μm pore membrane) and the association of Ni^{2+} with larger size particulates. The larger CV is consistent with opportunistic trapping of larger particulates by filter type C. The Ni^0 particles seem to have wider size distributions and are less affected by the filter type used. All in all, the results of both filter types attest to substantial heterogeneity of the airborne nickel species in the whole building.

Airborne Total Nickel and Dust Concentrations by Filter Types and Locations. In order to explain the

above differences in nickel speciation, a comparison of airborne dust and total nickel concentrations by filter types and locations is given in Table IV. The filter dust sample weights and the total nickel determined either by AAS or from the sum of nickel species by AdSV analysis are normalized over the volume of air flow through the filters to obtain their air concentrations. The weight percent of total nickel in dust is then calculated. From filter type G, there is a regular decreasing trend in all three categories with increasing elevations, with CV ranging from 4% to 33%. This trend is similar to that of Ni^0 and NiO$_x$ shown in Table II. Also, the filter type C samples in Table IV produce more data variation, with CV ranging from 8% to 83%. Levels 1 and 2 are similar in dust, total nickel, and percent nickel, while level 3 is lower in all the means. Although on level 1 the average dust weight and total Ni with filter type C were less than that of type G, the dust and total Ni weights at level 2 PL and level 3 DC are about twice as large with type C. This opposite result indicates that both filter type and location are significant variables.

Statistical Significance of Filter Type and Location. Analysis of variance was performed to determine the statistical significance of source variation for each of the eight variables below: Ni^{2+}, Ni^0, NiO$_x$, Ni^{2+}/NiO$_x$, Ni^0/NiO$_x$, Ni$_{total}$, filter dust, and Ni$_{total}$/dust. A data set of 12 observations from Tables II and III was used in the ANOVA procedure for the first five variables. The data set for the remaining three was expanded to 18 by including the results of six samples analyzed by AAS. The

observed P values are reported in Table V for these eight variables. Not listed in the table is the test result of method variation (AdSV and AAS analysis of total Ni) by the 18 data point set, which gave observed P values of 0.3–0.7. Thus, having found no statistical significance in this method factor, and because of the closely similar accuracy of AAS and AdSV in determining total nickel, it is deemed justifiable in averaging data from the two analytical methods in Table IV and using them to construct Figure 1. This figure is based on the statistical significance ($P < 0.05$) of location for Ni_{total} and filter dust as reported in Table V. The two intersecting pairs of curves illustrate the significance of the interaction of filter type and location (FT × LO) for Ni_{total} and filter dust. Although filter type G with the smaller membrane pore size retained more dust and Ni_{total} on level 1 than the larger pore type C, the reverse happened on levels 2 and 3. At higher elevations where air particulates are more dilute, opportunistic trapping of larger particulates by the 8-h type C becomes more likely than by the 1-h type G filter. This interaction effect of FT and LO appears to play a similar role regarding nickel species, e.g., NiO_x decreased with elevations on filter type G, which also retained more NiO_x than type C on level 1 only. Furthermore, Table V shows that the filter type variation is significant ($P \leq 0.05$) for filter dust as a mixture of particulates as well as for the nickel species Ni^{2+} and Ni^{2+}/NiO_x, but marginally significant ($P = 0.08$) for NiO_x only. This statistical finding is consistent with the above suggestion of smaller NiO_x and the association of Ni^{2+} with larger size particulates.

Conclusions

The nickel speciation and concentration data shown in Tables I–IV as well as Figure 1, supported by the analysis of variance summarized in Table V, have shown for the first time the significant variations in the workplace of airborne nickel species and concentration. The usual assumption that replicative analysis of samples from the same location should be reproducible was not obtained. The time-weighted averages from the personal monitor may have introduced bias because of opportunistic trapping where air particulates are more dilute. Its larger pore membrane may favor the larger size particulates (e.g., Ni^{2+}) and retain less of the smaller NiO_x. The area station monitor appears to give more internally consistent nickel data with elevations, but this will not yield representative exposure data because of the air particulate heterogeneity. Further work is necessary to determine more precisely the effects of filter pore size, sampling site, duration of sampling, etc. on nickel exposure profiles, which are needed in occupational dose–response studies.

Literature Cited

(1) Sunderman, F. W., Jr. *Ann. Clin. Lab. Sci.* **1984**, *14*, 93.
(2) Costa, M.; Simmons-Hansen, J.; Bedrossian, C. W. M.; Bonura, J.; Caprioli, R. M. *Cancer Res.* **1981**, *41*, 2868.
(3) Norseth, T. *J. Toxicol. Environ. Health* **1980**, *6*, 1219.
(4) Wu, T. G.; Wong, J. L. *Anal. Chim. Acta* **1990**, *235*, 457.
(5) *SKC Guide to NIOSH/OSHA Air Sampling Standards*; SKC Comprehensive Catalog and Guide; SKC, Inc.: PA, 1989. OSHA Standards for General Industry (29 CFR Part 1910), Subpart Z—Occupational Health and Environmental Control. CCH Editorial Staff Publication, Commerce Clearing House, Inc., Chicago, IL, July 31, 1986. OSHA Instruction CPL 2-2.20A, Office of Health Compliance Assistance, March 30, 1984.
(6) Snedecor, G. W.; Cochran, W. G. *Statistical Methods*, 7th ed.; The Iowa State University Press: Ames, IA, 1980; Chapter 14.
(7) *SAS Version 5*; SAS Institute, Inc.: Carry, NC.