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Determination of nickel carbonyl by charcoal tube collection and furnace atomic absorption spectrophotometry

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A method for the determination of nickel carbonyl has been developed using acid-washed coconut shell charcoal for sample collection and graphite furnace atomic absorption spectrophotometry for measurement. The estimated relative standard deviation of the method is 0.099 and recoveries averaged 93.0%. The working range is 2 to 50 μg $Ni(CO)_4/m^3$ (0.4 to 7 ppb) for a 20-L air sample taken at 0.2 lpm or less. **Eller, P. M.**: Determination of nickel carbonyl by charcoal tube collection and furnace atomic absorption. *Appl. Ind. Hyg. 3*:115-118; 1986.

Introduction

Nickel carbonyl is an extremely toxic gas used in the Mond Process for production of high-purity nickel and in the synthesis of methyl and ethyl acrylate monomers.[1] A total of 500 to 5000 workers may be exposed.[1] It may also be formed in tobacco smoke[2] and in nickel catalysts in the presence of carbon monoxide.[3,4] Because of its high toxicity, a maximum occupational time-weighted average exposure limit of 1 ppb (7 $\mu g/m^3$) was proposed as early as 1954 and remains the OSHA standard today. At ppb levels, several instrumental methods including chemiluminescence,[5] Fourier transform infrared spectrometry,[6] and plasma chromatography[6] have excellent sensitivity and have been applied successfully as direct-reading process monitors.

Portable methods suitable for industrial hygiene use have been very limited, however. Detector tubes have a lower useful limit of 50 ppb, and the only collection devices available for personal sampling involve liquid-filled bubblers.[1,3,7] The current work was undertaken because of the need for a solid sorbent method useful for personal sampling of sub-ppb-levels of nickel carbonyl.

Experimental

Reagents

All nitric acid solutions were prepared from J. T. Baker Ultrex concentrated nitric acid. The mean nickel content of 3% (w/v) solutions of nitric acid prepared by diluting 31 mL of this concentrated nitric acid to 1 L with deionized water was found to be 0.003 μg/mL (standard deviation = 0.002 μg/mL). Reagent grade 2-propanol (Burdick & Jackson) and iodine were used to prepare 5% (w/v) solutions of iodine for use in bubblers.[7] Nickel carbonyl was obtained from Pfalz and Bauer. Compressed air and 10% (v/v) carbon monoxide in nitrogen were used as received, except that 200-g activated charcoal traps were added to the outlets of the cylinders to purge the gases of any $Ni(CO)_4$ during use.

Sorbent

The sorbent used was a Calgon coconut-based charcoal distributed by Mine Safety Appliances, Inc. as MSA Lot No. 4. As received, the nickel content extractable by ultrasonic leaching in 3% nitric acid for 30 min was 0.25 μg Ni/g charcoal. Before use in the sampling tubes, a batch of the charcoal was allowed to stand overnight in 3% (w/v) nitric acid, rinsed with deionized water, and heated at 600°C in still air for 1.5 hours. The washed charcoal had a blank value of 0.05 μg Ni/g charcoal (standard deviation = 0.025 μg Ni/g charcoal). Sampling tubes containing 120-mg front and 60-mg backup sections of the charcoal were used throughout the work

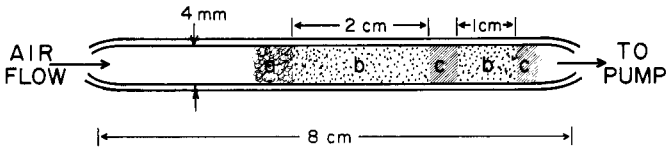

Figure 1—Sorbent tube. (a) silylated glass wool, (b) acid-washed coconut shell charcoal (120-mg front section, 60 mg back section), (c) polyurethane foam.

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(Figure 1). The tubes were capped with conventional plastic caps for storage. Other solid sorbents which were tried unsuccessfully included iodine-coated silica gel, which was rejected because of low breakthrough capacity for nickel carbonyl, and several commercially-available charcoal tubes, which contained unacceptably high concentrations of acid-leachable nickel even after several treatments.

Test atmosphere generation

A working mixture containing 6 ppm $Ni(CO)_4$ was prepared by injecting several microliters of the liquid into 10% carbon monoxide/90% nitrogen and pressurizing to about 40 psig in a pressure vessel. The purpose of adding carbon monoxide to this working mixture and to all generated atmospheres was to stabilize $Ni(CO)_4$.[3,5] (NOTE: Nickel carbonyl is highly toxic and should be used only in a fume hood or glove box.)

The pressure vessel containing the 6 ppm $Ni(CO)_4$ working mixture served as the source of $Ni(CO)_4$ in the generation system (Figure 2). A needle valve and rotameter were used to regulate and indicate the flow of working mixture from the pressure vessel. The working mixture was combined with humidified air and 10% CO in nitrogen to produce the desired atmospheres. All experiments were conducted at ambient temperature (20 to 25°C). Carbon monoxide content of the test atmosphere was estimated by triplicate Draeger detector tube determinations. Weights of Drierite tubes before and after sampling known volumes of test atmosphere were used to determine humidity in the sampling manifold. The effluent of the generation system was bubbled through a Greenburg-Smith impinger filled with 5% (w/v) iodine in isopropanol to remove any residual $Ni(CO)_4$ before exhausting to the fume hood.

The concentration of $Ni(CO)_4$ in the test atmosphere was determined independently by sampling in midget impingers containing 5% (w/v) iodine in isopropanol.[7] These solutions were analyzed directly by atomic absorption spectrophotometry. Groups of six sorbent tubes were exposed for periods ranging from 15 minutes to 4 hours. Flow rates through the sorbent tubes were controlled by 0.2 lpm critical orifices. The range of nickel carbonyl concentrations studied was from about 2 $\mu g/m^3$ to 140 $\mu g/m^3$ (0.3 ppb to 20 ppb). The mass of nickel carbonyl collected in these sample sets varied from about 0.1 μg per sample to about 0.6 μg per sample, i.e., the amounts that would be collected in 14-L samples at one-third to twice the OSHA standard. Breakthrough experiments were conducted by sampling a given test atmosphere at three different sampling rates in the range 0.07 to 0.6 L/min, in duplicate. Sample stability was assessed by storing exposed, capped sample tubes from a given sample set at room temperature for 1, 16, or 17 days before analysis.

Analysis of samples

The front and backup charcoal sections of a sample tube were placed in separate 2-mL, acid-washed glass vials. The glass wool and urethane foam plugs were discarded. Exactly one mL of 3% nitric acid was added by pipet. The vial was capped with a plastic-lined cap and placed in an ultrasonic water bath for 30 min. Aliquots of the sample solution were analyzed by graphite furnace atomic absorption spectrometry, using standards prepared from nickel nitrate in 3% (w/v) nitric acid. Analyses were done on a Perkin-Elmer Model 603 Atomic Absorption Spectrophotometer equipped with a Model HGA-2200 graphite furnace and AS-1 autosampler. Only non-pyrolytic graphite tubes were used. The measurement parameters used were as follows: injection volume, 20 μL; D_2 background correction used; dry 30 s at 105°C; ash 15 s at 800°C; atomize 10 s at 2850°C with MAX PWR. Under these conditions, the instrumental limit of detection was approximately 0.003 μg Ni (equivalent to 0.01 μg of $Ni[CO_4]$).

Desorption efficiencies were determined for aqueous nickel nitrate solutions spiked onto charcoal sorbent sections and carried through the desorption and measurement procedures.

TABLE I
Desorption of nickel (as $Ni(NO_3)_2$) from charcoal[a]

Concentration[b]								
0.4 ppb			1 ppb			2.5 ppb		
μg Ni taken	μg Ni found	DE[c]	μg Ni taken	μg Ni found	DE[c]	μg Ni taken	μg Ni found	DE[c]
0.0800	0.0734	0.918	0.200	0.195	0.975	0.500	0.454	0.908
0.0800	0.0758	0.948	0.200	0.200	1.000	0.500	0.448	0.896
0.0800	0.0681	0.851	0.200	0.196	0.980	0.500	0.442	0.884
0.0800	0.0704	0.880	0.200	0.192	0.960	0.500	0.468	0.936
0.0800	0.0734	0.918	0.200	0.204	1.020	0.500	0.472	0.944
0.0800	0.0716	0.895	0.200	0.197	0.985	0.500	0.459	0.918
n = 6					6			6
mean = 0.902					0.987			0.914
std. dev. = 0.0339					0.0209			0.0231
RSD = 0.0376					0.0212			0.0252
RSD = 0.029								

[a]Nickel nitrate standard solution added to 120 mg charcoal.
[b]Expressed as ppb of nickel carbonyl in an 83-L air sample.
[c]DE = Desorption efficiency.

Results and discussion

Nickel carbonyl is readily oxidized by alcoholic iodine or dilute hydrochloric or nitric acids. This property has formed the basis of collection methods using solutions in impingers.[3,7] In the present work, an acid-cleaned activated charcoal was investigated as a more convenient sampling device.

Nickel ion, in the form of nickel nitrate solutions, was chosen as a surrogate for desorbed samples of nickel carbonyl. Desorption of nickel nitrate standard solutions from the activated charcoal was studied in the range 0.08 to 0.5 μg Ni^{2+} per sample (Table I). The

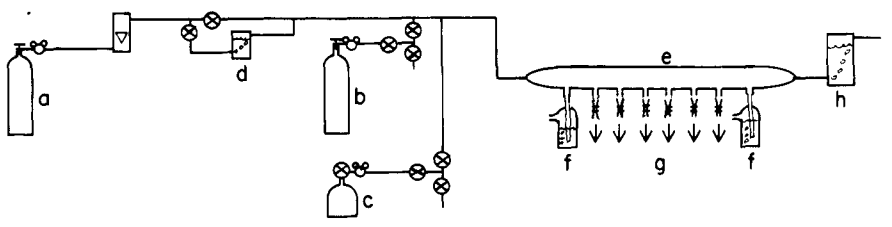

Figure 2—Generator for nickel carbonyl atmospheres. (a) compressed air, (b) 10% CO/90% N_2, (c) 6 ppm $Ni(CO)_4$ in 10% CO/90% N_2 (v/v), (d) water-filled bubbler, (e) sampling manifold, (f) midget impingers with 10 mL 5% (w/v) I_2/2-propanol, (g) sample tubes, (h) scrubber, I_2/2-propanol.

average desorption efficiency (DE) found was 0.934, and this value was used as a correction factor in subsequent analyses of generated nickel carbonyl samples.

The breakthrough volume of the sorbent tubes was sufficiently large for 8-hour sampling at ppb-levels of nickel carbonyl. Results from two runs at different humidities (Table II) showed that the 5% breakthrough volume varied from more than 4 μg nickel carbonyl per sample at low humidity to about 1 μg nickel carbonyl per sample at high humidity.

In order to estimate accuracy and precision of the overall sampling and measurement method, four sets of samples were taken, representing a range of concentrations of $Ni(CO)_4$, at a range of carbon monoxide concentrations and humidities. The results, shown in Table III, show an overall bias, relative to 5% (w/v) iodine in isopropanol, of -7%. This bias may be due in part to incomplete desorption of nickel carbonyl from the sample tubes (i.e., lower desorption efficiency for $Ni(CO)_4$ than for $Ni(NO_3)_2$). No measurable nickel was found on any of the backup charcoal sections in these experiments. The levels of carbon monoxide and humidity also had no apparent effects on the results. An estimate, 0.099, of the overall relative standard deviation of the sampling and measurement method was obtained by combining the pooled relative standard deviations from Tables I and III.

Sample stability was acceptable for the loaded sample tubes when capped and stored at room temperature for at least 17 days, as seen in Table IV.

Nickel carbonyl was observed to pass quantitatively through a 37-mm cellulose ester membrane filter at high humidity (Table V). No detectable nickel above the 0.022-μg Ni blank (standard deviation = 0.003 μg Ni) was found on any of the prefilters, and good agreement was found between sampling tubes with and without prefilters.

Recommendations

This solid sorbent method makes possible, for the first time, convenient, personal, integrated air samples in the range 2 to 50 μg $Ni(CO)_4/m^3$ (0.4 to 7 ppb) for a 20-L air sample.[8] Larger air volumes, up to 80 L, may be taken at 0.2 L/min or less. If the sampling for nickel carbonyl is to be done in atmospheres

TABLE II
breakthrough tests

Flow rate, L/min	Liters	ppm CO	H_2O, mg/L*	$Ni(CO)_4$ found μg Front	μg Back	μg/m³	Percent breakthrough
0.0821	19.7	50	3.3	0.803	0.0	40.8	0.0
0.0657	15.8			0.589	0.0	37.3	0.0
0.193	46.3			1.46	0.0	31.5	0.0
0.184	44.2			1.37	0.0	30.9	0.0
0.613	147.			4.45	0.0	30.3	0.0
0.475	114.			3.87	0.0	33.8	0.0
0.186	3.72	305	15.3	0.523	0.016	145.	3.0
0.194	3.88			0.646	0.005	168.	0.8
0.185	8.33			1.067	0.017	131.	1.6
0.183	8.24			1.212	0.028	150.	2.3
0.177	15.9			1.856	0.264	133.	12.5
0.191	17.2			2.280	0.090	138.	3.8

*Saturated air at 22°C contains 17.3 mg/L H_2O.

TABLE III
Determination of nickel carbonyl in air

$Ni(CO)_4$ Found μg	Corr. μg[a]	Liters	μg/m³	$Ni(CO)_4$ Taken μg/m³	Percent recovery	ppm CO	H_2O mg/L
0.189	0.202	43.7	4.64	5.45		6	10.4
0.218	0.233	43.7	5.20				
0.192	0.206	41.5	4.96				
0.233	0.249	44.6	5.59				
0.212	0.227	43.2	5.27				
0.195	0.209	45.4	4.59				
			mean = 5.04		92.5		
			SD = 0.39				
			RSD = 0.077				
0.558	0.597	14.4	41.6	45.4		150	8.5
0.576	0.617	14.1	43.9				
0.503	0.539	13.2	40.8				
0.582	0.623	14.0	44.5				
0.460	0.493	14.1	34.8				
0.582	0.623	14.9	41.8				
			mean = 41.2		90.8		
			SD = 3.5				
			RSD = 0.084				
0.1076	0.1152	2.46	46.9	47.6		90	15.3
0.1076	0.1152	2.41	47.9				
0.1076	0.1152	2.34	49.3				
0.1018	0.1090	2.52	43.3				
0.0960	0.1028	2.39	43.0				
0.0960	0.1028	2.52	40.8				
			mean = 45.2		95.0		
			SD = 3.3				
			RSD = 0.073				
0.466	0.499	3.59	139.2	129.7		250	8.5
0.404	0.433	3.52	122.9				
0.407	0.436	3.31	131.7				
0.387	0.414	3.53	117.3				
0.361	0.387	3.50	110.3				
0.373	0.399	3.72	107.4				
			mean = 121.5		93.7		
			SD = 12.3				
			RSD = 0.102				
			pooled RSD = 0.085 (n = 24)				

[a]Corrected for desorption efficiency of 0.934 (Table II).

TABLE IV
Table stability tests

Liquid spikes[a]—μg Ni Recovered / μg Ni Taken ± SD	
Day 1	Day 16
0.934 ± 0.031	0.875 ± 0.050
Gas spikes[b]—μg $Ni(CO)_4$ Recovered / Taken ± SD	
Day 1	Day 17
0.930 ± 0.085	0.977 ± 0.026

[a]Aliquots of standard nickel nitrate solutions added to charcoal.
[b]Aliquots of standard 6 ppm $Ni(CO)_4$ in 10% CO / 90% N_2 (v / v) added to charcoal.

TABLE V
Effect of Prefilter

Run	μg $Ni(CO)_4$ Found Filter	Tube	Liters	μg/m³	ppm CO	H_2O, mg/L
I	0.0000	0.0809	5.70	13.3	40	8.5
	0.0000	0.0717	5.16	13.0		
	0.0000	0.0717	5.40	12.4		
				mean = 12.9		
				SD = 0.5		
				RSD = 0.036		
	--*	0.0621	5.55	10.5	40	8.5
	--*	0.0809	5.58	13.6		
	--*	0.0717	5.88	11.4		
				mean = 11.8		
				SD = 1.6		
				RSD = 0.135		
II	0.0000	0.597	4.65	128.6	290	15.3
	0.0000	0.566	4.43	127.9		
	0.0000	0.623	4.58	136.0		
				mean = 130.8		
				SD = 4.5		
				RSD = 0.034		
	--*	0.258	1.91	135.3	290	15.3
	--*	0.613	4.85	126.6		
	--*	0.654	4.78	136.8		
				mean = 132.9		
				SD = 5.6		
				RSD = 0.042		

*No prefilter used.

containing particulate nickel species, a prefilter must be used.

The success of this sensitive method for determination of nickel carbonyl depends in large part on a low Ni blank value for the sorbent charcoal used. Each batch of charcoal used as sorbent should contain less than 0.1 μg Ni/g charcoal, as determined by ultrasonic leaching in 3% nitric acid and analysis for nickel.

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Answers to "The Action Level" questions

1. (d)
2. (b)
3. naphthalene-Diisocyanate
4. (c)
5. wheezing
6. (d)
7. (d)
8. (a)
9. (a)
10. See TLV and BEI Booklet