SHIMADZU APPLICATION NEWS

LAAN-A-AA-E014

● SPECTROPHOTOMETRIC ANALYSIS

No.A384

Ni Analysis by Atomic Absorption

■ Introduction

Nickel is obtained by combusting various nickel-containing ores, such as garnierite, niccolite, pentlandite, etc., and then reducing the oxide using carbon. Ni is a silver-white metal with abundant malleability and ductility, however, since it is extremely stable at ambient temperatures, it is widely used for plating. The alloys of nickel include stainless steel (Ni 8%, Cr 18%, with the main constituent being Fe), cupronickel used for coin (Ni 25%, Cu 75%), white metal used for art objects, musical instruments, tableware, etc. (Ni 10 – 20%, Cu 40 – 70%, Zn 20 – 30%), nichrome used in heating elements (Ni 60 – 80%, Cr 10 – 20%, Mn 1 – 2%), etc. In addition, it is used in a wide range of fields, including electrode materials in Ni-Zn batteries and Ni-Cd batteries, as a catalyst in organic synthesis, etc.

Ni is present at the rate of about 143μg/kg in the human body, with its greatest concentration in bones. Since there is almost no absorption of Ni from the intestine, it is presumed that oral toxicity is low, although nickel sulfide and nickel oxide, etc. are carcinogenic and can cause allergies. Nickel alloys used in accessories become ions when in contact with skin, and when they form bonds with biological substances, they act as haptens (weak antigens) showing strong antigenicity. As a result, an immune reaction occurs in the body, causing skin inflammation and other symptoms.

Ni has a high melting point and high boiling point, and it cannot be easily atomized. Thus it is one of the elements for which it is difficult to obtain good sensitivity. However, we introduce here an example of high sensitivity analysis using concentration-boosting inside the furnace.

■ Basic Data of Nickel

Atomic mass	58.69	
Melting point	1453˚C ($NiSO_4$ 99˚C)	
Boiling point	2732˚C	
Oxidation number	−1 $[Ni_2(CO)_6]^{2-}$	
	0 $[Ni(CO)_4]$	
	+1 $[Ni(PPh_3)_3Br]$	
	+2 NiO, $NiCl_2$	
	+3 Ni_2O_3	
	+4 NiO_2	
	+6 K_2NiO_4	
Solubility	$NiCl_2 \cdot 6H_2O$	67.8g/100gwater (26˚C)
	$Ni(NO_3)_2 \cdot 6H_2O$	94.2g/100gwater (25˚C)
	$NiSO_4 \cdot 7H_2O$	39.7g/100gwater (20˚C)

Reference : New Ideas about 111 Elements, Physics and Chemistry Dictionary, etc.

■ Wavelengths of Ni

nm	Sensitivity ratio
232.0	1.0
341.5	0.51
352.5	0.5
231.1	0.2
351.5	0.09

■ Furnace Analysis of Ni

One method of increasing the sensitivity in furnace analysis is to boost concentration in the furnace. The amount of sample injected into the graphite cuvette can be increased with the aim of improving sensitivity, however, since the injection volume is limited by the internal capacity of the cuvette, normally, about 80μL per injection is the maximum volume that can be injected. The hot injection method is also available, in which the sample is dried through heating of the cuvette while sample is injected. However, when the injection volume is increased, the temperature of the tube decreases, and the sample may be measured before being sufficiently dried. Concentration boosting inside the furnace is a method in which a fixed amount of sample is injected into the cuvette, and drying and re-injection are repeated to increase the amount of sample in the furnace. When there are few coexisting substances in the sample, re-injection is performed after drying is completed, however, when the sample contains many coexisting substances, it is preferable to perform re-injection after completion of ashing to eliminate the interfering substances. When conducting concentration boosting in the furnace, it is necessary to note that the risk of contamination is higher than in measurements with single injection, due to the repeated operations of the autosampler and comparatively long analysis time. However, concentration in the furnace creates a smaller number of contamination sources than concentration using a hotplate and other tools, where care must be taken to prevent contamination from the sample containers and the environment.

In this investigation, we conducted furnace analysis of Ni using concentration boosting in the furnace. A pyrolyzed tube was used for the cuvette, and analysis↘

↘was conducted with the heating conditions shown in Table 1. The injection volume for each injection was 80µL, and the concentration boosting injections were repeated 5 times. Therefore, the obtained sensitivity is approximately equivalent to the sensitivity obtained when 400µL of sample is injected. Specifically, after first injecting 80µL, the first line of Table 1 was conducted (drying step), heating was stopped temporarily, 80µL was next injected to repeat the first step, and after the fifth injection, heating was conducted until the final step.
Fig.1 shows the calibration curve with five concentration-boosting injections, and Fig.3 and 4 show the peak profiles at 0.1ppb and 1ppb, respectively. The calibration curve with one injection is shown in Fig.2 for reference. The lower quantitation limit with the five concentration-boosting injections is about 0.02ppb.

Table 1 Heating Conditions

Temperature (˚C)	Time (s)	Heating mode	Gas flow rate (L/min)
150	20	RAMP	0.1
250	10	RAMP	0.1
800	10	RAMP	1.0
800	10	STEP	1.0
2500	3	STEP	0.0
2600	2	STEP	1.0

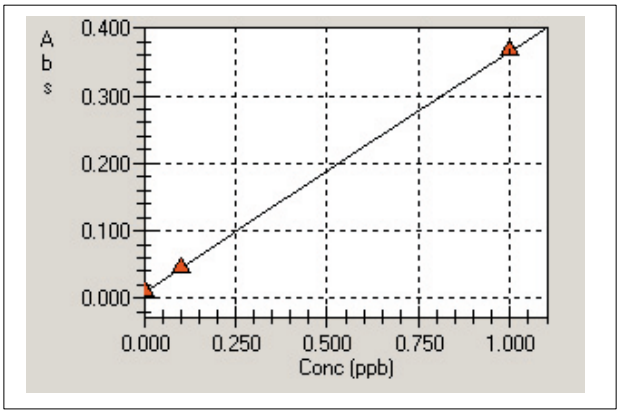

Fig.1 Calibration Curve (5times injection)

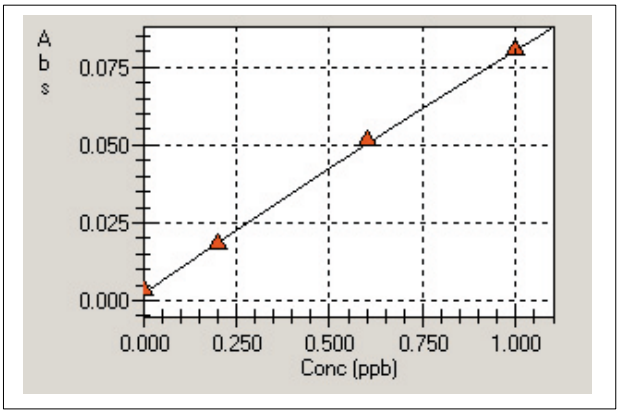

Fig.2 Calibration Curve (1time injection)

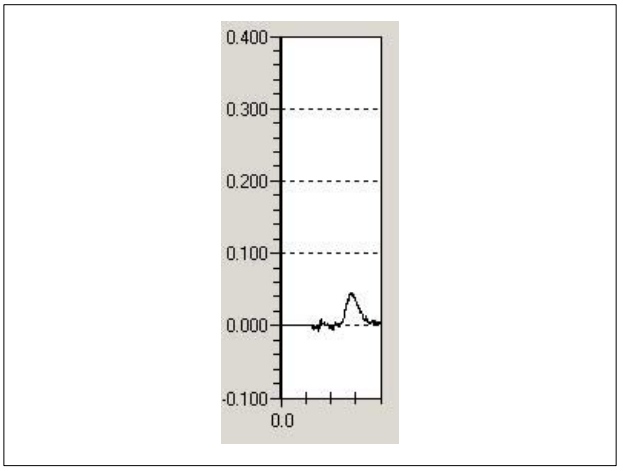

Fig.3 Peak Profile (0.1ppb)

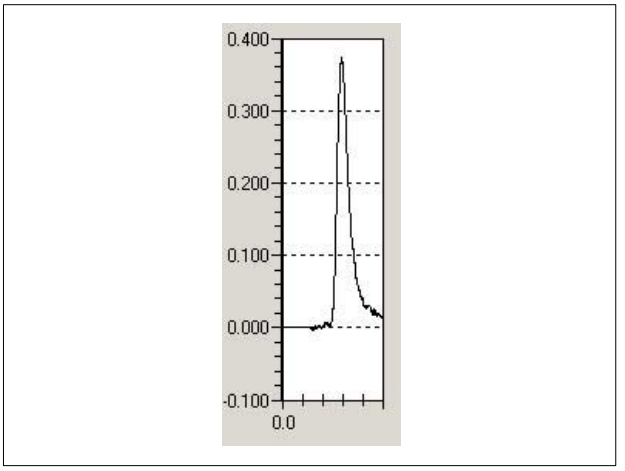

Fig.4 Peak Profile (1ppb)

■ Conclusion

Ni exists at a concentration of about 0.004% in soil, and about 0.002mg/L in sea water. Since the concentrations are low, it is not easily affected by contamination from the environment. Ni displays catalytic activity, and because it forms alloys easily, it is employed, like Pd, as a matrix modifier in furnace analysis. However, Ni has many absorbance lines, making it a source of spectral interference in some cases. For example, the 228.8nm wavelength of Ni is the cause of background in the Cd measurement at wavelength 228.84nm. This is a typical combination that generates background caused by adjacent lines, which cannot be compensated for using the D_2 method. However, high accuracy compensation is possible with the SR method.

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