Preliminary study on a vapor generation technique for nickel without using carbon monoxide by inductively coupled plasma atomic emission spectrometry

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Abstract

The authors found that volatile nickel species could be generated by reaction in an aqueous solution with sodium or potassium borohydride under appropriate conditions at room temperature without using carbon monoxide. After vapor generation and gas–liquid separation, the volatile species was carried into an inductively coupled plasma (ICP) by argon gas, and the quantity of nickel determined by atomic emission spectrometry. The intensities of the Ni lines were strongly affected by the acidity of samples, the flow rate of argon carrier gas and the length of the transfer tube between the gas–liquid separator and ICP. A detection limit of 0.5 ng/ml and a precision of <5% was obtained under the following conditions: 0.12 M HCl acidified sample solution; 3% potassium borohydride solution with 0.5% potassium hydroxide added; sample uptake rate 2.8 ml/min; argon carrier gas flow 500 ml/min; and the length of the transfer tube kept as short as possible. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Vapor generation; Nickel volatile species; Inductively coupled plasma atomic emission spectrometry

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1. Introduction

The vapor generation (VG) method, with its advantages of high sensitivity and minimized spectral interference, has been widely used in atomic spectrometry. However, the elements that can be determined by this technique are still limited to just a few so far; this has led to attempts to develop new VG systems for more elements. Over the past 20 years, the reaction of nickel and carbon monoxide (CO) to form a stable gaseous carbonyl has been used as a gaseous sample introduction method for the determination of nickel by atomic spectrometry [1–8]. In all of these methods, nickel was reduced to its elemental form by addition of sodium borohydride into the sample solution; then by reacting with carbon monoxide (CO) in the Ar–CO or He–CO mixture added to the solution, nickel carbonyl was formed, stripped from solution, and subsequently detected spectrometrically. In these methods, a CO supply was needed, the reaction time was relatively long (min), and usually a trapping technique was used. It should be pointed out that nickel carbonyl is extremely toxic.

It is well-known that hydride generation techniques based on the reaction between sodium tetrahydroborate (borohydride) and the acidified sample solution are susceptible to severe interference from transition metal ions such as Ni$^{2+}$, Co$^{2+}$, and Cu$^{2+}$. However, in this work, it was found for the first time that volatile nickel species could be generated by reaction in an aqueous solution with sodium or potassium borohydride at room temperature without using carbon monoxide. After vapor generation and gas–liquid separation, the volatile species could be detected by inductively coupled plasma atomic emission spectrometry (ICP-AES). This paper describes the results of preliminary studies on the optimization of experimental parameters affecting nickel vapor generation and determination, as well as the analytical performance of this method.

2. Experimental

2.1. Instrumentation

The instrument used was an ICP 2070 sequential ICP emission spectrometer (Baird, MA), coupled with a home-made continuous flow vapor generator (Fig. 1). The latter consisted of a manually controlled peristaltic pump to feed the acidified sample and borohydride solutions to a Y-tube connected to a gas–liquid phase separator, and to remove the waste liquid from the separator chamber. The gas–liquid separator was a cylindrical vessel of approximately 60 mm long, with an i.d. of approximately 14 mm. The inlet was 25 mm

Fig. 1. Schematic of the vapor generation manifold.
from the top of the vessel, and the gas outlet was at the top of the vessel. The drainage was pumped out by the peristaltic pump at the same time as the inlet mixture was pumped in, as shown in Fig. 1. The generated analyte vapor was swept into the ICP via a length of tygon tubing, using the existing nebulizer Ar gas flow from the spectrometer as the carrier gas. The argon and sample flow rates were carefully selected to match the requirements of the gas–liquid separator and the plasma.

2.2. Reagents

A stock solution of Ni (1000 mg l⁻¹) was prepared from nickel nitrate. Working standard solutions were freshly prepared daily by diluting appropriate aliquots of the stock solution in high-purity water containing 0.1 mol l⁻¹ HCl. A 3% (m/v) solution of potassium borohydride was prepared by dissolving KBH₄ (Aldrich) in de-ionized water stabilized in a 0.5% m/v KOH solution. All of the mineral acids used were of the highest quality. High-purity water was used throughout.

2.3. Procedures

The sample and reducing reagent solution (KBH₄) were pumped at flow rates of 4 and 2 ml min⁻¹, respectively, into the vapor generator. VG was accomplished in a continuous-flow mode at the merge point of the Y-tube. Once the ICP was stabilized, the vapor generator was switched on-line to the ICP. A standard solution containing 0.5 or 2 µg/ml Ni was used for experiments, and the spectrometer was tuned at Ni II 221.65 nm for maximum response. A number of variables were optimized, including the carrier gas flow rate, the acid and reductant concentrations, and the length of the transfer tubing between the vapor generator and the ICP torch. A calibration curve was obtained by using aqueous standards without a matrix. The volatile species was transported by the evolved H₂ and Ar gas purged from the gas–liquid separator through the transfer tubing to the plasma. The operating parameters used for ICP-AES are listed in Table 1.

3. Results and discussion

3.1. Effect of acids

To examine the effects of acid concentration and acid type, the most common acids used for sample preparation, such as HCl, HNO₃, H₂SO₄, and HClO₄, were studied. The Ni line intensity was strongly affected by the acidity of the sample solution. It was surprising that not only HCl, but also HNO₃, H₂SO₄, and HClO₄ could be used in this reaction. This is very similar to the findings by Sturgen et al. [9] for copper vapor generation. This fact was an advantage, because in many digestion procedures, particularly for biological samples, acids other than HCl are often used. In our case, however, 0.12 M of HCl was found to be optimal, as shown in Fig. 2. The concentration–intensity curves for other acids tested have trends similar to that of Fig. 2.

3.2. Reductant concentration

A higher concentration of the reductant may be beneficial for forming nickel volatile species, at least to some extent. To investigate this, various concentrations of NaBH₄ were used for the Ni vapor generation (at the same NaOH concentration of 0.5% m/v). The results showed that the Ni intensity increased with NaBH₄ concentration. However, excessive hydrogen, and hence plasma instability, also increased at the same time, and a

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Vapor generation ICP-AES operating parameters</th>
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<tbody>
<tr>
<td>RF generator frequency</td>
<td>27.12 MHz</td>
</tr>
<tr>
<td>Plasma RF power</td>
<td>1400 W</td>
</tr>
<tr>
<td>Reflected power</td>
<td>≤ 5 W</td>
</tr>
<tr>
<td>Working gas</td>
<td>Ar</td>
</tr>
<tr>
<td>Outer gas flow rate</td>
<td>14 l/min</td>
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<tr>
<td>Intermediate gas flow rate</td>
<td>0.8 l/min</td>
</tr>
<tr>
<td>Carrier gas flow</td>
<td>550 ml/min</td>
</tr>
<tr>
<td>Sample acidity</td>
<td>0.12 M HCl</td>
</tr>
<tr>
<td>Sample uptake rate</td>
<td>4 ml/min</td>
</tr>
<tr>
<td>KBH₄ concentration</td>
<td>3.0% (m/v)</td>
</tr>
<tr>
<td>KBH₄ flow rate</td>
<td>2 ml/min</td>
</tr>
<tr>
<td>Observation height</td>
<td>11 mm above load coil</td>
</tr>
<tr>
<td>Integration time</td>
<td>5 s</td>
</tr>
<tr>
<td>Ni wavelength</td>
<td>221.647 nm</td>
</tr>
</tbody>
</table>
Fig. 2. Effect of HCl acidity on the intensity of Ni II 221.65 nm (1 μg/ml).

NaBH₄ concentration higher than 4% (m/v) would extinguish the plasma. Eventually 3% NaBH₄ (m/v) was used for further experiments.

3.3. Effects of RF power and argon carrier gas flow

When the hydride and hydrogen produced by vapor generation were introduced into the ICP, the plasma became very bright and unstable. This was mainly due to the introduction of excessive hydrogen gas.

The effect of hydrogen has been studied in detail [10,11]. It was found that for obtaining the best detection limits, the plasma for hydride generation should be operated at a power higher than that for a nebulization method. Studies on the effect of RF forward power on the ICP in this work verified that higher forward power not only provided higher sensitivity, but also better precision. The power–intensity curve is shown in Fig. 3. Since the RF generator of the 2070 spectrometer has a nominal power limit of 1.6 kW, the operating power used this work was set at 1.4 kW for the sake of safety.

Fig. 3. Effect of RF forward power on the intensity of Ni II 221.65 nm (0.5 μg/ml).
It was also found that the waste liquid should be removed from the liquid–gas separator as soon as possible to ensure a stable plasma.

The effect of the argon carrier gas flow rate has also been studied. The results are shown in Fig. 4. From the figure it can be seen that at low carrier gas flow rates, e.g. 0.3 l/min, the signal intensity was decreased, implying that the carrier gas flow was too low to smoothly transport the volatile species to the plasma. With the continuous introduction of hydrides, a flow of 0.55 l/min was found to be best.

3.4. Length of the reaction tube

The length of the transfer tubing between the gas–liquid separator and the ICP torch is a crucial factor in nickel vapor generation, as shown in Fig. 5. Clearly, the emission intensity decreases drastically as the transport distance increases, reflecting the additional losses of the analyte due to collisions with the inner wall surfaces of the tubing. In order to obtain a high transfer efficiency, the length of tubing between the

![Figure 4: Effect of Ar carrier gas flow rate on the intensity of Ni II 221.65 nm (1 µg/ml).](image1)

![Figure 5: Influence of the length of Tygon transfer tube between the generator and the ICP torch on the intensity of Ni II 221.65 nm (1 µg/ml).](image2)
The liquid separator and the ICP should be kept as short as possible. The fact that reasonable transport can be achieved only at a tube length of less than 10 cm suggests that this analyte species is very unstable. Transfer efficiency was probably the main factor preventing previous workers from getting a Ni vapor species signal directly without employing carbonyl.

The length of the reaction coil is also of importance. It was found that the Ni signals became less intense if the tubing was longer, and a black Ni precipitate formed rapidly on the inner wall of the tubing. It appears that inside the long reaction coil, the Ni volatile species has enough time to reduce to metallic form, and the Ni precipitate would probably adsorb the volatile species, thus decreasing the Ni signal intensity further. Hence, the length of the reaction coil should also be as short as possible and emit the volatile species out of the tubing as soon as possible after it was produced.

### 3.5. Analytical performance

The detection limit (DL) and precision (expressed by RSD) have been evaluated under ‘optimized’ operating conditions, as listed in Table 1. A DL of 0.5 ng/ml ($n = 10$) and an RSD of $< 5\%$ ($n = 10, 0.1 \mu g/ml Ni^{2+}$) were obtained.

The Ni intensity scans obtained under the vapor generation mode and the direct nebulization mode, respectively, are shown in Fig. 6. A standard solution of 2 $\mu g/l Ni^{2+}$ was used in this experiment. It can be seen from the scans that the intensity was enhanced by more than four times by VG as compared with direct nebulization. However, the sample uptake rate for VG was 4 ml/min, whereas for nebulization it was only 1.5 ml/min. So there was not much gain in sensitivity from VG. This suggests that the efficiency of volatile species generation was quite low at the present stage.

#### 3.6. Verification of nickel vapor generation

Wickström et al. [12] reported that the matrix (‘non-hydride forming’) elements such as Ni, Co, Cr, and Fe could be transported to the atom cell as an aerosol, formed during hydride generation. Therefore, the following experiment was performed to evaluate how much nickel would be transported as an aerosol to the ICP. Both the Ni and Mg intensities were measured in VG mode with a 0.1 $\mu g/ml Ni$ solution spiked with 1 mg/ml nickel.

![Intensity scans of Ni II 221.65 nm by using ICP-AES. A, vapor generation method; B, nebulization method. (2 $\mu g/ml Ni$).](image)
Mg. Mg is a non-hydride forming element, but it is much more sensitive than Ni in ICP-AES. Only a weak signal of Mg was recorded in this experiment. A semi-quantitative estimation showed that only a very small amount of Mg (≤ 10% of the amount introduced by normal nebulization) had been transported to the ICP in the form of an aerosol. This means that most of the Ni contained in the solution was transported to the ICP as some kind of volatile species.

Another experiment was performed to verify the existence of Ni volatile species formed in vapor generation. Two calibration curves were obtained by vapor generation ICP-AES with two sets of standard solutions, with and without EDTA, respectively. The curves are shown in Fig. 7. Curve (a) was for solutions containing EDTA, and curve (b) was for solutions with no EDTA added. In the presence of the EDTA, which is a strong chelator for masking metal ions, it was believed that Ni$^{2+}$ could not react with KBH$_4$, and that no volatile species could be formed. However, a small amount of Ni$^{2+}$ could still be transported to the plasma as a form of aerosol, so curve (a) still has a small slope, though much smaller than that of curve (b), in which no chelator was added. The much larger slope of the curve (b) is a manifest of the existence of the Ni volatile species.

4. Conclusions

This work demonstrates for the first time that nickel volatile species can be formed by reacting with tetrahydroborate in aqueous solution without the presence of CO. The volatile species remains unidentified, and is very unstable, but it seems that the method should be potentially useful for analytical purposes. However, this technique is still in its infant state, and further work is required to make it mature. For instance, the further improvement of the VG setup and optimization of the operating conditions, the collection of nickel volatile species in a cold trap or in a graphite tube as a pre-concentration step, and the application of some kind of enhancement reagent [13], etc., should be considered to attain a much better detection limit and precision. Presumably, this technique, when matured, should be...
applicable to other techniques such as atomic absorbance spectroscopy and atomic fluorescence spectrometry.

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References


