Determination of Tin in Nickel-based Alloys by Electrothermal Laser-excited Atomic Fluorescence With Confirmation of Accuracy by Inductively Coupled Plasma Mass Spectrometry and Atomic Absorption Spectrometry

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The determination of tin in nickel-based alloys by laser-excited atomic fluorescence in a graphite furnace was investigated. The concentrations of tin in four nickel-based alloys from Pratt & Whitney Aircraft were determined. The nickel in the alloys was found to behave as a permanent chemical modifier that remained in the graphite tube during analyses. The use of a mixture of hydrochloric, hydrofluoric and nitric acids proved to be the most efficient dissolution method. In order to confirm the accuracy of the results, Zeeman-effect background corrected ETAAS and ICP-MS methods were also used. The results from these different methods were compared by use of the Student's t-test. The laser-excited atomic fluorescence method was found to be as accurate as the other techniques. The precision of the techniques varied from 4 to 12% RSD. For the dissolution of 100 mg of nickel alloy in 100 ml of aqueous solution, the effective atomic fluorescence detection limit in the original nickel alloy samples was 1.5 ng g⁻¹. The atomic fluorescence method was simple to develop and did not need a sophisticated background correction technique to perform the analyses.

Keywords: Tin, nickel alloy; laser; atomic fluorescence; atomic absorption; graphite furnace; inductively coupled plasma mass spectrometry.

Despite the sensitivity and accuracy inherent in atomic spectroscopy, many analysts have found tin determinations in refined metal alloys to be troublesome, owing to the complicated chemistry of many tin compounds that necessitates the use of time-consuming sample preparation steps prior to analysis. Manshlin et al. employed a continuous hydride generator to remove tin from copper alloys in the form of a gaseous hydride, before introduction of the sample into an inductively coupled plasma atomic emission spectrometer. Nakahara and Wasa followed a similar separation procedure prior to the analysis of low-alloy steels for trace amounts of tin by conventional source AFS and achieved a detection limit of 1.2 ng. In both cases, hydride generation increased the sample introduction efficiency and reduced the severity of matrix interferences. Del Monte Tamba and Luper developed ETAAS methods for the determination of tin in steels that eliminated the need for separation steps. Ratcliffe et al. reported detection limits of 800 pg. ETAAS, coupled with either dissolution or direct solid sampling, has been the most frequently employed technique for the determination of tin in nickel-based alloys. The use of solid certified reference materials has been demonstrated for the determination of antimony, arsenic, bismuth, cadmium, indium, lead, selenium, silver, tellurium, thallium and zinc in nickel-based alloys by ETAAS with direct solid sampling. Relative standard deviations were between 6 and 15%, and detection limits were in the sub-μg g⁻¹ region. Marks et al. used ETAAS with solid sampling to determine tin in nickel-based alloys. Calibration was based on solid standards, and a detection limit of 0.3 μg g⁻¹ was obtained. Complete atomization of tin from the alloys was not achieved, and a poor relative standard deviation of 25% resulted.

The work presented here was a continuation of an evaluation in the authors’ laboratory, of electrothermal laser-excited atomic fluorescence spectrometry (ET-LEAFS) in a graphite furnace as a sensitive and selective technique for the analysis of nickel-based alloys for a variety of elements. The high sensitivity of ET-LEAFS, compared with many other techniques, allows not only more sensitive analyses, but also analyses that are easier to develop and use because of the low incidence of spectral and matrix interferences. ET-LEAFS uses the same technology as ETAAS, except for the laser, but has been demonstrated to have detection limits 1-4 orders of magnitude better than ETAAS, and a linear dynamic range up to four orders of magnitude longer than ETAAS. ET-LEAFS has been shown to be effective for the determination of thallium, lead, tellurium and phosphorus, but not antimony, in nickel-based alloys by direct solid sample analysis with aqueous calibration, while all these elements could be determined by aqueous calibration if the samples were first dissolved. Also, it has been found that nickel alloy residue in the graphite tube acts as a permanent chemical modifier for methods that use either dissolution or solid sampling for both ETAAS and ET-LEAFS, while a chemical modifier is unnecessary for aqueous calibration standards if the graphite tube is pre-treated with nickel or melted alloy.

Here, the determination of tin in nickel-based alloys by use of ET-LEAFS is reported, and the accuracy of the analyses was verified by use of ETAAS. In addition, two non-furnace methods, ICP-MS and GDMS, were used to corroborate the accuracy of the results. Three different dissolution methods, and the role of nickel as a permanent chemical modifier for the furnace methods, were studied. Solid sampling was attempted but was not successful.
EXPERIMENTAL

ETAAS

The instrumentation included a Perkin-Elmer 430ZI Zeeman atomic absorption spectrometer (Perkin-Elmer, Norwalk, CT, USA), equipped with a transversely heated graphite atomizer (THGA) and an AS-70 autosampler. A Perkin-Elmer DEC 425c computer station (Digital Equipment, Maynard, MA, USA), equipped with GEM-BASED PEALAB. Version 7.3 software (Perkin-Elmer), was used for data acquisition. A tin hollow cathode lamp (Perkin-Elmer, Part No. 303-6274) was operated at 50 mA. Pyrolytically coated, transversely heated, graphite furnaces were used with L'vov platforms. Integrated absorbance signals were measured at 286.8 nm with the monochromator spectral band-width set at 0.7 nm.

ET-LEAFS

The ET-LEAFS instrumentation has been described previously.16 An excimer laser operated with xenon chloride at a wavelength of 308 nm was used to pump a tunable dye laser. A repetition rate of 500 Hz was used for all real sample analyses. Rhodamine 575 [(6-ethylamino-3-ethylimino-2,7-dimethyl-3H-xanthen-9-y1)] benzoic acid (Exciton, Dayton, OH, USA) was used as the laser dye in concentrations of 0.91 and 0.30 g l\(^{-1}\) in the oscillator and amplifier dye cells, respectively. The laser was frequency-doubled by the use of a KDP-B second harmonic generation crystal. The energy of the laser beam was measured to be 2–3 \(\mu\)J after it exited from the furnace. A beam expander was used to increase the diameter of the beam to 2–3 mm before passage through a hole in a plane mirror situated at an angle of 45° with respect to the tube furnace. The resulting fluorescence was collected at an angle of 180° onto the same mirror, and focused by a lens onto the slit of a monochromator and into the detection system. The detection system included an end-on, 2 in diameter, photomultiplier tube, a preamplifier based on the peak areas produced from 20 \(\mu\)l aliquots of standard or sample solutions followed by subtraction of the blank. Direct solid sample analysis was performed by the introduction of a solid chip, with a mass between 0.1 and 50 mg, directly onto the L'vov platform. Solid sampling was conducted without a dry or char step, and quantification of the analyte was achieved through aqueous calibration.

ICP-MS

In order to corroborate the results obtained by the electrother-.

Slavin17 reported that the ETAAS characteristic mass of tin is 20 pg and the detection limit is likely to be slightly lower. The ET-LEAFS detection limit for tin has been determined by Wei et al.10 to be 30 fg. For the dissolution of 100 mg of nickel alloy into 100 ml of aqueous solution, the effective detection limit in the original alloy sample was calculated to be 1.5 ng g\(^{-1}\). Nevertheless, the concentrations of tin in the P&W samples used here were at least two orders of magnitude higher than the ET-LEAFS detection limits. Hence, sensitivity was not an important issue in these analyses. It can be seen, from Table 1, that the detection limit for tin by LEAFS was at least two orders of magnitude better than ETAAS, and about the same as ICP-MS. The detection limit for solid sampling ETAAS (ref. 10) was based on rigorous measurements in real sample analysis while the ETAAS measurement in this work was calculated based on aqueous standards. Compared with the solid sampling ETAAS method, the dissolution ETAAS method had poorer sensitivity owing to dilution of the analyte. The detection limits of ET-LEAFS and ICP-MS in this work were also calculated based on aqueous standards. ET-LEAFS has so few spectral interferences that the detection

<table>
<thead>
<tr>
<th>Instrumental conditions for ICP-MS</th>
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<tbody>
<tr>
<td>Ag power</td>
</tr>
<tr>
<td>Nebulizer gas flow rate</td>
</tr>
<tr>
<td>Solution uptake rate</td>
</tr>
<tr>
<td>Resolution</td>
</tr>
<tr>
<td>Sweeps/readings</td>
</tr>
<tr>
<td>Readings/replicates</td>
</tr>
<tr>
<td>Replicates</td>
</tr>
<tr>
<td>Dwell time per U</td>
</tr>
<tr>
<td>Integration time per U</td>
</tr>
<tr>
<td>Internal standard</td>
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<tr>
<td>Analyte</td>
</tr>
</tbody>
</table>

Reagents

All standards and samples were prepared in a Class 100 (US Federal 209b) clean air hood and on a Class 100 clean bench. De-ionized water was used for preparation of all standards and samples. All glassware and plasticware were soaked in 20% nitric acid for 24 h and then rinsed with de-ionized water. A stock solution of 1000 ppm tin in 5% hydrochloric acid and 5% nitric acid was prepared by the dissolution of 1.000 g of high-purity tin powder (HiPurge grade, Spex Industries, Metuchen, NJ, USA) in the minimum amount of concentrated hydrochloric acid (reagent grade, Baker, Jackson, TN, USA) followed by dilution to 1 l with 5% hydrochloric and 5% nitric acid (reagent grade, Baker). The stock solution was diluted with 1% ultrapure nitric acid served as the blank.

Sample Preparation

Three dissolution methods were investigated for the preparation of the Pratt & Whitney (P&W) nickel-based alloys (Pratt & Whitney Aircraft, East Hartford, CT, USA). In each of the three cases 100.0 mg of alloy were weighed into a Teflon beaker, to which were added 2 ml of water and 2 ml of ultrapure nitric acid. In the first method, a 1% solution of ultrapure nitric acid served as the blank.
Role of Nickel in the Char and Atomization Temperature

RESULTS AND DISCUSSION

Optical Saturation

Plots of the relative fluorescence signal versus laser pulse energy were constructed in order to determine the laser energy needed to ensure optical saturation with the greatest signal-to-noise ratio. Optical saturation is considered to be complete when such a curve reaches a plateau. For tin, the point of intersection between the linear behavior and the saturation plateau was found to be approximately 2 μJ. The saturation curves obtained for tin contained in a standard solution and in a P&W nickel alloy sample were similar, which demonstrated that the presence of nickel did not appear to affect the laser energy required for saturation.

RESULTS AND DISCUSSION

Role of Nickel in the Char and Atomization Temperature

Optimization

The optimization of the char step, or thermal pre-treatment, was investigated for three cases: a standard tin solution, with and without a chemical modifier, atomized from a graphite platform; a standard solution of tin, without chemical modification, atomized from a tantalum platform; and tin contained in a dissolved P&W nickel alloy atomized from a graphite platform. The integrated absorbances versus the char temperatures (°C) were plotted as shown in Fig. 1.

For the standard tin solution atomized from a fresh graphite platform without chemical modification, a maximum char temperature of 1000 °C could be used without loss of signal. The addition of a conventional chemical modifier, a mixture of palladium and magnesium nitrate, caused a decrease in signal by approximately 40% but increased the optimum char temperature to 1600 °C. For tin atomized from a solution of dissolved P&W nickel alloy, a maximum char temperature of 1600 °C could be used without a significant loss of signal. It was found that chemical modification was not necessary since the nickel within the alloy stabilized the analyte at higher char temperatures and did not change the magnitude of the absorbance signal. Signal enhancement through the use of a tantalum platform was also investigated since these platforms have been shown to improve the absorbance profiles for many elements by preventing reduction of the analyte by carbon. In this study, tin atomized from a tantalum platform without chemical modification displayed a maximum signal between 200 and 1000 °C that was 30% lower than that for tin atomized from a graphite platform without chemical modification.

Optimization of the atomization temperature was performed in an analogous fashion to the char temperature, and similar results were obtained. Plots of relative absorbance (A4) versus atomization temperature (°C) for the same solutions discussed above were plotted as shown in Fig. 2. Tin atomized from a graphite platform without chemical modification produced a maximum signal between 2100 and 2500 °C. The addition of palladium and magnesium nitrate decreased the signal intensity by approximately two-thirds and delayed the atomization of tin. The maximum signal was not obtained until the furnace reached a temperature of 2400 °C. This delay was consistent with XTPF technology since the presence of the chemical modifier stabilized the analyte at higher temperatures. From Fig. 2, it can be seen that tin in nickel alloy generated a signal that was double the size of that of an aqueous tin solution without chemical modifier over a wide atomization temperature range (from 1900 to 2500 °C). In the experiment, fresh graphite tubes were used when the chemical modifiers were changed, in order to eliminate any possible influence from the previous chemical modifier or nickel alloy in the old graphite tubes. The results obtained for the optimization of the char and atomization temperatures demonstrated that quantitative analyses could be carried out in a graphite furnace without chemical modification by taking advantage of the nickel in the samples. The heating programme used for the real sample analyses is shown in Table 3.

For the standard tin solution, the concentration of nickel was about five orders of magnitude higher than that of the tin in the alloy samples, which

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**Table 2** Comparison of the detection limits of tin by various methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Sample</th>
<th>Detection limit ng g⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ET-LEAFS</td>
<td>Nickel alloy</td>
<td>1.5*</td>
<td>This work</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Nickel alloy</td>
<td>1†</td>
<td>This work</td>
</tr>
<tr>
<td>ETAAS</td>
<td>Nickel alloy 300°C</td>
<td>10*</td>
<td>This work</td>
</tr>
<tr>
<td>ETAAS</td>
<td>Nickel alloy 1000°C</td>
<td>This work</td>
<td></td>
</tr>
</tbody>
</table>

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* 100 mg of nickel alloy in 100 ml solution. Volume used, 20 μl.
† 1 g of nickel alloy in 200 ml solution. Volume used, 20 μl.
‡ 1 mg nickel alloy chip was used for solid sampling.

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Fig. 1 ETAAS char temperature optimization for 1 ng of tin atomized from a graphite platform without chemical modification (A), from a graphite platform with a Pd-Mg(NO₃)₂ chemical modifier (B), from a tantalum platform without chemical modification (C), and from a standard tin solution (D). The heating program used for the real sample analyses is shown in Table 3.

Fig. 2 ETAAS atomization temperature for 500 pg of tin atomized from a graphite platform without chemical modification (A), from a graphite platform with a Pd-Mg(NO₃)₂ chemical modifier (B), from a tantalum platform without chemical modification (C), and from a standard tin solution (D).
Table 3 Furnace heating programme for determination of tin in nickel alloys by ETAAS and ET-LEAFS

<table>
<thead>
<tr>
<th>Step</th>
<th>Parameter</th>
<th>Temperature/°C</th>
<th>Ramp/s</th>
<th>Hold/s</th>
<th>Internal Ar flow rate/ml min−1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>200</td>
<td>1</td>
<td>30</td>
<td>300</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>800</td>
<td>1</td>
<td>20</td>
<td>300</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>2000</td>
<td>1</td>
<td>10</td>
<td>300</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>2300</td>
<td>1</td>
<td>5</td>
<td>300</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>2650</td>
<td>1</td>
<td>5</td>
<td>300</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>2000</td>
<td>1</td>
<td>10</td>
<td>300</td>
</tr>
</tbody>
</table>

* Maximum power heating rate (approximately 1500 °C s−1).

meant that a large amount of nickel was injected onto the graphite platform to form the permanent chemical modifier during the analyses. In order to maintain similar chemical modifier conditions during calibration, a nickel pre-treated graphite platform was used for the construction of the aqueous tin calibration graphs. The same chemical modification phenomena were observed by Irwin and co-workers11,13,15 who successfully determined the concentrations of thallium, bismuth, selenium, antimony and lead in nickel-based alloys by LEAFS and ETAAS by use of nickel as a built-in chemical modifier.

Excitation Spectrum and Background Signals in ET-LEAFS

One of the advantages of ET-LEAFS is its relative freedom from spectral interferences due to the narrow laser line width of typically 3 pm. To confirm the lack of spectral interferences, the dye laser was systematically tuned through the wavelength region of the tin excitation line. The fluorescence signal from separate furnace firings was measured at each excitation wavelength. The resulting excitation spectra (Fig. 3) were obtained for both an aqueous tin standard and a dissolved P&W alloy solution. No spectral backgrounds were observed in the excitation spectrum for the standard tin solution as shown in Fig. 3. The excitation spectrum obtained for the nickel-based alloy revealed the presence of only tin and another element with a fluorescence transition at a wavelength 70 pm longer than that of tin. This second element was determined to be cobalt by reference to the MIT Wavelength Tables.25 Experimental confirmation was achieved by the addition of cobalt to the alloy solution, which caused an increase in the signal intensity of the second element. Cobalt did not interfere with the determination of tin since the two transitions were well resolved.

Solid Sampling

Solid sampling of the P&W nickel-based alloys with aqueous calibration was attempted. The results demonstrated that quantitative analysis was not feasible owing to a poor recovery, which resulted from incomplete atomization. Optimization of the atomization temperature for solid sampling revealed that only 1% of the tin present in the alloy was vaporized at the maximum atomization temperature of 2650 °C. The lack of success of this approach for solid sampling for the determination of tin was similar to a previous attempt to determine antimony36 by solid sampling, but in contrast to thallium and lead,11 phosphorus12 and tellurium,13 which were successfully determined in nickel alloys by direct solid sampling and aqueous calibration. Marks et al.10 were more successful at quantifying tin in nickel-based alloys by direct solid sample analysis. The alloys tested (modified B-1900) were prepared by means of a melt procedure conducted at 2700 °C, which involved the addition of known amounts of tin to the alloy. A change in the characteristics of the alloy due to the melt procedure may have aided the atomization of tin. Furthermore, the calibration was performed with solid nickel-based alloy standards prepared in their laboratory by the same melt procedure.

Comparison of Dissolution Methods

Different combinations of oxidizing and non-oxidizing acids were investigated in order to find one that would completely dissolve the alloy and not affect the tin absorbance signal. The results obtained for the determination of tin by different dissolution methods, for the P&W 2A alloy, are shown in Table 4. The values represent the average and standard deviation of 4–7 trials for ETAAS and ET-LEAFS with aqueous calibration and standard additions. Three pairs of Student’s multiple-t-tests were carried out between all pairs of the three dissolution methods; the statistical results showed no significant difference among the three dissolution methods. However, a mixture of nitric, hydrochloric and hydrofluoric acids proved to be the most efficient dissolution method, as the solid alloy was completely dissolved in this acid mixture in less than 10 min. Therefore, this acid mixture was used to dissolve all of the nickel alloy samples in the experiment.

Table 4 Comparison of dissolution methods for the determination of tin (μg g−1) in P&W 2A alloy by the aqueous calibration and standard additions methods for ET-LEAFS and ETAAS*.

<table>
<thead>
<tr>
<th>Dissolution method</th>
<th>Aqueous calibration</th>
<th>Standard additions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ET-LEAFS</td>
<td>ETAAS</td>
</tr>
<tr>
<td>HNO3–HCl</td>
<td>12.7±1.4(8)</td>
<td>14.7±1.1(3)</td>
</tr>
<tr>
<td>HNO3–HF</td>
<td>13.3±1.3(7)</td>
<td>13.2±1.2(3)</td>
</tr>
<tr>
<td>HNO3–HCl–HF</td>
<td>13.3±1.3(5)</td>
<td>13.1±1.2(3)</td>
</tr>
</tbody>
</table>

* Data expressed as mean ± one standard deviation. The number of replicates is given in parentheses.
† A reference value of 13 μg g−1 obtained from GDMS data was provided by Pratt & Whitney.
Determination of Tin in the Nickel-based Alloys

The concentrations of tin in the P&W 1A–4A nickel-based alloys were determined by ETAAS, ET-LEAFS and ICP-MS. The results are presented in Table 5. The GDMS results had been obtained previously by Pratt & Whitney Aircraft, and no standard deviations were available. Student’s t-tests were conducted among the results from the four analytical methods (ETAAS, ET-LEAFS, ICP-MS and GDMS) at the 95% confidence level. Student’s multiple sample t-test was used between all four methods in order to find any statistical differences. The multiple sample t-tests indicated that there was no statistical difference among ETAAS, ET-LEAFS and GDMS. Results from ICP-MS agreed with those from ETAAS and GDMS, but there was a statistical difference between ICP-MS and ET-LEAFS based on the multiple sample t-tests. From Table 5, it can be seen that the tin concentration of each of the four nickel alloy samples (1A–4A) determined by ICP-MS tended to have lower values than the ET-LEAFS results, which gave rise to the overall difference in the multiple t-tests. The reasons for the discrepancies are still not known.

Pared t-tests were carried out for each nickel alloy sample between all pairs of the above methods, for which more than 91% of the pairs agreed with each other statistically. Generally, the results from the four different analytical methods agreed with each other. Some inherent spectral interference in ICP-MS, a sample inhomogeneity in GDMS, or an unknown effect in the electrothermal techniques might have caused the discrepancies between a few of the results. While it may be worthwhile to track down some of the discrepancies, the relative error was not more than 18% for those few comparisons that failed the t-test.

Precision

From Table 5, it appears that the precision of the ET-LEAFS measurements was slightly worse for two or three of the samples than the precision of the other techniques. This may have been a result of poor pulse-to-pulse stability of the laser, which was typically about 12%. Some of this variation was averaged during the integration of the furnace pulses but may still have played a part in the precision of the analyses.

CONCLUSIONS

The ET-LEAFS method that was developed here was no more complicated than electrothermal atomic absorption methods and just as accurate. A significant feature of these analyses was that Zeeman-effect background correction, which is usually essential for atomic absorption analyses, was not necessary for the ET-LEAFS analyses. Indeed, the ability to tune the laser off-line allowed verification that there was no background that might have interfered with quantitative analysis. ET-LEAFS

Table 5 Determination of tin (µg g⁻¹) in P&W 1A–4A alloys by ET-LEAFS, ETAAS and ICP-MS

<table>
<thead>
<tr>
<th>Alloy</th>
<th>GDMS</th>
<th>ET-LEAFS</th>
<th>ETAAS</th>
<th>ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>P&amp;W 1A</td>
<td>6.7</td>
<td>6.8 (6.4%) (4)</td>
<td>6.8 (6.4%) (5)</td>
<td>6.8 (4.4%) (3)</td>
</tr>
<tr>
<td>P&amp;W 2A</td>
<td>13</td>
<td>12.9 (4%) (4)</td>
<td>13.3 (6.0%) (4)</td>
<td>12.4 (4.8%) (3)</td>
</tr>
<tr>
<td>P&amp;W 3A</td>
<td>21</td>
<td>22 (9.1%) (6)</td>
<td>21 (4.8%) (4)</td>
<td>21 (4.8%) (3)</td>
</tr>
<tr>
<td>P&amp;W 4A</td>
<td>4.6</td>
<td>5.0 (12%) (4)</td>
<td>4.8 (8.3%) (4)</td>
<td>4.2 (7.1%) (3)</td>
</tr>
</tbody>
</table>

* Data expressed as mean (relative standard deviation) (number of replicates)

REFERENCES


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