# The Determination of Trace Elements in Stainless Steel by Forked Platform GFAAS

## Application Note

Atomic Absorption

## Author

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## Introduction

The metallurgical behavior of stainless steel is affected not only by the concentration of major constituents but also by the presence of trace elements. The high sensitivity of the graphite furnace AAS technique makes it ideal for the analytical monitoring of trace elements. In this study three stainless steel samples were analyzed for seven elements utilizing forked platform atomization.

The approximate concentration of the major metal constituents of the stainless steel samples were: Fe -75%, Cr - 13%, Ni, - 8%, MO - 2%, and Al - 1%. Other elements at less than 0.1% included Si, Mn, P, W, V, Co, Cu, Ti, Sb, Pb, Sn, As, Ag, Se, Bi, Cd and Zn. Of particular interest were the very low concentrations (< 0.01%) of As, Se, Pb, Cd, Sb, Bi and Ag. These elements are relatively volatile. Their determination by graphite furnace technique can be subject to chemical and background interferences due to the high metal sample matrix. The very high iron matrix can cause spectral interference in the determination of some elements, particularly Se. Zeeman background correction eliminates this interference.

The graphite platform atomization technique minimizes chemical and background interferences. The graphite platform is placed in the graphite tube and sample atomization takes place from the platform rather than from the tube wall. The temperature of the platform lags behind the temperature of the tube wall and that of the gaseous environment. This temperature lag causes delayed sample vaporization and analyte atomization. This reduces chemical and background interferences, particularly in the determination of volatile elements.

This AA-at-Work describes the determination of As, Se, Pb, Cd, Sb, Bi and Ag in stainless steel utilizing a new forked platform design for the Agilent GTA graphite furnaces. The forked platform is installed into a partitioned style tube. The partitions are "notched" and the platform is designed to "catch" in the partition notches. This provides minimal physical contact between the platform and tube wall. Platform rotation is prevented during insertion of the tube into the graphite furnace. The tube and platform are shown in Figure 1. Advantages include simple positioning of the tube and platform within the furnace, easy alignment of the sample dispensing capillary tip (relative to the platform) and stability of the platform during operation. An evaluation of the forked platform has been reported in Agilent AA-at-Work number 99 [1].

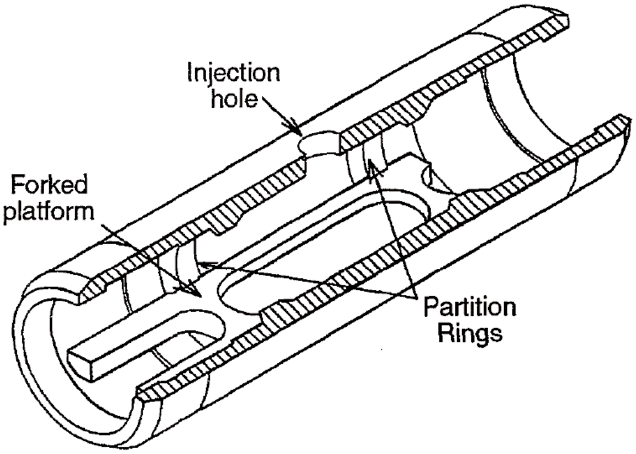

*Figure 1.*

## Methodology

For each sample solution, two grams of stainless steel shavings were dissolved in 25 mL 1:1 HCl/$HNO_3$, with gentle heating. After complete dissolution, the solutions were diluted to 200 mL with deionized water. This 1% solution was analyzed for As, Se, Pb, Cd, Sb, Bi and Ag by Zeeman graphite furnace AAS.

An Agilent SpectrAA-400 Zeeman Spectrometer Graphite Tube Atomizer and Programmable Sample Dispenser were used for this study. Table 1 lists the instrument operating parameters.

*Table 1. Instrument Operating Parameters*

| Element | Wavelength | SBW | Lamp current | Measurement mode |
|---|---|---|---|---|
| As | 193.7 | 0.5 | 8 | Peak area |
| Se | 196.0 | 1.0 | 10 | Peak height |
| Pb | 283.3 | 0.5 | 5 | Peak area |
| Cd | 228.8 | 0.5 | 4 | Peak area |
| Sb | 217.6 | 0.2 | 12 | Peak area |
| Bi | 223.1 | 0.2 | 10 | Peak area |
| Ag | 328.1 | 0.5 | 4 | Peak area |

Hollow cathode lamps were utilized. Peak area absorbance measurements were used for all element determinations except Se. The Se concentrations were very close to the detection limit and the precision of replicate signals was better by peak height measurement. The furnace parameters are summarized in Table 2.

*Table 2. Furnace Parameters*

| Element | Dry (all elements) | Ash 25 sec. | Atomize 2.7 sec. READ |
|---|---|---|---|
| As | | 1100 °C | 2700 °C |
| Se | | 900 °C | 2700 °C |
| Pb | Hot inject 130 °C | 700 °C | 2500 °C |
| Cd | Injection rate 5 | 700 °C | 2400 °C |
| Sb | Ramp to 350°/40 second | 800 °C | 2500 °C |
| Bi | Ramp to ash/20 second | 700 °C | 2500 °C |
| Ag | | 700 °C | 2400 °C |

Injection and dry parameters were the same for all elements. Maximum atomization ramp rate (2000 °C/sec) was used for all elements. The high metal matrix resulted in broadened peak profiles. Thus, atomization hold time and "read" was extended to 2.7 seconds to achieve complete peak area measurement.

Solutions of very high metal content cause considerable signal suppression in graphite furnace AAS. These interference effects can be minimized by the use of platform atomization and appropriate chemical modifiers. The modifier solutions used in this study are listed in Table 3.

*Table 3. Chemical Modifiers*

| **Element** | **Modifier** | **Modifier Volume - µL** |
|---|---|---|
| As | 1% $Mg\ (NO_3)_2$ | 4 |
| Se | 1% $Mg\ (NO_3)_2$ | 5 |
| Pb | 1% $H_3P\ O_4$ | 5 |
| Cd | 1% $H_3P\ O_4$ | 5 |
| Sb | 1% $Mg\ (NO_3)_2$ | 8 |
| Bi | 10% $H_2S\ O_4$ | 5 |
| Ag | – | – |

Volumes were optimized for maximum sensitivity. Nickel nitrate is a commonly used chemical modifier for As and Se determinations and it also delays Sb atomization. The sample solutions contained approximately 800 mg/L Ni. No additional nickel was added. A modifier of 1% $Mg(NO_3)_2$ improved sensitivity and precision for As, Se, and Sb. $Mg(NO_3)_2$ had no effect on the Bi signal. Ten per cent $H_2SO_4$ was found to improve sensitivity and precision for Bi.

One method of dealing with severe matrix interference effects is dilution of the sample. Rather than dilution, a reduction of the sample volume injected, minimized the severity of the matrix interferences. The sample volume and modifier volume were chosen to provide the optimum signal. Sample volumes ranged from 3 to 5 µL. It was found that sample volumes over 5 µL resulted in severe signal suppression. Standard additions calibration was used for all determinations.

# Results

Seven elements were determined in 3 stainless steel samples (0204M-TOP, 2298B-TOP, 2305B-TOP): the results are listed in Table 4.

*Table 4. Stainless Steel Analysis Results*

| **Element** | **0204M-Top** | **2298B-Top** | **2305B-Top** | **Estimated method detection limit** |
|---|---|---|---|---|
| **mg/L Analysis solution** | | | | |
| As | 161 | 173 | 189 | 3 |
| Se | <2 | 2 | 2 | 2 |
| Pb | 8 | 7 | 7 | 2 |
| Cd | <0.2 | <0.2 | <0.2 | 0.2 |
| Sb | 16 | 27 | 26 | 3 |
| Bi | 8 | 6 | 6 | 5 |
| Ag | 0.6 | 0.7 | 0.7 | 0.2 |
| **mg/g Solid stainless steel** | | | | |
| As | 16.1 | 17.3 | 18.9 | 0.3 |
| Se | <0.2 | 0.2 | 0.2 | 0.2 |
| Pb | 0.8 | 0.7 | 0.7 | 0.2 |
| Cd | <0.02 | <0.02 | <0.02 | 0.02 |
| Sb | 1.6 | 2.7 | 2.6 | 0.3 |
| Bi | 0.8 | 0.6 | 0.6 | 0.5 |
| Ag | 0.06 | 0.07 | 0.07 | 0.02 |

Results are reported two ways, µg/L in the dissolved samples solution and mg/g in the solid stainless steel. All results are the mean of two determinations. An estimated method detection limit is also shown. Se results on samples 2298B-TOP and 2305B-TOP were very close to the detection limit. For all elements detection limits were less than 0.5 µg/g in the solid stainless steel. The very sensitive elements, Cd and Ag, had detection limits less than 0.05 µg/g.

A standard additions calibration and signal graphics display for the determination of Sb in sample 2305B-TOP is shown in Figure 2. Calibrations for all elements determined are not included in this AA-at-Work. Sb is representative of the sensitivity and precision attainable in the analysis of stainless steel. Similarly, the determination of As in sample 2298B-TOP is shown in Figure 3.

| Sample | Conc ppb | %RSD | Mean ABS | Readings | | |
|---|---|---|---|---|---|---|
| Blank | 0 | | -0.001 | 0.000 | -0.001 | -0.001 |
| Addition 1 | 50 | 5.3 | 0.052 | 0.049 | 0.052 | 0.055 |
| Addition 2 | 100 | 1.5 | 0.090 | 0.091 | 0.089 | 0.091 |
| Addition 3 | 200 | 1.6 | 0.162 | 0.160 | 0.165 | 0.160 |
| 2305B-Top | 26 | 9.8 | 0.020 | 0.018 | 0.021 | 0.022 |

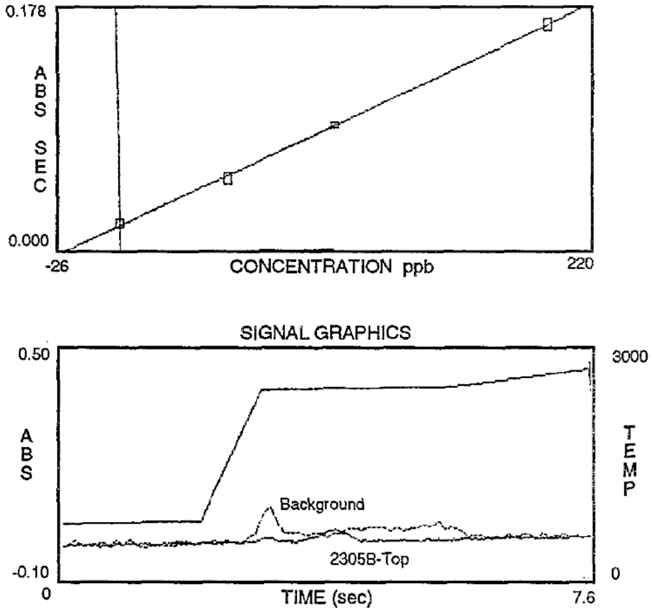

*Figure 2. Antimony calibration and signal graphics for sample 2305B-Top.*

| Sample | Conc ppb | %RSD | Mean ABS | Readings | | |
|---|---|---|---|---|---|---|
| Blank | 0 | | 0.003 | 0.007 | 0.004 | -0.001 |
| Addition 1 | 50 | 2.7 | 0.188 | 0.183 | 0.187 | 0.193 |
| Addition 2 | 100 | 2.6 | 0.230 | 0.226 | 0.237 | 0.228 |
| Addition 3 | 150 | 1.8 | 0.272 | 0.278 | 0.270 | 0.269 |
| 2298B-Top | 171 | 0.7 | 0.145 | 0.146 | 0.144 | 0.145 |

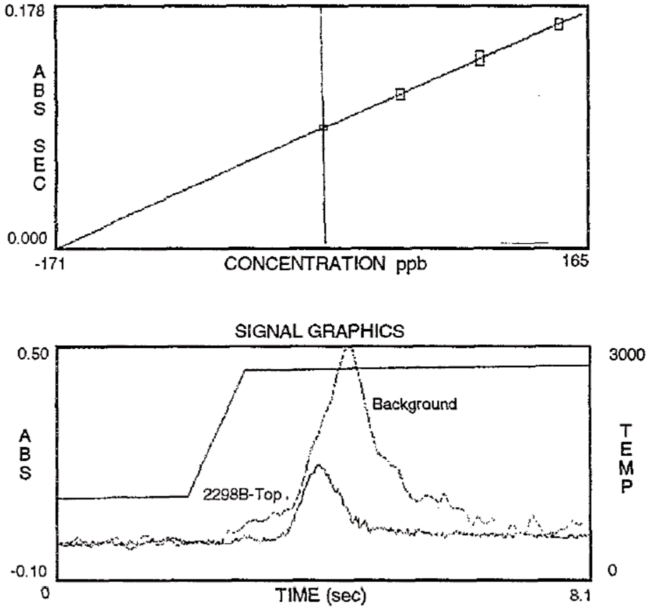

*Figure 3. Arsenic calibration and signal graphics for sample 2298B-Top.*

## Conclusion

Due to high sensitivity, graphite furnace AAS techniques are the most suitable method for the determination of trace elements in stainless steel. Zeeman background correction eliminates spectral interference problems associated with high Fe matrices. Platform atomization and the use of chemical modifiers minimize chemical interferences. In this work a newly designed forked platform was utilized. The platform was easily positioned within the graphite tube. Alignment of the tube in the furnace and positioning of the sample dispensing capillary were simple. The mechanical stability maintained during operation contributed to baseline stability and to excellent precision for these difficult samples.

## Acknowledgement

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## Reference

1. L. M. Beach, AA-at-Work number 99

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