# Direct Determination of As, Cu and Pb in Seawater by Zeeman Graphite Furnace Atomic Absorption Spectrometry

Application Note

Atomic Absorption

## Author

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## Introduction

Environmental pollution is becoming an increasingly important issue and receiving world wide attention. There is a great need to monitor our living environment and protect it from further deterioration. In particular, seawater analysis is important because the coastal region and oceans are at times being used as the dumping area for environmental wastes. Therefore, reliable analytical data for trace elements in seawater are required for environmental monitoring as well as for geochemical studies.

The normal concentrations of several trace elements in seawater are very low, near or slightly above the detection limit for graphite furnace AA [1]. In addition, seawater has a very high dissolved solids content, about 3.5% salts of which the sodium chloride content is typically about 80%. This matrix can cause substantial background and chemical interferences during the analysis. Hence, the quantitation of low analyte levels requires a very sensitive and accurate analytical technique. A method using Zeeman graphite furnace atomic absorption spectrometry (GFAAS) has been developed for the determination of trace elements (As, Cu, Pb) in seawater samples with the use of chemical modifiers.

Agilent Technologies

# Experimental

## Instrumental

An Agilent SpectrAA 400 Zeeman graphite furnace atomic absorption spectrometer with programmable sample dispenser was used. The instrument was equipped with an IBM PS/2 Model 30 computer.

The instrument operating parameters are listed below.

*Table 1. Instrument Operating Parameters*

| **Element** | **As** | **Cu** | **Pb** |
|---|---|---|---|
| Instrument mode | Absorbance | Absorbance | Absorbance |
| Calibration mode | Standard addition | Standard addition | Standard addition |
| Measurement mode | Peak height | Peak height | Peak height |
| Wavelength (nm) | 193.7 | 327.4 | 283.3 |
| Lamp current (mA) | 20 | 4 | 5 |
| Slit width (nm) | 0.2 | 0.5 | 0.5 |

## Sample Preparation

Seawater contains substantial amounts of dissolved solids and it was necessary to filter each sample through a 0.45 µm membrane filter. It was then acidifed to pH 2 with nitric acid and stored in a polyethylene bottle which had previously been cleaned [2].

# Analytical Method

The determination of As, Cu and Pb in seawater by Zeeman GFAAS was carried out directly on the sample solution.

## Determination of Arsenic

The determination of arsenic in seawater by Zeeman GFAAS required the use of a pyrolytic platform. A Super Lamp* was found to give better sensitivity than the normal hollow cathode lamp with this particular element. Matrix modification is necessary to stabilize the analyte and to reduce background levels. A 1000 mg/L nickel nitrate in 5% nitric acid solution was found to be the most efficient chemical modifier. For 5 µL of the sample, 5 µL of the $Ni(NO_3)_2$ modifier was added. Hot injection at 150 °C was employed in order to accelerate the drying process and to keep the total analysis time to a minimum. An ashing temperature of 1200 °C was used in conjunction with the platform atomization temperature of 2600 °C. A cool-down stage was included in the program to ensure the platform returned to a reproducible temperature between furnace firings. The furnace parameters and sampler parameters are listed in Table 2. The technique of multiple sample injection is recommended to improve the sensitivity and enhance the analyte signal. An addition signal of As in 5 µL of seawater is shown in Figure 1.

*Table 2. Furnace Parameters and Sampler Parameters for the Determination of Arsenic in Seawater (Platform Atomization)*

**Furnace parameters**

| **Step no.** | **Temperature (C)** | **Time (sec)** | **Gas flow (L/min)** | **Gas type** | **Read command** |
|---|---|---|---|---|---|
| 1 | 350 | 20.0 | 3.0 | Normal | No |
| 2 | 600 | 15.0 | 3.0 | Normal | No |
| 3 | 1250 | 10.0 | 3.0 | Normal | No |
| 4 | 1250 | 15.0 | 0.0 | Normal | No |
| 5 | 1250 | 2.0 | 0.0 | Normal | No |
| 6 | 2600 | 1.3 | 0.0 | Normal | Yes |
| 7 | 2600 | 2.7 | 0.0 | Normal | Yes |
| 8 | 2600 | 2.0 | 3.0 | Normal | No |
| 9 | 40 | 13.0 | 3.0 | Normal | No |

**Sample parameters**
**Volumes (µL)**

| | **Standard** | **Sample** | **Blank** | **Modifier** |
|---|---|---|---|---|
| Blank | – | – | 10 | 5 |
| Addition 1 | 2 | 5 | 3 | 5 |
| Addition 2 | 4 | 5 | 1 | 5 |
| Sample | – | 5 | 5 | 5 |
| Recalibration rate | 0 | | | |
| Multiple inject | No | | | |
| Hot inject | Yes | | | |
| Pre inject | No | | | |
| Temperature | 150 | | | |
| Inject rate | 7 | | | |

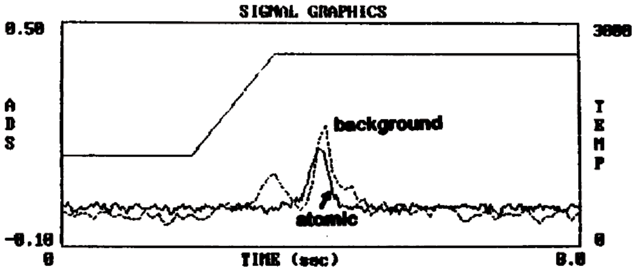

*Figure 1. Standard addition signal of 20 ng/mL in 5 µL of seawater sample.*

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* Super lamps have been superceded by Agilent UltrAA lamps, which are high intensity, boosted discharge hollow cathode lamps.

By increasing the spectral bandwidth (from 0.2 nm), the baseline noise level will be reduced even further than shown in Figure 1.

## Determination of Copper

Copper is an element for which platform atomization does not offer an advantage. The determination of copper in seawater was performed by wall atomization. Ammonium nitrate has been used as a chemical modifier in seawater analysis [3–6] in reducing sodium chloride interference by the formation of ammonium chloride and sodium nitrate which volatilizes at a lower temperature. In this work, a 2% w/v ammonium nitrate solution was used. Because ammonium nitrate contains Cu as a contaminant, a preliminary extraction of the modifier was necessary (see Appendix 1). For 5 µL of the sample, 20 µL of the $NH_4NO_3$ modifier was added. Correct drying of the seawater sample before ashing leads to a better signal, and a total drying time of 135 seconds was therefore employed. Ashing temperature was 1050 °C and the atomization temperature was 2350 °C. The furnace parameters and sampler parameters are listed in Table 3. An addition signal of Cu in 5 µL of seawater is shown in Figure 2. Multiple sample injection can also be employed to enhance the signal.

*Table 3. Furnace Parameters and Sampler Parameters for the Determination of Copper in Seawater (Wall Atomization)*

**Furnace parameters**

| Step no. | Temperature (C) | Time (sec) | Gas flow (L/min) | Gas type | Read command |
|---|---|---|---|---|---|
| 1 | 75 | 5.0 | 3.0 | Normal | No |
| 2 | 90 | 120.0 | 3.0 | Normal | No |
| 3 | 120 | 10.0 | 3.0 | Normal | No |
| 4 | 1050 | 10.0 | 3.0 | Normal | No |
| 5 | 1050 | 20.0 | 3.0 | Normal | No |
| 6 | 1050 | 2.0 | 0.0 | Normal | No |
| 7 | 2350 | 1.0 | 0.0 | Normal | Yes |
| 8 | 2350 | 2.0 | 0.0 | Normal | Yes |
| 9 | 2350 | 2.0 | 3.0 | Normal | No |

**Sample parameters**
**Volumes (µL)**

| | Standard | Sample | Blank | Modifier |
|---|---|---|---|---|
| Blank | – | – | 10 | 20 |
| Addition 1 | 2 | 5 | 3 | 20 |
| Addition 2 | 5 | 5 | | 20 |
| Sample | – | 5 | 5 | 20 |
| Recalibration rate | 0 | | | |
| Multiple inject | No | | | |
| Hot inject | No | | | |
| Pre inject | No | | | |

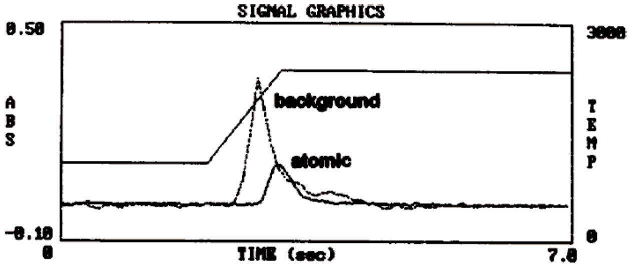

*Figure 2. Standard addition signal of 20 ng/mL Cu in 5 µL of seawater sample.*

## Determination of Lead

The determination of lead in seawater by Zeeman GFAAS was performed with a pyrolytic platform. A 2% w/v ammonium oxalate solution was used as a matrix modifier. Ammonium oxalate is an organic chemical modifier which was found to be efficient for high salt matrix samples in decreasing chloride interferences by forming ammonium chloride [5]. The ammonium oxalate contains Pb as a contaminant, therefore a preliminary extraction of the modifier was necessary (see Appendix 1). The use of ammonium oxalate required a lower ashing temperature, an ashing temperature of 500 °C was used. For 5 µL of the sample, 20 µL of the modifier was added. Hot injection at 150 °C assisted in minimizing the drying time. The platform atomization temperature was 2100 °C. The furnace parameters and sampler parameters are listed in Table 4. An addition signal of Pb in 5 µL of seawater is shown in Figure 3. A typical analytical signal is shown in Figure 4. The technique of multiple sample injection is recommended in order to measure very low levels.

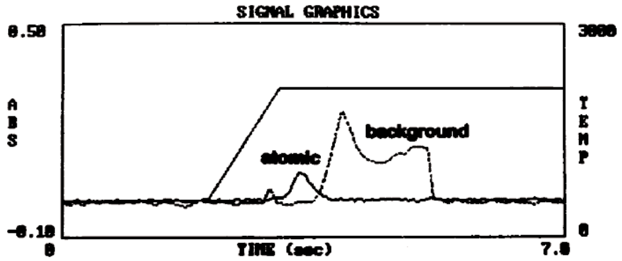

*Figure 3. Standard addition signal of 20 ng/mL Pb in 5 µL of seawater sample.*

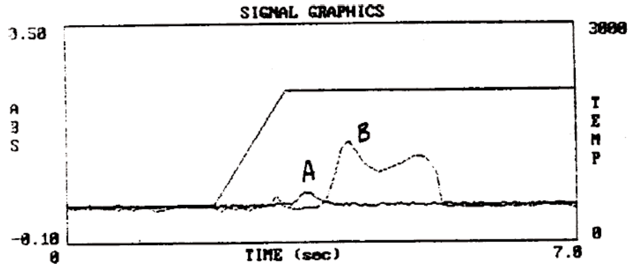

*Figure 4. Lead in seawater - typical analytical signal. A. The corrected signal. B. The background signal.*

*Table 4. Furnace Parameters and Sampler Parameters for the Determination of Lead in Seawater. (Platform Atomization)*

**Furnace parameters**

| Step no. | Temperature (C) | Time (sec) | Gas flow (L/min) | Gas type | Read command |
|---|---|---|---|---|---|
| 1 | 300 | 30.0 | 3.0 | Normal | No |
| 2 | 300 | 60.0 | 3.0 | Normal | No |
| 3 | 500 | 10.0 | 3.0 | Normal | No |
| 4 | 500 | 0.0 | 3.0 | Normal | No |
| 5 | 500 | 2.0 | 0.0 | Normal | No |
| 6 | 2100 | 1.0 | 0.0 | Normal | No |
| 7 | 2100 | 2.0 | 0.0 | Normal | Yes |
| 8 | 2100 | 2.0 | 3.0 | Normal | No |
| 9 | 40 | 12.0 | 3.0 | Normal | No |

**Sample parameters**
**Volumes (µL)**

| | Standard | Sample | Blank | Modifier |
|---|---|---|---|---|
| Blank | – | – | 10 | 20 |
| Addition 1 | 2 | 5 | 3 | 20 |
| Addition 2 | 5 | 5 | | 20 |
| Sample | – | 5 | 5 | 20 |
| Recalibration rate | 0 | | | |
| Multiple inject | No | | | |
| Hot inject | Yes | | | |
| Pre inject | No | | | |
| Temperature | 150 | | | |
| Inject rate | 7 | | | |

## Results

A standard addition method was employed for the calibration. Typical results for the analysis of seawater samples are listed in Table 5.

*Table 5. Typical Results of Seawater Analysis*

| Element | Concentration (ng/mL) | Characteristic mass (pg) |
|---|---|---|
| Arsenic | 0.15 | 10 |
| Copper | 0.21 | 4 |
| Lead | 3.50 | 5.5 |

## Conclusion

Arsenic, copper and lead in seawater have been determined by Zeeman GFAAS. Arsenic and lead required the use of the pyrolytic platform, whereas copper can be determined using wall atomization. The use of a chemical modifier is necessary. Multiple sample injections are recommended for better sensitivity and to enhance the analyte signal.

## References

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3. R. D. Ediger, G. E. Peterson, J. D. Kerber, At. Absorption Newsl., 13, 61 (1974).
4. W. Slavin, The determination of trace metals in seawater, At. Spectrosc., 1, 66-71 (1980).
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## Appendix 1

### Ammonium Nitrate and Ammonium Oxalate Modifier Preparation

Prepare a solution of 2 g of $NH_4NO_3$ or 2 g of ammonium oxalate in 100 mL of deionized distilled water.

Dissolve 1.5 g of ammonium pyrolidine dithiocarbamate (APDC) in 100 mL of deionized distilled water and filter through a Whatman 541 filter paper into a flask, then stopper. Add 5 mL of the filtered APDC solution to a 2% ammonium nitrate solution or 2% ammonium oxalate solution with 30 mL of di-isobutylketone (DIBK) and shake vigorously for three minutes in a separation funnel. Leave to stand to permit separation of the phases. Remove the lower aqueous phase and discard the organic layer. The extraction is repeated twice more. The ammonium nitrate or ammonium oxalate is then ready for use as a modifier. Store the purified reagent in a clean polyethylene container.

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