

# Graphite Tube Atomizer Performance — ASTM Graphite Furnace Round Robin for Water

# **Application Note**

**Atomic Absorption** 

#### **Authors**

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#### Introduction

With the increasing awareness of the significance of many metals at ultratrace as well as toxicological levels, there is a continuing need for improvement of existing methods for determining those elements. For a large number of elements, graphite furnace techniques are more sensitive than flame methods, and concentrations typically one hundred times lower than those possible by flame can be determined. Sample volumes in the microlitre range can normally be analyzed and the preparation of samples may be relatively simple.

Analysts over the last decade have increasingly used graphite furnace atomizers to allow them to determine metals in the  $\mu g/L$  and sub- $\mu g/L$  range. Federal and state regulatory agencies, for example, the EPA, have approved furnace methods for the determination of many metals [1]. However, furnace techniques are not troublefree and may require procedures such as matrix modification of the sample and calibration by the method of standard additions.

Recently, the American Society of Testing and Materials (ASTM) conducted a graphite furnace round robin for fourteen metals in water samples. The purpose of this round robin was to determine whether graphite furnace techniques could be included as ASTM standard methods for the determination of these metals in water

Twenty-one labs around the US, including Agilent's Atomic Absorption Resource Center (AARC) in Park Ridge, IL, participated in the round robin. However, all labs did not submit data for all fourteen elements. Concentrated unknowns were supplied to each lab by ASTM. Instructions for sample preparation including specific dilution factors to be used were provided with the unknowns.

Three different concentration levels ( $\mu g/L$ ) for the elements of interest were supplied along with a quality control check sample containing known concentrations of the elements of interest. The unknown levels were prepared and diluted once in



distilled water and once in a lab water of choice producing seven different solutions to be analyzed for each of the fourteen elements. Lab tap water was chosen as the AARC's water of choice.

This application note presents the performance of Agilent's GTA 95 Graphite Tube Atomizer with programmable sample dispenser in the ASTM round robin. AAWC values are compared to ranges and means of values reported by all participants

#### Instrumentation

Two separate furnace systems were used by the AARC for the ASTM round robin. The first was an Agilent 975 AA and GTA 95 with programmable sample dispenser. The second was an Agilent AA-875 and GTA 95 with sample dispenser.

The GTA 95 with sampler embodies computerized furnace control and sample handling in a totally integrated system. A video display guides the operator in setting up a program, displays the current status of the sampling and atomization process, and graphically superimposes the atomization signal over the temperature vs time profile. The sampler can automatically generate up to five standards from a single stock standard solution, prepare a range of standard addition solutions on every sample, and add a chemical modifier when required. This capability not only saves time but also leads to more accurate answers as dilution and contamination errors are virtually eliminated.

Normally, for each participating lab in a round robin, the unknowns are analyzed by two different operators on three different days and average results are submitted. Due to time considerations, the results reported by the AARC were based on a single analysis. The fourteen elements were divided between two operators on the two GTA 95 systems. Thus, AARC results should be indicative of results attainable in a routine lab environment. Also, all calibration and addition of matrix modifiers was accomplished utilizing the automatic capabilities of the GTA 95 system.

#### **Instrument and GTA 95 Parameters**

Standard recommended parameters for the most sensitive resonance line for each element were used. Hollow cathode lamps were used for all analyses.

Table 1 presents a list of the fourteen elements included in the round robin along with Ash and Atomize temperatures used for each. Dry steps were the same for all elements:

- Ramp Ambient to 75 °C in 5 seconds
- Ramp 75 °C to 120 °C in 45 seconds

Ash steps involved a Ramp of 1 to 5 seconds and a hold of 4 or 5 seconds. Atomize steps involved a Ramp of 0.6 to 3 seconds and a hold of 1 to 4 seconds.

Programmed sample volumes ranged from 3  $\mu$ L to 60  $\mu$ L depending upon element sensitivities and concentration of unknowns. In most cases 10  $\mu$ L sample volumes were used. Matrix modification was performed for As and Se. Standard additions calibration was utilized for Ba and Pb in the water of choice.

Table 1. ASTM Round Robin

Element	Ash (°C)	Atomize (°C)	
Al	1300	2600	
As*	1000	2500	
Be	1100	2300	
Cd	300	1800	
Cr	1300	2500	
Co	900	2300	
Cu	900	2300	
Fe	800	2300	
Pb	400	2000	
Mn	700	2400	
NI	700	700 2400	
Se*	700	2400	
V	1500	2600	
Ba	500	2500	

<sup>\*</sup>Matrix modification

#### Results

The following results are based on values reported to ASTM by the participating labs. Mean values and standard deviations were calculated using all data reported. Values for "All Labs" included those reported by AARC.

Standard deviation ( $\sigma$ ) and relative standard deviation (RSD) were calculated as follows:

1. 
$$\sigma = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}}$$

$$x = \text{individual value}$$

$$\bar{x} = \text{mean value}$$

$$n = \text{number of individual values}$$
2. 
$$RSD = \frac{\sigma}{\bar{x}}$$

$$\bar{x} = \text{mean value}$$

## Copper

One of the elements for which quite scattered results were reported by participating labs was copper. Figure 1 shows the ranges reported (|-|) true values (■) and the values reported by AARC (•) for the seven samples. D, E, and F were the unknowns prepared with distilled water and D\*, E\*, and F\* were the unknowns prepared with lab water of choice. QC signifies the quality control check sample.

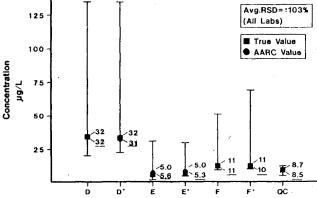


Figure 1. Copper.

The range of concentrations reported was quite large producing an average RSD of ± 103%. No significant difference between distilled water and lab water of choice was seen for Cu or the remaining thirteen elements. True values are shown along with AARC values (underlined). Concentrations shown are µg/L Cu. The correlation between AARC values and true values is excellent.

The average error in values reported by all labs for Cu (■) is shown in Figure 2. There is a definite positive bias in results indicating the possibility of contamination problems. Also shown is the error in values reported by AARC for Cu ( ) The average error of 1% for AARC indicates that contamination was not a problem with the GTA 95.

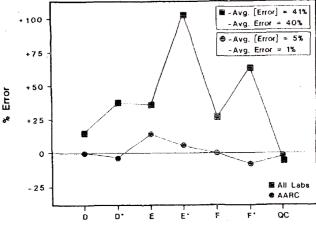


Figure 2. Copper.

#### **Nickel**

One of the elements for which more precise results were reported was nickel. Ranges reported (|-|) true values (■) and AARC values (●) are shown in Figure 3.

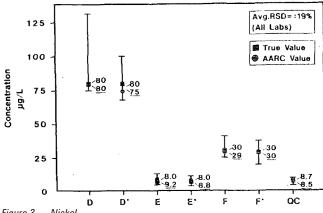


Figure 3. Nickel.

The range of concentrations reported produced an average RSD of  $\pm$  19%. As with copper, the correlation between AARC values (underlined) and true values for Ni is excellent.

The average error in values reported by all labs for Ni (■) is shown in Figure 4: No consistent bias is seen. The average error of 2% for values reported by AARC for Ni (●) is a factor of three (3) better than that for all labs.

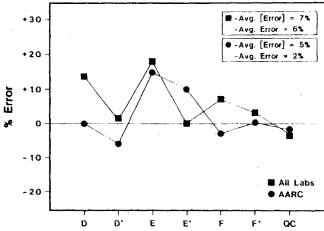


Figure 4. Nickel.

#### **All Elements**

Figure 5 presents condensed results for all fourteen elements determined in the ASTM round robin. Average absolute error ([error]) is shown for all labs (■) and for AARC (●). Data for all elements and all samples was used to calculate [error]. Again, significantly better results were produced by the GTA 95.

As part of EPA recommendations for a quality control program, values determined for quality control check samples and recovery or interference check determinations should fall within a window of  $\pm$  10% of the true value in order to be deemed acceptable. Figure 6 shows results reported for all elements and all samples as presented in Figure 5 with the  $\pm$  10% window of acceptance highlighted. The all lab data ( $\blacksquare$ ) indicates problems, positive bias for several elements, while AARC data ( $\blacksquare$ ) shows good acceptability for all elements.

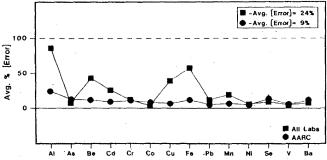


Figure 5. All samples..

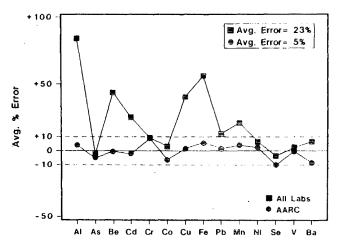


Figure 6. All samples.

As may have been noticed on Figures 1 and 3, the range of values reported for the QC check sample was smaller than ranges reported for unknowns. Figure 7 shows this graphically. This is to be expected since concentration levels for the QC sample were known to participants. However, reported results still show an average RSD of  $\pm$  20%, perhaps indicating incorrect use of the QC sample or inability of labs to accurately measure concentrations at the  $\mu g/L$  level.

Table 2 lists the elements determined in the QC check sample along with ranges reported by participating labs, average values reported, true values, and AARC values reported. Barium was not included in the QC sample. Values reported by AARC are in excellent agreement with the true value and

show significantly less error than the average values for all participating labs.

Table 2. ASTM Round Robin QC Check Sample (µg/L)

Element	Range	Average	True	AARC
Al	62–129	86	61	65
As	19–26	23	24	24
Be	24-37	27	24	25
Cd	5.2-8.3	6.6	6.5	6.6
Cr	3.0-6.9	4.7	4.4	4.6
Co	28-37	32	30	30
Cu	2.8-11	8.4	8.7	0.5
Fe	-1.4–26	15	16	16
Pb	26-42	31	30	30
Mn	6.4-10.6	7.9	7.9	8.1
Ni	5.7–11	8.4	8.7	8.5
Se	1–9	7.3	8.7	9.0
V	50-83	70	78	76
Ва	NA	NA	NA	NA

Values reported are plotted in Figure 8. Average reported values for AI, Be, and Se fall outside the  $\pm$  10% window of acceptance when all lab data ( $\blacksquare$ ) is plotted. AARC values ( $\bullet$ ) fall well within the acceptable range showing an average error of only 3%.

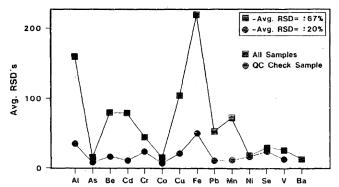


Figure 7. All labs.

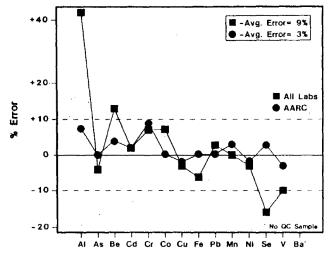


Figure 8. Q.C. check sample.

## **Conclusion**

The results presented for the ASTM graphite furnace round robin for water show that the GTA 95 with sampler can be used for the accurate determination of fourteen elements in water samples at the  $\mu g/L$  concentration level. Agilent's AARC values were overall significantly better than those reported by other participating labs. The GTA 95 with sampler offers automatic capabilities of standard and sample dilution, calibration, and matrix modification which save analyst time and also lead to more accurate answers as dilution and contamination errors are virtually eliminated.

#### References

1. US EPA, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 (1979).

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