Determination of Lead in Urine by GFAAS–Deuterium and Zeeman Background Correction

Application Note

Atomic Absorption

Authors

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Introduction

A growing number of children in the U.S. are testing positive for lead poisoning. The Centers for Disease Control (CDC), Atlanta, GA, have set specific guidelines for corrective action for various levels. Children with blood lead levels > 24 µg/dL who show symptoms of lead poisoning are treated with chelation therapy. There are many chelating agents commercially available today. The basic mechanism is the same for all of them – to form a stable lead compound which is then excreted in the urine. The urine is collected and analyzed for lead [1].

This study deals with the determination of lead in urine. The method is based on the work of Dr. Patrick J. Parsons, New York State Department of Health, Albany, NY[2]. Initially the procedure was created for the measurement of lead in blood, however, it is found to work extremely well for urine as well. The method permits these biological samples to be run against aqueous calibration standards.

Both Zeeman and Deuterium background correction was used. Methods include graphite furnace programs for platform atomization (forked platform tube) and wall atomization (partition tube).

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Experimental

Instrumentation

The instrumentation used for the determination of lead in urine was an Agilent SpectrAA-400Z with Zeeman background correction and an Agilent SpectrAA-400P with deuterium background correction. Each spectrometer was equipped with a Agilent GTA-96 graphite tube atomizer and PSD-96 programmable sample dispenser. Ultra high purity argon was used as the inert gas.

Reagents Required

Triton X-100

Ammonium diHydrogen Phosphate ($NH_4H_2PO_4$), a grade suitable for trace metal analysis.

Concentrated Nitric Acid (HNO_3), a grade suitable for trace metal analysis.

Reagent Preparation

- 10% Triton X-100 (v/v) – Pipet 10 mL of Triton X-100 into ~ 70 mL D.I. water. Stir for ~1 hour. The solution may need to be gently warmed or sonicated for complete dissolution. Make up to 100 mL. (Stable for 1 month.)
- 20% $NH_4H_2PO_4$ (w/v) – Dissolve 20 g of $NH_4H_2PO_4$ in ~ 75 mL D.I. water. Make up to 100 mL. (Stable for 6 months.)
- Working Modifier – To ~ 400 mL D.I. water add 25 mL 10% Triton X-100 solution, 5.0 mL 20% $NH_4H_2PO_4$ solution and 1.0 mL conc. HNO^3. Make up to 500 mL. (Stable for 3 weeks.)

If absorbance values start to degrade, make a fresh solution of working modifier as your first corrective action.

Standards Required

1000 µg/mL stock lead solution (Pb) - atomic absorption standards can be purchased from any major chemical supplier.

- 10 µg/mL intermediate Pb standard – Pipet 1.0 mL stock Pb standard and 2.0 mL conc. HNO3 into ~75 mL D.I. water in a 100 mL volumetric flask. Carefully make up to volume (100 mL).
- Calibration Standards – All prepared weekly in 2% v/v HNO_3. Final volumes are 100 mL, made in volumetric flasks utilizing glass pipettes.

  100 µg/L – Pipet 1.0 mL intermediate standard and dilute to 100 mL with 2% v/v HNO_3.

  200 µg/L – Pipet 2.0 mL intermediate standard and dilute to 100 mL with 2% v/v HNO_3.

  300 µg/L – Pipet 3.0 mL intermediate standard and dilute to 100 mL with 2% v/v HNO_3.

  400 µg/L – Pipet 4.0 mL intermediate standard and dilute to 100 mL with 2% v/v HNO_3.

  600 µg/L – Pipet 6.0 mL intermediate standard and dilute to 100 mL with 2% v/v HNO_3.

Urine Samples

Urine controls were purchased to be used as urine samples. Controls were prepared per included instructions. The urine was obtained from New York State Department of Health, Wadsworth Center Lead Poisoning Laboratory, Empire State Plaza, Albany, NY 12201-0509.

Working Standard and Sample Preparation

All calibration working standards and urine controls were prepared in the same manner. They should be prepared fresh daily. A glass 1.0 mL pipette (graduated in 100 µL increments) was used to add 900 µL of the working modifier to a 2.0 mL graphite furnace sample dispenser cup. Next, 100 µL of the urine control or calibration standard was added to the working modifier. The urine controls and standards were pipetted with a 100 µL micropipettor. All working solutions were carefully mixed with a transfer pipet to ensure homogeneity.

Results and Discussion

Table 1 lists the instrument parameters used for both Zeeman background correction and deuterium background correction systems. The measurement mode is dependent on the type of tube atomization used.

Table 1. Instrument Parameters

Instrument mode	Absorbance
Calibration mode	Concentration
Measurement mode	*
Lamp current (mA)	5.0
Slit width (nm)	0.5
Slit height	Normal
Wavelength(nm)	283.3
Sampler introduction	Sampler premix
Time constant (sec)	0.05
Replicates	2
Background correction	On

* Peak height was used for wall atomization and peak area was used for platform atomization.

The furnace parameters for the SpectrAA-400Z are given in Table 2 for platform atomization. Because analyte peaks are broad and asymmetrical with platform atomization, peak area is the measurement mode used. In Table 3 the parameters for wall atomization on the Zeeman system are presented.

Table 2 Forked Platform Tube - Zeeman Cyclic Program Time ~ 93 Secs

Step no.	Temp (°C)	Time (sec)	Gas flow (L/min)	Gas type	Read command
1	150	20.0	3.0	Normal	No
2	250	20.0	3.0	Normal	No
3	600	10.0	3.0	Normal	No
4	600	5.0	3.0	Normal	No
5	850	10.0	3.0	Normal	No
6	850	1.0	0.0	Normal	No
7	2300	1.5	0.0	Normal	Yes
8	2300	2.0	0.0	Normal	Yes
9	2500	6.0	3.0	Normal	No

Table 3 Partition Tube - Zeeman Cyclic Program Time ~ 78 Secs

Step no.	Temp (°c)	Time (sec)	Gas flow (L/min)	Gas type	Read command
1	95	20.0	3.0	Normal	No
2	130	15.0	3.0	Normal	No
3	350	7.0	3.0	Normal	No
4	650	5.0	3.0	Normal	No
5	650	4.0	3.0	Normal	No
6	650	1.0	0.0	Normal	No
7	2100	1.0	0.0	Normal	Yes
8	2100	2.0	0.0	Normal	Yes
9	2300	6.0	3.0	Normal	No

Analyte peaks from wall atomization are generally more symmetrical and the peak height is proportional to the concentration of analyte present. Therefore, peak height is used with wall atomization.

Table 4 gives the furnace parameters for the SpectrAA-400P for platform atomization. Table 5 gives the furnace parameters for wall atomization on the deuterium system. The (normal) inert gas type in all cases was ultra high purity argon.

Table 4 Forked Platform Tube - Deuterium Cyclic Program Time ~ 90 Secs

Step no.	Temp (°C)	Time (sec)	Gas flow (L/min)	Gas type	Read command
1	130	15.0	3.0	Normal	No
2	150	20.0	3.0	Normal	No
3	550	5.0	3.0	Normal	No
4	550	10.0	3.0	Normal	No
5	800	15.0	3.0	Normal	No
6	800	1.0	0.0	Normal	No
7	2200	1.3	0.0	Normal	Yes
8	2200	2.0	0.0	Normal	Yes
9	2400	3.0	3.0	Normal	No

Table 5 Partition Tube - Deuterium Cyclic Program Time ~ 76 Secs

Step no.	Temp (°c)	Time (sec)	Gas flow (L/min)	Gas type	Read command
1	95	20.0	3.0	Normal	No
2	130	15.0	3.0	Normal	No
3	450	7.0	3.0	Normal	No
4	600	5.0	3.0	Normal	No
5	600	4.0	3.0	Normal	No
6	600	1.0	0.0	Normal	No
7	2000	1.0	0.0	Normal	Yes
8	2000	2.0	0.0	Normal	Yes
9	2200	4.0	3.0	Normal	No

The solution volume injected was 12 mL and two replicate readings were taken for all solutions.

The rinse solution for the sample dispenser was 10% isopropyl alcohol in D.I. water with 3 drops of 10% Triton X-100 added. The capillary remained clean inside and outside. Carryover problems were non-existent.

Forked Platform Tube Atomization

Figure 1 illustrates a typical calibration curve andsample run for the SpectrAA-400Z with platform atomization. The absorbance values for the Zeeman and deuterium system were similar. Notice that thein run precision is very good for aqueous standards and urine samples. Each urine sample shown was individually prepared. Both systems showed in run precisions < 5%. The characteristic concentration was 1.5 µg/dL for the Zeeman system and 1.3 µg/dL for the deuterium system using peak area measurements.

Precision and accuracy of results were equivalent for both background correction systems. Results for platform atomization are presented in Table 6.

Table 6 Urine Control Results - Platform Atomization

Control sample DOH-NY	True (µg/dL)	Zeeman (µg/dL)	Deuterium (µg/dL)
Human urine	40 ± 6	42.0 ± 0.7	43.0 ± 0.6
Human urine	15 ± 5	15.0 ± 1.6	14.0 ± 1.7

It was observed that with a platform tube, and either background correction system, lead could be determined in urine and blood samples with the same furnace parameters. This is due to the fact that the platform (therefore, the sample) is not heated by the power applied to the tube but via heat transfer from the tube. Thus, differences in matrices are better handled.

Partition Tube Atomization

Figure 2 illustrates a typical calibration curve and sample run for the SpectrAA-400P with wall atomization. As with the platform tube, the absorbance values are similar for both background correction systems. Again each urine sample shown was individually prepared. The characteristic concentration with peak height measurement was 0.45 µg/dL on both systems.

The results obtained for wall atomization are compared on Table 7. Both systems produced accurate, precise results.

Table 7. Urine Control Results - Wall Atomization

Control sample DOH-NY	True (µg/dL)	Zeeman (µg/dL)	Deuterium (µg/dL)
Human urine	40 ± 6	43.0 ± 0.5	44.0 ± 0.4
Human urine	15 ± 5	13.0 ± 0.5	15.0 ± 0.7

It is not possible to run urine samples and blood samples against the same furnace parameters using wall atomization. Unlike the platform tube, the partition tube and sample are heated directly by the power supplied. Ashing and atomization temperatures are more matrix dependent with wall atomization.

Conclusion

The found values for the urine samples on the Zeeman and deuterium systems are both precise and accurate. Either platform tube atomization or partition tube (wall) atomization can be used. However, if the lead analysis is to be performed on both urine and blood, the platform tube may increase laboratory productivity.

References

1. "Preventing Lead Poisoning in Young Children", A Statement by the Centers for Disease Control, Atlanta, GA (October **1991**).
2. "Blood Lead Determination by Electrothermal Atomization Atomic Absorption Spectrometry", New York State Department of Health, Albany, NY (February **1991**).

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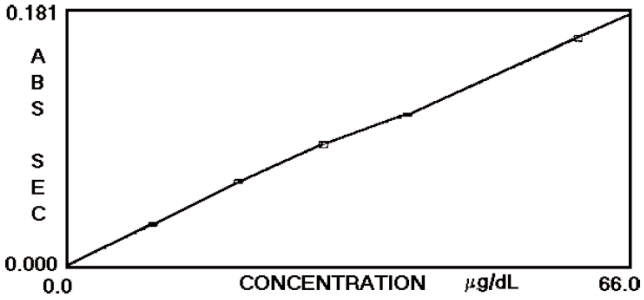
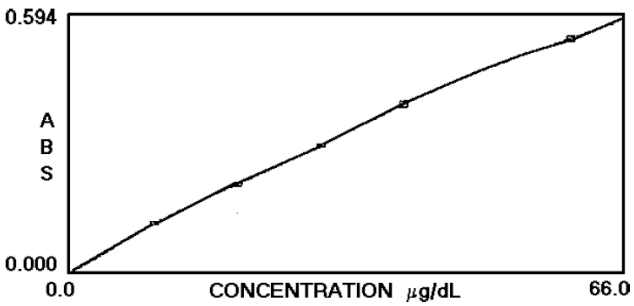
SAMPLE	CONC µg/dL	%RSD	MEAN ABS	READINGS	
BLANK	0.0	0.001	0.001	0.001	
STANDARD 1	10.0	0.9	0.029	0.030	0.029
STANDARD 2	20.0	0.1	0.060	0.060	0.060
STANDARD 3	30.0	0.6	0.087	0.087	0.086
STANDARD 4	40.0	0.1	0.109	0.109	0.109
STANDARD 5	60.0	0.3	0.165	0.165	0.164



40 µg/dL	43.3	0.6	0.118	0.118	0.119
15 µg/dL	13.0	0.3	0.039	0.038	0.039
15 µg/dL	16.4	0.4	0.049	0.049	0.049
15 µg/dL	13.2	1.7	0.039	0.039	0.040
15 µg/dL	16.3	0.9	0.049	0.049	0.048
40 µg/dL	42.3	0.2	0.115	0.115	0.115
15 µg/dL	13.2	0.4	0.039	0.039	0.039
15 µg/dL	16.0	0.8	0.048	0.048	0.048
15 µg/dL	13.2	0.8	0.039	0.039	0.039
40 µg/dL	44.3	3.5	0.121	0.124	0.118

Figure 1. Calibration for lead with platform atomization and typical sample analyses - Zeeman background correction.

SAMPLE	CONC µg/dL	%RSD	MEAN ABS	READINGS	
BLANK	0.0		0.020	0.020	0.021
STANDARD 1	10.0	0.5	0.113	0.113	0.113
STANDARD 2	20.0	0.2	0.203	0.203	0.203
STANDARD 3	30.0	0.1	0.293	0.292	0.293
STANDARD 4	40.0	1.1	0.388	0.392	0.385
STANDARD 5	60.0	0.4	0.540	0.542	0.539



40 µg/dL	43.4	0.6	0.418	0.420	0.416
15 µg/dL	15.2	0.6	0.162	0.163	0.161
15 µg/dL	14.3	1.6	0.154	0.153	0.156
15 µg/dL	15.8	3.4	0.168	0.164	0.172
15 µg/dL	14.3	0.2	0.154	0.154	0.155
40 µg/dL	43.0	0.5	0.415	0.417	0.414
15 µg/dL	15.3	0.5	0.163	0.164	0.162
15 µg/dL	15.7	2.4	0.167	0.169	0.164
15 µg/dL	14.6	2.3	0.157	0.159	0.154
40 µg/dL	43.5	0.1	0.419	0.418	0.419

Figure 2. Calibration for lead with wall atomization and typical sample analyses - deuterium background correction.

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