Determination of Lead in Seasoning Salts

Ben Hui and Steve Gradus, City of Milwaukee Health Department Laboratory, 841 North Broadway, Room 201, Milwaukee, WI 53202 USA

OBJECTIVE

The objective of this study was to use atomic absorption spectrometry to determine ppm of lead in seasoning salts produced in Mexico. Chloride in salt has been known to decrease the lead signal. Using a 5 step temperature program in graphite furnace atomic absorption with Zeeman background correction and calibration of ppb lead standards in 1% nitric acid, less than 1 ppm of lead in seasoning salts was determined in argon gas in one minute. A 2% ammonium dihydrogen phosphate was found to be a suitable matrix modifier. Nitric acid digested samples were measured directly or by standard addition method. In split samples, results compared favorably with a reference lab's ICP-MS data.

In July 2004, the City of Milwaukee Health Department (MHD) became aware of lead contamination of certain brands of seasoning salts, also used by children as candy. The MHD Lead Poisoning Prevention Program under guidance from the Commissioner of Health and input from the City Attorney, acted in response to this public health problem. The MHD Public Health Laboratory, with an environmental and blood lead program, validated a practical and relatively rapid assay to measure lead in a high salt content matrix. The laboratory's role contributed to the removal of suspect items from retail shelves in Milwaukee and a voluntary national recall of these products.

EXPERIMENTAL

1) Sampling and preparation

Thirteen plastic unopened bottles of seasoning salt, each weighing 25 grams were collected by the MHD lead inspectors from local grocery stores. Samples were analyzed in duplicate. Approximately 0.5 g of each seasoning salt was dissolved in 3 ml deionized water and 2 mL concentrated nitric acid and heated in a 70°C water bath for 15 minutes. Samples were cooled to room temperature before 2 mL of 30% suprapure hydrogen peroxide was added drop wise. Five mL of nitric acid was added and samples were heated in hot block (Environmental Express) at 106°C for 3 hours. Samples were diluted with DI water to 50 mL and centrifuged for 10 minutes. An aliquot of supernatant was then pipetted into the AA's graphite tube by auto sampler.

2) Matrix Modifier

The matrix modifier consisted of 2% ammonium dihydrogen phosphate dissolved in 1% nitric acid. It was added to the sample after the sample was dried in a graphite tube.

3) Instrumentation

The instrument used was a Perkin-Elmer 4100 ZL graphite furnace AA spectrometer with Zeeman background correction, lead HCL and transversely-heated graphite tube.

Table 1: Graphite Furnace AA operation parameters

Wavelength (nm):	283.3
Slit width (nm):	0.7
Read time (sec):	5
Injection volume (µL):	12
Matrix volume (µL):	12
Signal measurement:	Peak area

Furnace Conditions

Step	Temp (°C)	Ramp time(s)	Hold time(s)	Internal flow	Read step
1	110	1	15	250	
2	170	5	20	250	
3	750	1	15	250	
4	1700	0	5	0	x
5	2300	1	2	250	

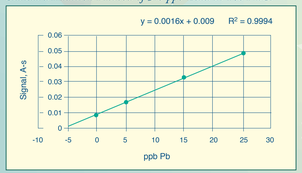
Injection temperature: 85°C

Sequence

StepAction and Parameters

A Pipet sample/standard
B Run furnace step 1 to 2
C Pipet modifier
D Run furnace step 1 to end

Figure 2a
Standard Addition Method of 5.0 ppb Lead in 1% NaCl



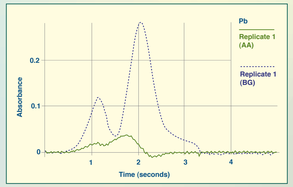
RESULTS and DISCUSSION

1) Effect of Chloride

In a 1% NaCl solution, the lead signal for a 10 ppb standard was decreased by 30% in the absence of ammonia dihydrogen phosphate. The analytical peak was asymmetrical and background peak was split into 2. *(See Figure 1)*

Figure 1 Sample ID: 1g NaCl + 10 ppb Pb

Signal reduction effect of chloride without ammonia dihydrogen phosphate



Repl #	SampleConc µg/L	StndConc µg/L	BlnkCorr Signal	Peak Area
1	6.7	6.7	0.0226	0.0253

Peak Height	Bkgnd Area	Bkgnd Height	Time	Peak Stored
0.0377	0.2502	0.2845	10:57:37	Yes

2) Effect of Matrix Modifier

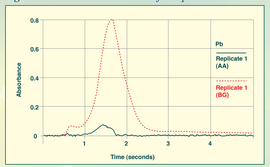
Effect of 2% ammonium dihydrogen phosphate matrix modifier in the presence of 0.5% NaCl:

Prepared lead conc.	Measured lead conc.	% of meas/prep
20.0 ppb	20.4 ppb	102
30.0	29.0	97
40.0	36.7	92

3) Direct Measurement vs. Standard Addition Method *(see Figures 2a and 2b)*

Sample	Direct Measure	Std Add. Method	Direct/SAM
a) 5.0 ppb	5.5 ppb	5.2 ppb	106%
b) #4018	12.0 ppb	15.0 ppb	80%

Figure 2b: Direct measurement of sample #4018



Repl #	SampleConc µg/L	StndConc µg/L	BlnkCorr Signal	Peak Area
1	11.6	11.6	0.0242	0.0298

Peak Height	Bkgnd Area	Bkgnd Height	Time	Peak Stored
0.0710	0.6437	0.8055	09:56:54	Yes

4) QA/QC Reference Samples

Sample	Measured lead conc.	% Recovery
Bone meal (SRM 1486)	9.7 ppb	101

SUMMARY of lead found in 13 seasoning salts

Table 2

Sample*	Avg GFAA‡, ppb	ICP-MS†, ppb	Cal.Conc**, ppm
1	5.8	3.6	0.55
2	5.5		0.53
3	5.5		0.54
4	5.3		0.50
5	5.3		0.51
6	10.9	11	1.05
7	4.2		0.41
8	4.8		0.46
9	4.0		0.39
10	8.1	8.0	0.79
11	8.1		0.80
12	4.4		0.42
13	7.5		0.73

* About 0.5 g sample diluted with water to 50.0 mL after digestion

‡ Average % RSD for duplicates: 4.7

† Split samples were measured by University of Wisconsin – Madison Soil and Plant Analysis Lab

** Calculated lead concentration in samples.
Average: 0.59 ppm
Minimum: 0.39 ppm
Maximum: 1.05 ppm

FDA recommends maximum lead levels in candy not exceed 0.5 mg/kg (ppm). FDA proposes to lower the lead limit guidance to 0.1 ppm in candy.

CONCLUSION

Less than 1 ppm lead determination by the GFAA method presented here offers:

1) Direct measurement in 1 minute.
2) Calibration standards in 1% nitric acid without matching chloride concentration of the samples.
3) No need to use a mixture carrier gas such as argon and hydrogen
4) A 2% ammonium dihydrogen phosphate solution was sufficient as a matrix modifier.

References

1) Standard Operating Procedures (SOP) for Lead in Food Using Graphite Furnace Absorption Spectrometry, City of Milwaukee Health Department Chemistry Section, November 2004.

2) FDA Elemental Analysis Manual for Food and Related Products, Analytical Methods, January 2002.

3) Lihua Jianyan-Huaxue Fence, PTCA, part B: Chemical Analysis, Volume 37, Number 11, p522, November 2001.

4) FDA's Laboratory Information Bulletin, Volume 21, Number 4, April 2005.

5) Milwaukee Journal Sentinel, July 29, 2004. Kawanza L. Griffin. Officials urge retailers to pull candy. http://www.jsonline.com/news/metro/julo4fr247498.asp?format=print

6) US Food and Drug Administration, Center for Food Safety and Applied Nutrition, December 2005. Guidance for Industry. Lead in Candly Likely to be Consumed Frequently by Small Children: Recommend Maximum Level and Enforcement Policy. Draft Guidance. http://ww.cfsan.fda.gov/~dms/pbguid2.html

Acknowledgement

This work was possible through grant support from the Childhood Lead Poisoning Prevention Program, Amy Murphy, Manager, Home Environmental Health Division, City of Milwaukee Health Department

Think Health Act Now!
CITY OF MILWAUKEE HEALTH DEPARTMENT
Serving Milwaukee Since 1867

Tom Barrett, Mayor
Bevan K. Baker, Commissioner of Health
www.milwaukee.gov/health