

LEAD (CHELATING MEMBRANE CONCENTRATION AND GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY)**PRINCIPLE**

The sample is diluted to 10% solids and is filtered through a membrane containing a chelating resin in monovalent salt form whereby trace lead is retained quantitatively. The membrane is rinsed with water to remove residual carbohydrate and is treated with dilute nitric acid to release the lead. The resulting acid solution is analyzed by graphite furnace atomic absorption spectroscopy (GFAAS).

SCOPE

This method has been written based on an instrument-specific GFAAS technology and may need adjustments of parameters when used with equipment by other manufacturers. It is applicable to corn syrup, including high fructose corn syrup, and to blends of corn syrups with sucrose and invert sugar. It is also applicable to solutions of solid samples, including dextrose, sucrose and water soluble maltodextrins.

SAFETY NOTE

Analyst should be familiar with the corrosive and toxic properties of all reagents and should be capable of observing all safety precautions before performing this method, including protective equipment to be worn, spill prevention, spill management and waste disposal.

SPECIAL APPARATUS

1. GFAAS Atomic Absorption Spectrometer, Perkin Elmer Model 5100 PC or equivalent, capable of background correction and equipped with a computerized graphite furnace and an autosampler. Zeeman background correction with either L'vov platform atomization or Transverse Heated Graphite Atomizer (THGA) technology have been used successfully by CRA members, including Perkin-Elmer graphite tubes and platform-Part Number B050-4033 (Note 1).
2. Analytical balance capable of weighing to 0.01 grams.

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3. Plasticware: volumetric flasks, beakers and other general purpose container or dispenser should be made of plastic, preferably polypropylene. Soak all plasticware in 10% nitric acid overnight before use. Rinse with purified water before use. Glassware is not recommended. If unavoidable, glassware should be treated in the same way. Check all plastic Eppendorf or equivalent-type pipettes for actual delivery volume using purified water and apply correction as needed (Note 2).
4. Plastic syringes, 10 mL and 60 mL, with Luer-lock tip (Note 3)
5. Syringe pump: AflatestTM Pump Stand, Vicam, Watertown, MA (Figure 1) or Sage Instruments No. 351, available from Orion Research, Inc., Cambridge, MA 02139, or equivalent (Note 4)
6. EmporeTM Chelating Resin Extraction Disks, 3M Co. (1-800-440-2966), available from Fisher Scientific (No. 14378 24A) Varian Associates, Inc. and VWR Scientific (Note 5)
7. Polypropylene (PP) 25 mm in-line filter holder, for extraction disks above: featuring female Luer lock on the inlet and male Luer slip on the outlet; available from Cole-Parmer, Cat No. E-06623-32, as manufactured by ADVANTEC MFS, Inc., or equivalent (Note 6)

REAGENTS

1. This method requires the use of high purity reagents, including high grade purified water and special handling to avoid contamination.
2. Purified Water: deionized 18 M minimum resistivity. Run a blank according to this method. A total of 100 mL should contribute $\leq 1 \mu\text{g Pb}$. The water may be put through an EmporeTM chelating disc to remove any trace of lead.
3. Nitric Acid, 70% high purity: available as #621 from GFS Chemicals, or as UltrexTM from J.T. Baker, or equivalent

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4. Nitric Acid, 2% Solution, v/v
5. Magnesium Nitrate Matrix Modifier Reagent Solution, containing 10,000 mg/L magnesium (as Mg): available from Perkin-Elmer, Catalogue No. 0190634, or equivalent
6. Magnesium Nitrate Matrix Modifier Working Solution: Dilute 0.5 mL of reagent solution to 50 mL with purified water in volumetric flask. 5 μ L of this solution will provide 3 μ g Mg in the atomizer.
7. Lead Standard Solution: containing 1000 μ g/mL lead as (as Pb) in 2% nitric acid, available from Perkin-Elmer, Catalogue No. N930-0128, or equivalent. This standard must be within labeled expiration date, normally one year from standard preparation.
8. Lead GFAAS Working Standard Solution, 0.1 μ g/mL (0.1 ppm) Pb: Prepare fresh daily in two 1:100 dilution steps:
 - A) *10 μ g/mL Pb Standard:* Add 2 mL 70% nitric acid and about 20 mL purified water to a 100 mL volumetric flask and mix; add 1 mL of the 1000 μ g/mL Pb standard, mix and dilute to volume with purified water.
 - B) *0.1 μ g/mL Pb Standard:* Add 2 mL 70% nitric acid and about 20 mL purified water to a 100 mL volumetric flask, mix: add 1 mL of the 10 μ g/mL Pb standard from step (A) above, mix and dilute to 100 mL with purified water. This is the GFAAS working standard.
9. Lead Spiking Standard Solution, 5 μ g/mL (5 ppm) Pb: Add 2 mL nitric acid and about 20 mL purified water to a 100 mL volumetric flask, mix, add 0.5 mL lead standard solution, mix again and dilute to volume with purified water.

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10. Ammonium Hydroxide, reagent grade: Mallinckrodt, Catalogue No. 3256, or equivalent
11. Maleic Acid, reagent grade: Fisher Scientific, Catalogue No. 03417-500, or equivalent
12. Ammonium Maleate Buffer Solution: Dissolve 5.8 g maleic acid in about 60 mL of purified water. Adjust the pH of this solution to 6.5 with ammonium hydroxide, then dilute to 100 mL with purified water. Pass this solution through EmporeTM membrane filter to remove any lead that may be present. Store in an acid washed plastic bottle (Note 5).

PROCEDURE

Sample Preparation: Weigh 5 g of sample solids in a 50 mL beaker, add purified water to about 40 mL, and add buffer if necessary and dilute to volume. Attach chelating membrane disk to 60 mL plastic syringe (Note 2) with Luer lock tip, transfer solution to the syringe. Attach to syringe pump to obtain an even flow and let the sample solution pass through the membrane at a rate of 2-5 mL/min. Rinse the membrane with 3-4 mL of purified water. Discard effluent(s). Elute the lead ions (Pb^{++}) off the membrane by means of 8-9 mL of 2% nitric acid. Collect this fraction in a 10 mL volumetric flask and adjust to 10 mL with 2% nitric acid. This is the analytical sample solution for atomization and atomic absorption spectroscopy.

For a 50 ppb spike, add 50 μL lead spike standard solution to a separate 5 gram (solids basis) sample after dilution to 40 mL and before addition of buffer solution in sample preparation. Use 100 μL lead spike standard solution for a 100 ppb spike.

Standards for Calibration: Standards of 0, 10, 20, 40 and 60 ng/mL Pb should be used for calibration. These can be made individually or the autosampler can make them from the 100 ng/mL Pb standard. The calibration curve may not be linear beyond 50 ng/mL Pb, so a non-linear calibration may be necessary. The 0 ng/mL Pb standard is the 2% nitric acid used to make the standards and is from the same stock nitric acid used to strip the lead off the EmporeTM membrane. As stated

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above, 5 μL of the magnesium nitrate solution needs to be added at the furnace to all standards and samples.

Graphite Furnace Atomic Absorption Spectroscopy: The following furnace conditions are suggested for Perkin-Elmer THGA systems:

Step	Temp, °C	Ramp, sec	Hold, sec	ArgonFlow, mL/min	Read
1	90	30	30	250	
2	120	5	15	250	
3	200	5	10	250	*
4	400	10	10	250	
5	1600	0	5	0	
6	2400	1	5	250	

Suggested furnace conditions for HGA systems using PE B050-5057 graphite tube:

Step	Temp, Ambient	C	Ramp, sec	Hold, sec	Gas mL/min	Flow,
1	400		20	10	50-250	
2	20		1	15	250	
3	1800		0	15	250	
4	2600		1	5	0	
5				5	250	

Wavelength: 283.3 nm Mode: AA-BG Time: 5 seconds
 Peak area: 3 average Lamp: EDL or HCL* Slit: 0.7 nm L
 Inject Volume: 20 μL

* Detection limit may be reduced using HCL lamp.

Matrix modifier volume: 5 μL of magnesium nitrate solution is added to all standard and samples, usually done by the autosampler.

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The solution from sample preparation above contains the lead from 5 g of sample collected into 10 mL solution. From a calibration curve of ng/mL Pb vs peak area, determine the ng/mL Pb in this solution. The lead content in the sample is determined by $\text{ng/mL Pb} \times 10 \text{ mL}/5\text{g}$.

EXAMPLE CALCULATION

The lead from 5 grams of dextrose was chelated on the membrane, stripped off the membrane with 10 mL of 2% nitric acid. From the calibration curve, the solution contained 3 ng/mL Pb, then $3 \text{ ng/mL Pb} \times 10 \text{ mL}/5 \text{ g} = 6 \text{ ng/gram Pb}$.

NOTES AND PRECAUTIONS

1. While Zeeman background correction with either L'vov platform or THGA are effective in reducing matrix interference and achieving efficient atomization, this method should be amenable to less sophisticated instrumentation since the sample matrix will be essentially 2% nitric acid in water.
2. Plastic volumetric flasks need no verification due to negligible dilution error.
3. The large 60 mL syringe may be used during the lead concentration step and a smaller 10 mL syringe may be used during the lead elution step.
4. Vacuum may be used (in place of a syringe pump) to pull the carbohydrate solution through the membrane. However, the flow rate is difficult to control. A hand operated syringe pump may also be used.
5. The chelating membrane has a high degree of selectivity for lead as compared to other cations typically found in nutritive sweeteners. The selectivity is maintained by insuring that all carboxyl groups of the resin are in sodium or ammonium salt form. This is achieved by means of the ammonium maleate buffer solution to keep sample solution pH = 5.0. Addition of 1/mL buffer solution for each 5 g of sample solids is a good starting point.

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6. The holder from ADVANTEC, MFS, Inc. is a three piece unit that assembles easily without folding or tearing the membrane. This problem can occur with a conventional two piece filter holder when twisting top and bottom halves against the membrane.

REFERENCES

1. Pai, Su-Cheng, Whung, Pai-Yee and Lai, Ruei-Lung, *Pre-Concentration Efficiency of Chelex-100 Resin for Heavy Metals in Seawater, Part 1. Effects of pH and Salts on the Distribution Ratio of Heavy Metals*, *Analytica Chimica Acta* 211 (1988), 257-270.
2. Pai, Su-Cheng, *Pre-Concentration Efficiency of Chelex-100 Resin for Heavy Metals in Seawater, Part 2. Distribution of Heavy Metals on a Chelex-100 Column and Optimization of the Column Efficiency by a Plate Simulation Method*, *Analytica Chimica Acta* 211 (1988), 271-280.
3. Pai, Su-Cheng, Chen, Tsai-Chu and Wong, George T.F., *Maleic Acid/Ammonium Hydroxide Buffer System for Pre-Concentration of Trace Metals from Seawater*, *Anal. Chem.* (1990), 62, 774-777.
4. *Chelex-100 and Chelex-20 Chelating Ion Exchange Resin Instruction Manual*, LT 200 93-0778 0993 (1993), Bio-Rad Laboratories, 2000 Alfred Nobel Drive, Hercules, CA 94547.
5. Solid Phase Extraction of Lead and Other Metals from Maple Syrup Using an Empore™ Chelation Membrane. Louis C. Haddad, 3M I&C New Products Laboratories, 209-1C-30.
6. Stilwell, David E. and Musante, Craig L., *Lead in Maple Syrup Produced in Connecticut*, *J. Agric. Food Chem.* (1996), 44, 3153-3158.

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Figure 1

