The Measurement of Lead in Food Products by Graphite Furnace AA and SpectraAA-40

Application Note

Atomic Absorption

Author

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The widespread use of metals in modern industry has meant that traces of many elements are found throughout our environment. Some are essential to life while others are toxic, and it is often necessary to measure the levels of these metals in a variety of food types. Vapor generation AA has often been used to measure elements such as arsenic, selenium and antimony in foods and environmental samples at very low levels [1,2,3,4]. Graphite furnace atomic absorption is one of the most sensitive analytical techniques available for the detection of trace elements in solution. It is often necessary to use furnace AA in order to detect trace levels of metals in digested samples. Some samples may be measured directly without any pre-treatment, while other foods require vigorous digestion procedures prior to the analysis.

The use of pyrolytic graphite platforms to minimize vapor phase interelement interferences, and to significantly reduce background absorption has been exploited with certain samples [5,6,7].

This study shows that some food samples such as infant milk powder formula may be measured directly in solution while other analyses (for example fish digests) benefit from the use of the pyrolytic platform.

Agilent Technologies

Experimental

A SpectrAA 40 was used for this work together with the Agilent GTA-96 graphite furnace atomizer and automatic sample dispenser.

An Epson printer recorded the results and copied the signal graphics from the CRT video display.

Graphite tubes were of the partitioned pyrolytic coated type, except when the pyrolytic platform was used. In that case it was essential to use the plateau type graphite tube, which was also pyrolytically coated. Argon was used as the inert gas because it not only offers advantages for most elements in terms of sensitivity, but also provides better protection for the graphite than does nitrogen. A hollow cathode lead lamp was used at 283.3 nm.

Sample Treatment and Reagents

1.25 gm of infant milk power was simply dissolved in 25 mL de-ionized distilled water and the mixture vigorously agitated on a vortex mixer. The solution remained in a stable condition for at least one day. Some milk samples were prepared with about 0.001% Triton X-100 but there appeared to be little difference in the stability of the powder in solution.

The fish sample supplied had been digested by the following method [8].

1 gm of wet tissue (fat free) was digested slowly with heating in a conical flask using 5 mL of HNO_3 : $HCLO_4$ solution (6 : 1). It was heated slowly to 150 °C to continue the digestion. It was further heated to 220 °C to yield moist crystals and to remove most of the perchloric acid.

The crystals were dissolved in a minimum volume of 10% HNO_3 and made up to 2 ml final volume.

Water was distilled in a borosilicate vessel and then further purified through a Millipore Milli–Q system.

BDH standard solutions for AA in the form of nitrates were used to prepare the working standard for the programmable sample dispenser. The final concentration of nitric acid in these solutions was 0.1% v/v.

A.R. grade crystals of ammonium dihydrogen phosphate were dissolved in water to give a 0.5% w/v solution. This was used as a chemical modifier.

Results and Discussion

Infant Milk Powder

In order to establish the preferred analytical conditions for the sample, it was necessary to carry out an ashing study to determine the best furnace parameters for the 10 µL volume chosen.

Table 1 shows the instrument and furnace parameters used for the determination. In the ashing study, the temperature of steps 4 and 5 were changed while maintaining the same atomization ramp rate during atomization step 6.

Table 1. Instrument Parameters for Lead in Infant Milk Powder

INSTRUMENT MODE	ABSORBANCE
CALIBRATION MODE	STANDARD ADDITIONS
MEASUREMENT MODE	PEAK HEIGHT
LAMP POSITION	3
LAMP CURRENT (mA)	5
SLIT WIDTH (nm)	0.5
SLIT HEIGHT	NORMAL
WAVELENGTH (nm)	283.3
SAMPLE INTRODUCTION	SAMPLER AUTOMIXING
TIME CONSTANT	0.05
MEASUREMENT TIME (sec)	1.0
REPLICATES	2
BACKGROUND CORRECTION	ON

FURNACE PARAMETERS

STEP NO.	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	90	5.0	3.0	NORMAL	NO
2	100	65.0	3.0	NORMAL	NO
3	125	25.0	3.0	NORMAL	NO
4	650	20.0	3.0	NORMAL	NO
5	650	2.0	0.0	NORMAL	NO
6	2500	1.2	0.0	NORMAL	YES
7	2500	1.0	0.0	NORMAL	YES
8	2500	2.0	3.0	NORMAL	NO

By observing the background corrected (atomic) signal during atomization together with the background signal on the signal graphics screen, it was easily possible to observe the reduction in background signal, while ensuring that the analyte (lead) was not lost at that particular ashing temperature.

The results of the study are shown in Figure 1. It clearly shows that the ashing temperature should be not less than 600 °C to minimize background and not more than about 950 °C lest the analyte be lost during the ashing stage.

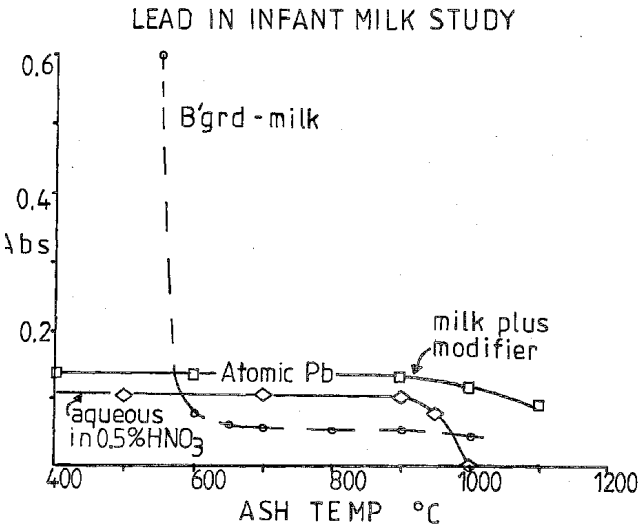

Figure 1. Ashing temperature study for the measurement of lead in infant milk.

Also shown is the atomic signal for an aqueous lead sample indicating that lead is lost at a lower temperature than in the milk sample. Further the presence of the ammonium dihydrogen phosphate modifier, increases the analytical signal for a given amount of lead in solution. The atomization temperature of 2500 °C selected in the furnace program was higher than that required to atomize lead, but ensured there was no build up of other matrix components in the tube.

Figure 2 shows a signal graphics trace of a typical determination of 10 µL of milk sample. The background signal remains low (at about 0.08 abs) while the atomic signal is shown as a well shaped peak.

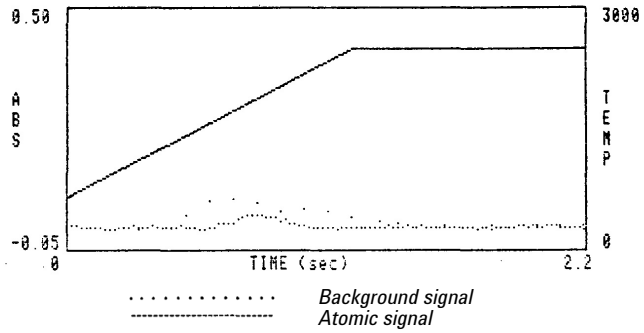

Figure 2. Signal graphics trace of lead in milk sample (10 µL volume).

In order to assess the amount of lead in the sample a standard additions calibration procedure was selected on the SpectrAA (see Table 1). Peak height -measurement mode was used. The automatic sample dispenser was programmed as follows:

> 10 µL of chemical modifier was added to 10 µL of the sample. The concentration of the standard solution used to create the calibration was 10 ng/mL Pb. 5 and 10 µL volumes were selected for the standard additions.

A blank volume was selected when required to maintain the total at 20 µL for all solutions dispensed. The error bars on the calibration in Figure 3 represent ± 1 standard deviation. The relative standard deviation is calculated automatically on SpectrAA instruments, and ranged from 0.5% to 7.6% for the samples. Absorbance was about 0.03.

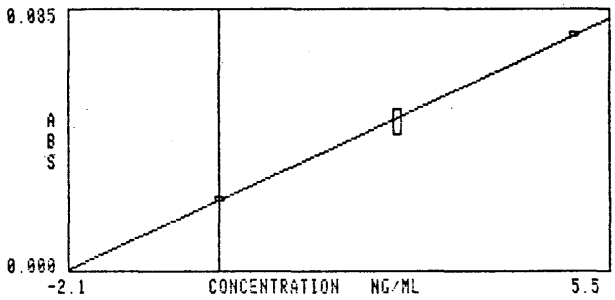

Figure 3. Standard additions calibration for lead in milk.

The concentration of lead in the milk solution was quite low at 2.1 ng/mL.

In the milk powder this represented 42 ng/gm.

It has recently been suggested that background correction difficulties have led to unsatisfactory results for lead in infant milk powders and formulas [9,10]. Although no standard reference material was available there were no apparent problems in carrying out this analysis on the GTA-96.

Fish Tissue

The analysis of a digested fish sample for lead was attempted on a pyrolytic coated graphite tube using a 10 µL volume. It became clear that the excessively high background (about 2 abs) was causing interference with the atomic peak – refer to Figure 4.

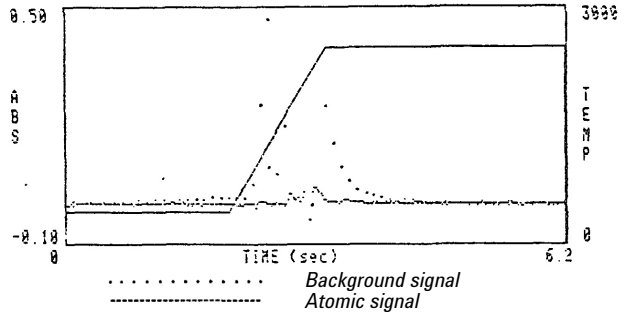

Figure 4. Signal graphics trace for lead in fish digest (10 µL sample) – wall atomization.

A pyrolytic platform was then used with the same sample volume and the magnitude of the background signal was significantly reduced while there was a well shaped atomic (background corrected) signal which had increased significantly in magnitude (Figure 5).

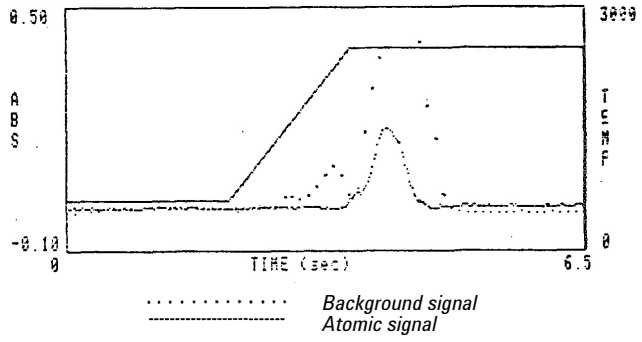

Figure 5. Signal graphics trace for lead in fish digest (10 µL sample) – platform atomization.

The background was still about 1.4 abs for a 10 µL sample.

The initial results suggested that the pyrolytic platform had worthwhile advantages and all further studies were carried out with the platform. Smaller sample volumes were used which not only reduced the magnitude of the background signal, but provided an atomic signal of sufficient absorbance on which to use a standard additions procedure.

The furnace parameters required during drying and ashing for the platform are slightly higher than those required for wall atomization. In addition a cool down step was included as shown in Table 2. This cool down step is desirable to ensure that the graphite tube has reached a sufficiently low temperature before the next sample is introduced.

Table 2. Instrument Parameters for Lead in Fish Digest —Platform Atomization

INSTRUMENT MODE	ABSORBANCE
CALIBRATION MODE	STANDARD ADDITIONS
MEASUREMENT MODE	PEAK HEIGHT
LAMP POSITION	8
LAMP CURRENT (mA)	5
SLIT WIDTH (nm)	0.5
SLIT HEIGHT	REDUCED
WAVELENGTH (nm)	283.3
SAMPLE INTRODUCTION	SAMPLER AUTOMIXING
TIME CONSTANT	0.05
MEASUREMENT TIME (sec)	1.0
REPLICATES	2
BACKGROUND CORRECTION	ON

FURNACE PARAMETERS

STEP NO.	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	150	5.0	3.0	NORMAL	NO
2	210	50.0	3.0	NORMAL	NO
3	260	10.0	3.0	NORMAL	NO
4	600	15.0	3.0	NORMAL	NO
5	600	2.0	0.0	NORMAL	NO
6	2500	1.5	0.0	NORMAL	YES
7	2500	1.0	0.0	NORMAL	YES
8	2500	2.0	3.0	NORMAL	NO
9	40	12.3	3.0	NORMAL	NO

An ashing temperature study over the range 400 °C to 1000 °C showed that the atomic signal was stable up to about 800 °C, while the background also remained fairly constant over the same range – (at about 0.27 abs for a 2 µL sample). An ashing temperature of 600 °C was therefore selected as shown in Table 2. Above about 800 °C ash, both atomic and background signals decreased in magnitude – as observed during atomization.

Standard additions calibrations were checked in both peak height and peak area for the sampler program as shown in Table 3.

Table 3. Sampler Parameters for Fish Digest Analysis Using Standard Additions

SAMPLER PARAMETERS
VOLUMES (uL)

	STANDARD	SAMPLE	BLANK	MODIFIER
BLANK	--	--	12	
ADDITION 1	5	2	5	
ADDITION 2	10	2		
SAMPLE	--	2	10	

The actual values for peak area (abs. sec. units) were about 3 times lower than the values for peak height (abs units), and it was not unexpectedly found that the %RSD or precision was also poorer.

It was of interest to examine the calibrations obtained for aqueous standards and the standard additions calibration in peak height and peak area modes for the fish digest to determine whether the digest matrix affected the calibration slope.

Coincidence of the aqueous and the standard addition calibration would indicate virtual freedom from interference in the measurement. It was found that a) for peak height mode, the standard addition calibration for the fish digest was about 5% lower than the aqueous calibration and b) for peak area the standard addition calibration for the fish digest was about 35% lower than the aqueous calibration.

This observation confirms that the peak height measurement is preferred and that aqueous calibrations would give a result within about 5% of the (true) standard additions calibration. Nevertheless the (automatically prepared) standard additions calibration was selected for this determination – refer to Figure 6.

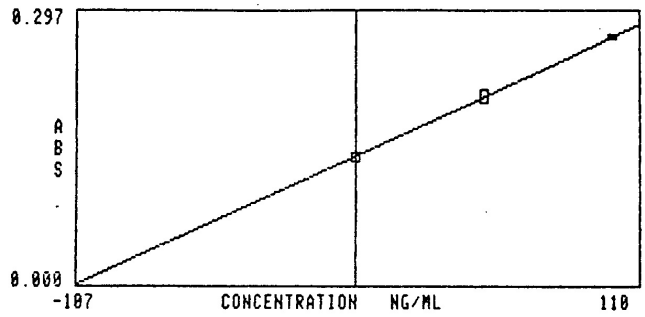

Figure 6. Standard additions calibration for fish digest by peak height measurement.

The SpectrAA automatically computes the calibration and displays the error bars for each measurement, giving a clear display of the precision of the measurements.

A signal graphics trace showing the atomic signal and background signal for the second standard addition appears in Figure 7. The magnitude of the background for this 2 µL sample volume was about 0.27 absorbance units.

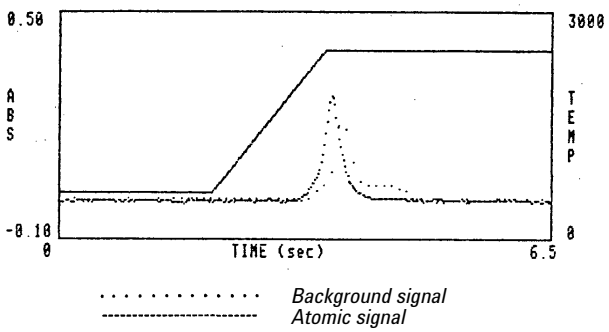

Figure 7. Signal graphics trace for the standard addition measurement of lead in fish digest (2 µL) – platform atomization.

The amount of lead found in the fish digest was 105 ± 2 ng/ml by peak height measurement. By peak area, the value found was 116 ± 12 ng/ml.

Peak height measurement is clearly preferred for this sample type. The amount found in the fish tissue was therefore 210 ng/gm.

Solubilized fish tissues have recently been determined by graphite furnace using a platform and an ammonium dihydrogen phosphate chemical modifier [11]. The procedure described here did not use a chemical modifier.

These studies show that the combination of SpectrAA and GTA-96 graphite tube atomizer with programmable sampler dispenser offer a number of advantages for such food analyses.

Real-time signal graphics and accurate background correction facilitate the choice of instrumental parameters for complex samples. Automatic sample dispensing with standard additions calibration established in a programmable manner by the sample dispenser, provides a simple means to measure low levels of lead in such samples. Reduced sample handling minimized possibilities of contamination. The pyrolytic platform was clearly beneficial for the fish digest, but unnecessary for the milk analysis.

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