Method Guide: 40186

Atomic Absorption Full Method Pb in Plant Materials

Key Words

- Lead
- Vegetable Material
- Plant Material
- Quadline Background Correction
- Graphite Furnace
- Atomic Absorption
- Matrix Modification
- Palladium
- Magnesium Nitrate
- Microwave Digestion

Introduction

Lead is a common environmental pollutant metal, and lead levels in plants are often used as an indicator of the lead contamination of the local environment. The lead content of food materials is strictly controlled, and the lead concentration in food plants grown for human consumption also has to be closely monitored.

Atomic absorption spectrometry is commonly used for the analysis of lead in plant material; the maximum levels specified for food materials are readily accessible by flame atomisation, but normal levels in uncontaminated materials and environmental samples require the graphite furnace technique.

It is common practice to perform an oxidative digestion of the plant material before analysis to destroy the organic material and take the lead into solution[1]. Dry ashing procedures are less suitable, as lead is a volatile metal, and can easily be lost during the ashing process[2]. Wet oxidative digestions in open vessels using concentrated acid mixtures can be successful, but require careful control to ensure complete destruction of the organic material and to avoid contamination. Digestion in sealed vessels reduces the likelihood of contamination and allows higher temperatures and pressures to be obtained, aiding the destruction of the organic material[3]. The use of microwave power, rather than a conventional oven, further increases the efficiency of the digestion, and shortens the time required[4].

A purpose designed high pressure microwave digestion system can be used to digest a wide range of plant materials quickly and easily. As the organic material is completely destroyed by the digestion, the final solution contains only inorganic salts, and can be analysed simply by Graphite Furnace Atomic Absorption Spectrometry with an appropriate choice of atomisation technique and matrix modifier.

Analytical range

A method for the determination of lead in samples of a wide range of plant material is presented. The 3 sigma detection limit for the method is 0.15 µg/g of lead in the dried sample and up to 20 µg/g can be measured. Sample masses can be reduced, or dilutions increased to handle higher concentrations if necessary.

Principle

0.5 g portions of dried plant material are digested with nitric acid in a high pressure microwave digestion system. The sample solutions are analysed for lead by Graphite Furnace AAS using platform atomisation with reduced palladium and magnesium nitrate matrix modifiers. Background signals are low, and Quadline background correction is used.

Method

Reagents:

Nitric acid (Spectrosol grade or equivalent).

Lead master standard (1000 mg/L Spectrosol or equivalent).

Hydroxylamine hydrochloride (AnalaR reagent).

Magnesium nitrate (SpecPure grade or equivalent).

All reagent examples available from:	Palladium matrix modifier (2 % Pd in 1 % v/v HNO3) obtained from:
Fisher Scientific Bishop Meadow Road Loughborough LE11 5RG UK	Aldrich Chemical Company New Road Gillingham Dorset UK

Standard reference materials from various sources.

The reduced palladium modifier solution contained 500 mg/L of palladium and 2 % m/v of hydroxylamine hydrochloride in water. The magnesium nitrate modifier solution contained 1 % m/v of magnesium nitrate in water.

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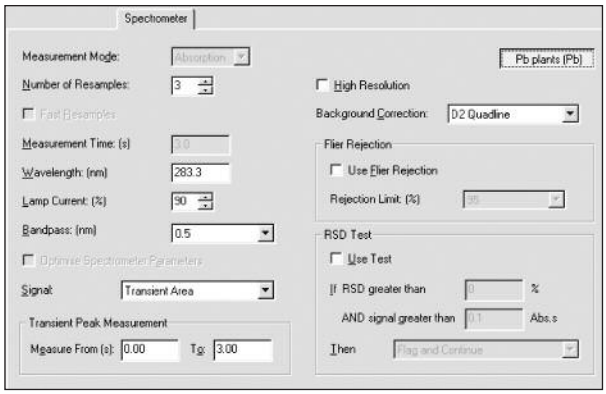

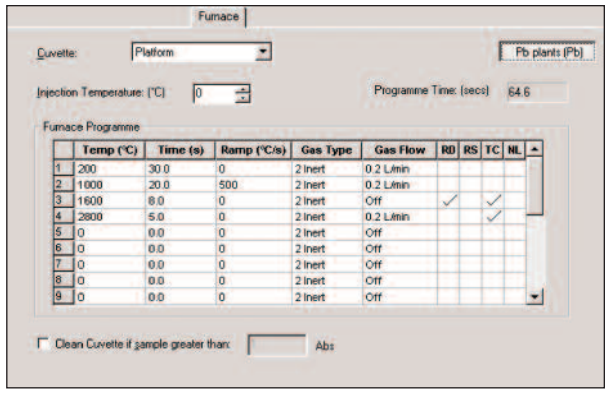

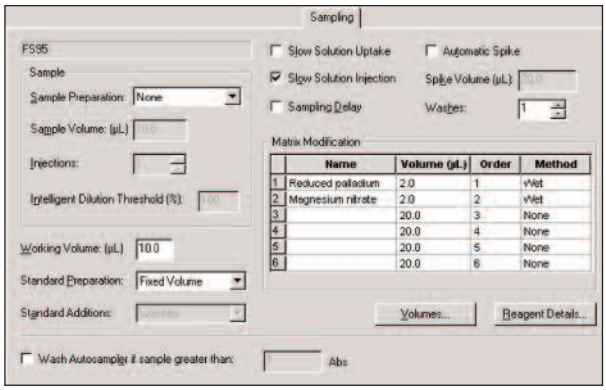

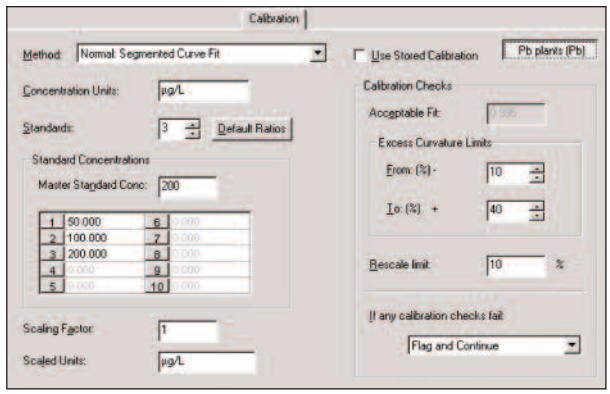

Figure 1: Analysis parameters

Sample collection

The samples were digested in a Milestone Mega 1200 microwave digestion system, using the MDR 1000/6/100/110 rotor. The reference materials were dried overnight at 85 °C. 0.5 g portions were weighed into the digestion vessels, and 6.0 mL of concentrated nitric acid were added. The vessels were closed and fitted into the rotor, and digested using the program shown in table 1. When the microwave program had finished, the rotor and digestion vessels were cooled in the Milestone Cooling System for 10 - 15 minutes. The vessels were then cautiously opened, the contents were transferred to 50.0 mL volumetric flasks and diluted to volume with deionised water.

Time (minutes)	Power (watts)
1	250
2	0
5	250
5	400
5	650

Table 1: Microwave programme

All of the samples gave completely colourless solutions after digestion, although a small quantity of white material, assumed to be silica, was observed in several of the solutions. This was allowed to settle out.

Reagent blanks were prepared by omitting the samples from two vessels.

A working standard containing 200 µg/L of lead was prepared by diluting the master standard with 10 % v/v nitric acid, and 10 % v/v nitric acid solutions were used for the diluent and calibration blank.

Method development

Atomisation

Platform atomisation was used throughout, using a pyrolytically coated graphite cuvette with an integrated pyrolytic graphite L'Vov platform.

Sample injection

The relatively high acid content of the samples initially caused some problems with the sample injection, leading to poor measurement precision. The GFTV image was used to observe the injection while adjusting the position of the furnace autosampler capillary tip, and the optimum position was found to be with the tip set just above the platform (figure 2), considerably closer to the platform than usual.

With a normal injection, the sample then ran back up the outside of the capillary tip. However, the slow injection facility of the furnace autosampler deposited the sample smoothly as a shallow pool in the platform cavity (figure 3), and good, reproducible results were then obtained when the rest of the parameters were optimised.

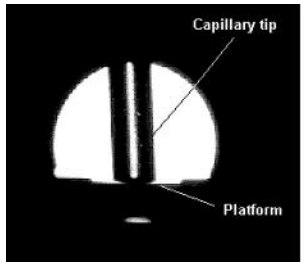

Figure 2: Capillary tip position

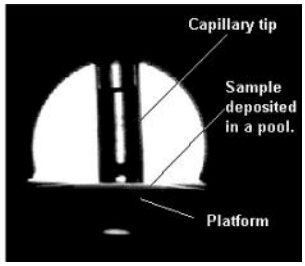

Figure 3: Sample injection

Matrix modifiers

Use of a matrix modifier is normally considered to be essential when platform atomisation is used to stabilise the analyte, permitting higher ash temperatures to be used, and to delay the analyte atomisation, reducing gas phase interferences by allowing the gas in the cuvette to reach a stable temperature before atomisation takes place.

An ash plot of a digested sample of the citrus leaves reference material without a modifier is shown in figure 4. The lead is stable up to 800 °C, but the peak shape (figure 5) is poor, the precision was not good, and low and variable recovery of the lead relative to the certified value was obtained.

Ammonium phosphate is a common modifier recommended for lead determinations, and the effect of this on the pine needles reference material digest is shown in figure 4. The lead is stabilised to 1200 °C, but the signals are slow, and show signs of double peaks (figure 5). Background signals were also significantly larger with this modifier. Recoveries relative to the certified values were again low and variable.

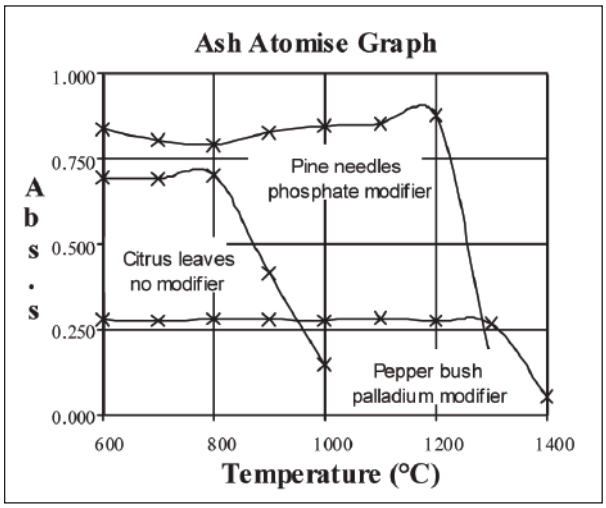

Figure 4: Ash temperature plots

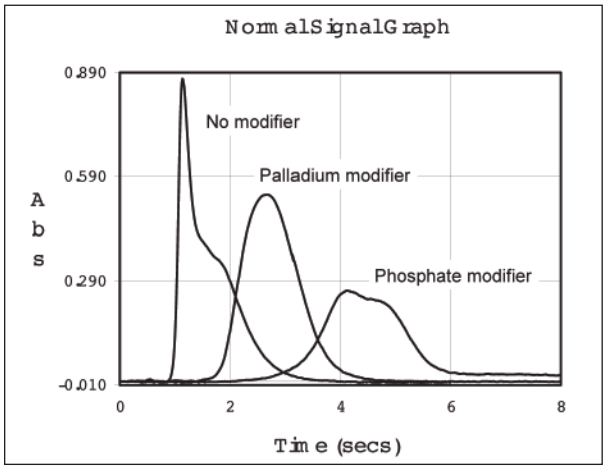

Figure 5: Atomisation signals

Palladium reduced in solution with hydroxylamine hydrochloride has recently been shown to be a very effective and easy to use modifier for selenium[5]. It also proved effective for lead, stabilising it to 1300 °C, and giving well shaped clean peaks. Similar peaks were only obtained from the standard solutions when the magnesium nitrate modifier was used as well. With both modifiers used, excellent recoveries from the CRM's were obtained. 2 µL volumes of the modifier solutions were found to give optimum results, equivalent to 1 mg of palladium and 20 mg of magnesium nitrate.

Method validation

The method was validated by analysing samples of eight certified reference materials of vegetable origin. Two reagent blanks were prepared with the samples, and the batch of ten sample solutions was analysed six times in a single run, utilising the full capacity of the furnace autosampler.

Results

The results from the validation experiment are shown in table 2 and figure 6. Note that the concentration results in figure 6 are plotted on a logarithmic axis, so that the trends in the results near the detection limit can be seen.

The mean results for the reference materials are shown in table 2, and are generally in excellent agreement with the certified values. The NIES Chlorella no. 3 CRM is not certified for lead; the value of 0.6 µg/g is a reference value only, and the result found in this work is much lower than that. The NBS Wheat flour 1567 is also not certified for lead, and the Rice flour 1568a contains less than 0.1 µg/g.

The results obtained for these samples could not be distinguished from the reagent blank.

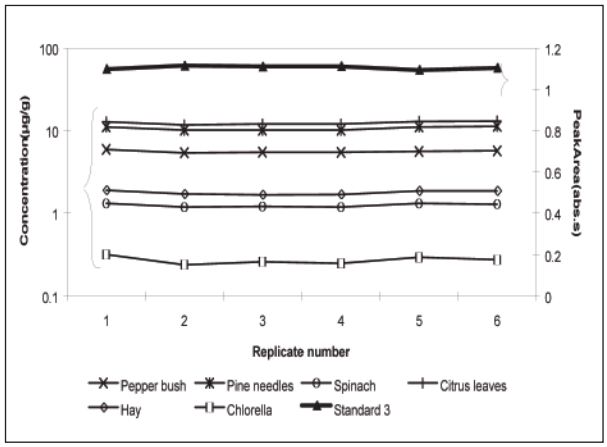

Figure 6: Validation experiment results

Sample	Certified value (µg/g)	Lead found (µg/g)
NIES Chlorella No.3	0.6 (ref. only)	0.18 ± 0.06
NBS 1567 Wheat flour		not detected
NBS 1575 Pine needles	10.8 ± 0.5	10.51 ± 0.49
NIES Pepper bush No.1	5.5 ± 0.8	5.57 ± 0.22
NBS 1568a Rice flour	< 0.01	not detected
NBS 1570 Spinach	1.2 ± 0.2	1.28 ± 0.11
NIST 1572 Citrus leaves	13.3 ± 2.4	12.78 ± 0.44
IAEA V10 Hay	1.6 (0.8 - 1.9)	1.8 ± 0.14

Table 2: Results for Certified Reference Materials

The calibration graphs were linear, with curvature coefficients below 5 %. The characteristic mass for lead measured under these conditions was found to be 8.4 pg for a signal of 0.0044 abs.seconds. The mean reagent blank was 0.5 µg/L, equivalent to 0.05 µg/g in the solid samples, and the 3 sigma method detection limit, calculated from the wheat flour, rice flour and chlorella results, was 0.15 µg/g.

Conclusions

A rapid, precise and accurate method for the determination of low levels of lead in plant materials has been developed. High pressure microwave digestion ensures the complete destruction of the organic matrix, and platform atomisation with the reduced palladium and magnesium nitrate modifiers permits precise and interference free determination of the lead concentration by Graphite Furnace Atomic Absorption Spectrometry.

References

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(5) Rock P.E 7th BNAAS , 1994, 'The Novel Use of Hydroxylamine Hydrochloride as a Reducing Agent for a Palladium Matrix Modifier in the Determination of Selenium by GFAAS.

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