Analysis of Plant Materials by VaporGeneration AA

Application Note

Atomic Absorption

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Introduction

Arsenic and antimony are widely used in modern industries although they are toxic to both man and animals. Significant levels of these elements can be found throughout our environment in such diverse sources as soils, plants, fish and animals. Selenium, on the other hand, is an essential trace element but can be toxic at higher levels. The essential role of selenium in animal nutrition was first demonstrated in 1957 [1] but man's requirements are not yet fully defined.

The concentration of these elements in foods is dependent on the soil conditions and ultimately on the methods of preparation of the food. The levels found in animal products is dependent on the plant material or other animal food source.

It is of considerable interest therefore to establish the level of these elements, as well as other toxic metals, in soils, plants and animal tissues.

Arsenic, antimony and selenium have been determined at very low levels by atomic absorption for many years, and vapor generation atomic absorption offers the most sensitive means by which they can be measured.

The results of extensive collaborative studies on acid digestion techniques, and hydride generation AA for the determination of arsenic and selenium in foods have been reported [2,3]. Several laboratories were involved in those reports.

Sample digestion procedures have ranged from ashing in a furnace with a magnesium nitrate solution [4], to hot digestion in acids usually comprising nitric and perchloric mixtures [5]. Agilent instruments have been used for the vapor generation measurement of selenium levels in plant and biological material after suitable acid digestion [5,6].

Many laboratories are reluctant to use perchloric acid with digestions of organic materials because of the potential risks involved [7,8]. For this reason a number of digestion procedures have been devised which have eliminated perchloric acid. Sulphuric acid increases the boiling point of an acid digestion mixture and improves the action of the other oxidizing acids such as nitric. The only disadvantage of sulphuric acid is the tendency to form insoluble compounds but the presence of nitric acid avoids the precipitation of trace metals with major components of the sample. Digestion mixtures of sulphuric, nitric and hydrogen peroxide have been used successfully for plant materials [7].

The results of the determination of arsenic, antimony and selenium in NBS orchard leaves (No 1571) by the vapor generation technique are reported here. A digestion procedure was prepared which did not contain perchloric acid.

Instrumentation

An Agilent AA-1475 with background correction and the VGA-76 were used in this study. The background signal was examined for all solutions, but no background was found. Measurements were therefore reported with the background corrector off. Hollow cathode lamps were operated at the recommended conditions and an Agilent 9176 strip chart recorder displayed the traces.

For development of this analytical technique samples were presented manually.

Absorbance mode was used and five 3-second integrations were taken.

The printer was an HP 82905A model. The reagents used for the VGA-76 were as follows:

Acid channel	Concentrated hydrochloric acid.
Sodium borohydride channel	0.6% NaBH4in 0.5% NaOH and 10% KI.

Sample Treatment

NBS orchard leaves (No. 1571) were dried at 80 °C and approximately 0.5 g samples were accurately weighed and prepared for analysis. The digestion procedure consisted of the addition of 5 mL concentrated sulphuric with swirling in a beaker. A 5 mL volume of 30% v/v hydrogen peroxide was added slowly and the reaction allowed to proceed. This addition of hydrogen peroxide was repeated, and when the reaction had subsided, the digestion mixture was heated on a hot plate.

After cooling, 2 mL of concentrated nitric acid was added and the mixture heated for about 2 hours to remove excess nitric acid. A further addition of nitric acid with heating may be required until the solution is a light straw color.

The digested mixture was made up to 25 mL to give a final solution in 7 M hydrochloric acid. This stock solution was used directly for the determination of selenium, but was diluted 1 in 10 with 7 M hydrochloric acid for the determination of arsenic and antimony.

Some quantities of powdered orchard leaves were also spiked with known amounts of arsenic, antimony and these samples were taken through the same digestion procedure. A standard additions calibration was thus established. Replicate samples were taken for each. Blank reagents were also prepared.

Samples were prepared in 7 M hydrochloric acid to ensure that any Se^{VI} formed in the digestion procedure, was reduced to the required Se^{IV} prior to analysis. This treatment is commonly used [5,6,9,10].

The reduction of As^{V} (or Sb^{V}) to As^{III} (or Sb^{III}) was achieved by the inclusion of potassium iodide in the sodium borohydride solution [9].

Results and Discussion

Figures 1 and 2 show chart recorder traces for the standard additions measurement of the digests for arsenic and antimony respectively. Approximately 40 seconds are required for the signal to reach an equilibrium value after introduction of the sample. Replicate absorbance readings were taken in the plateau region. It is apparent on Figure 2 that a spike appears on completion of the signal, and this is due to a brief introduction of air before the next solution is pumped. Such an occurrence is not uncommon.

Standard additions calibrations for arsenic and antimony are featured in Figures 3 and 4 respectively. The mean absorbance is shown and two values are represented by the error bars on the Figures.

That the standard additions technique was necessary, is demonstrated by aqueous calibrations for those elements on the same graphs. The calibration slopes are clearly different.

Table 1 shows the results obtained for arsenic and antimony in the orchard leaves. Agreement with the certificate was good.

Table 1 NBS Orchard Leaves No. 1571

Element	Certificate value µg/g	Found* µg/g
As	10 ± 2	11 ± 2
Sb	2.9 ± 0.3	2.7 ± 0.2

* Mean of replicate determinations.

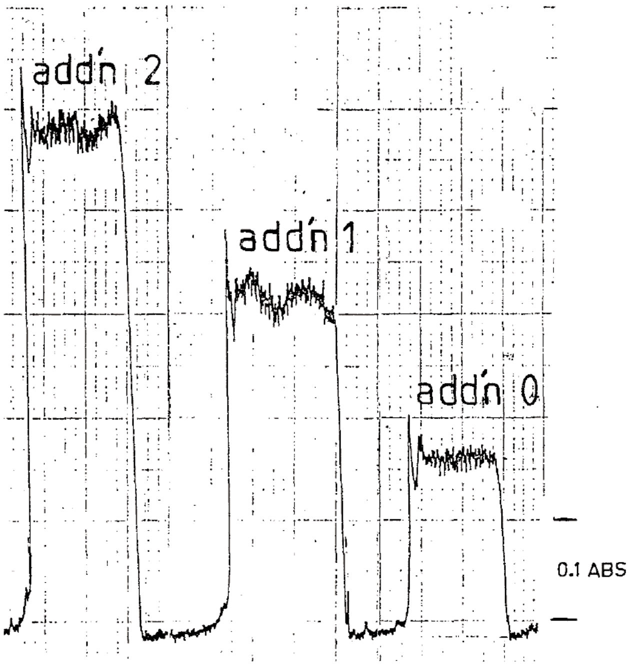

Figure 1. *Chart recorder traces for the measurement of arsenic in digested leaves.*

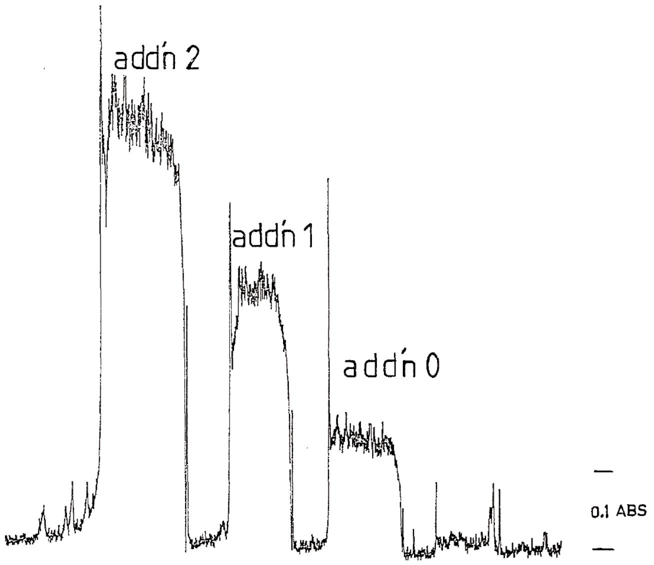

Figure 2. *Chart recorder traces for the measurement of antimony in digested leaves.*

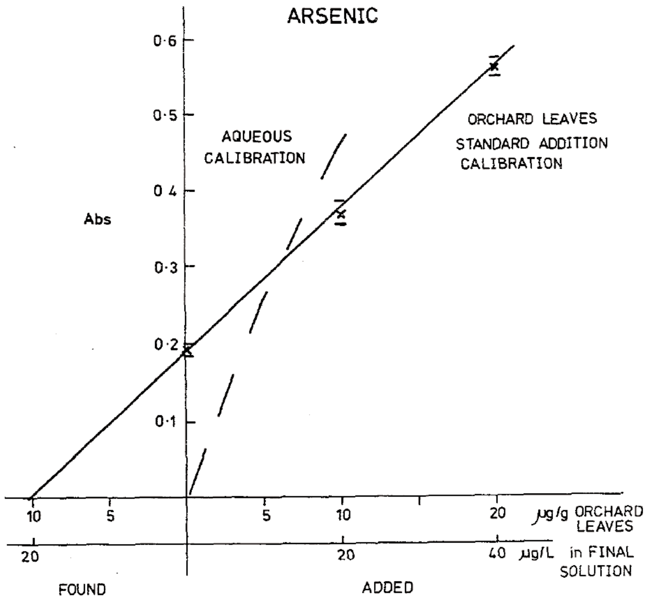

Figure 3. *Calibration for the determination of arsenic.*

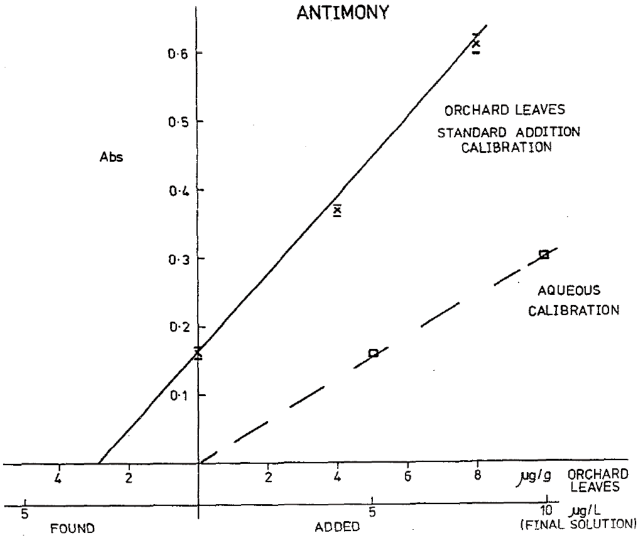

Figure 4. *Calibration for the determination of antimony.*

The level of selenium in the leaves was quite low (0.08 µg/gm) and a value of 0.05 was obtained from just one measurement by the standard additions technique.

No further study was made on selenium here but details of extensive work on selenium determination in agricultural materials by the VGA-76 has been recently reported [10].

An alternative digestion procedure was also attempted in which nitric and sulphuric acids only were used. The mixture was heated to remove excess nitric acid and the final solution was a light straw color. The recoveries from some samples analysed by this procedure were low, and this procedure was not pursued further.

Summary

The VGA-76 has been used to determine the amount of arsenic and antimony in digested orchard leaves. A digestion procedure was adopted which avoided the use of perchloric acid and it was necessary to use the standard additions calibration procedure.

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