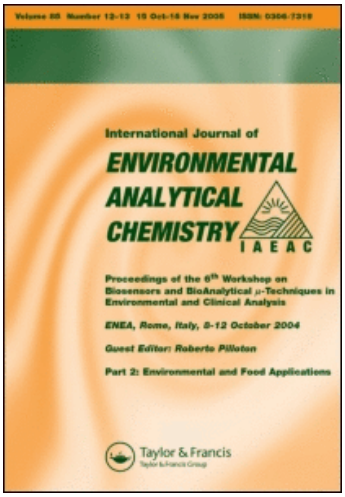

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Determination of Cadmium in Plant Tissues by Electrothermal Atomisation Atomic Absorption Spectrometry with Matrix/Analyte Modification and Smith-Hieftje Background Correction

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DETERMINATION OF CADMIUM IN PLANT TISSUES BY ELECTROTHERMAL ATOMISATION ATOMIC ABSORPTION SPECTROMETRY WITH MATRIX/ANALYTE MODIFICATION AND SMITH–HIEFTJE BACKGROUND CORRECTION

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Pressure decomposition in a microwave oven provides a rapid means of sample preparation for plant tissue analyses. The use of delayed atomisation cuvettes, Smith–Hieftje background correction and matrix/analyte modification enables accurate determinations of cadmium concentrations in plant materials to be made. However, care should be taken to restrict the concentrations of modifier used, as too high a concentration may lead to problems with both tube life and over-correction by the Smith–Hieftje background correction system.

KEY WORDS: Cadmium, delayed atomisation cuvettes, microwave dissolution, matrix/analyte modifiers.

INTRODUCTION

The aim of this study was to develop an accurate method for the determination of cadmium in plant samples from a range of contaminated soils. Matrix/analyte modification was evaluated in such a way as to optimise both tube life and analytical accuracy.

The routine use of electrothermal atomisation atomic absorption spectrometry (ETA-AAS) for the analysis of low levels of metals in a variety of environmental media is now an accepted part of monitoring and research procedures. However, with the increased sensitivity that ETA-AAS offers come a variety of problems, not the least of which are the interferences in the atomiser during signal measurement.[1,2] This paper will concentrate upon the analysis of plant materials for cadmium and will consider a specific problem inherent in the use of some matrix/analyte modifiers.

The primary problem with cadmium is its low appearance temperature in the furnace (ca. 580 °C); this means that the removal of matrix constituents during the ashing or char cycle is difficult without the associated loss of the analyte. Many papers have been published which deal specifically with the matrix effect problem and a wide variety of solutions are presented.[3,4,5]

Furnace interferences are often divided into two groups: (i) *vapour-phase*

interferences predominantly created by non-isothermal conditions in the furnace tube, and (ii) *solid-phase interferences*, a somewhat nebulous term which usually refers to the physical aspects of the volatilisation of the analyte itself. It should be noted that isothermality within the furnace tube has two components, (i) temporal and (ii) spatial.[6] Much attention has been paid to the former, but less to the latter. A very wide variety of techniques have been developed to deal with vapour-phase interferences. These mainly involve the creation of an isothermal environment in the tube prior to the samples atomisation. Developments include the L'vov or platform furnace,[7] delayed atomisation cuvettes,[8] the graphite probe,[9] the integrated contact furnace[10] and attempting to increase the thermal stability of the analyte.

With the exception of the standard additions procedure, the most commonly used technique is the use of matrix/analyte modifiers which are added to the sample in order to alter its thermal stability. In this paper an analyte modifier is considered to be any substance which alters the thermal stability of the analyte, this may either be an increase or decrease in stability; a matrix modifier is any substance which alters the thermal stability of the matrix. In most cases an analyte modifier will tend to be chosen in order to increase the stability of the analyte; however there are some exceptions to this.[11] The most widely used analyte modifier for the determination of cadmium is diammonium hydrogen or ammonium dihydrogen phosphate, which allow ashing temperatures up to ca. 700 °C to be employed without the loss of the analyte.[4,12,13] The addition of magnesium nitrate to the sample as a matrix modifier helps to raise the maximum ashing temperature to ca. 1000 °C. An alternative to magnesium nitrate is the addition of sodium chloride[4] which enables a similar maximum to be attained. The addition of either of these two matrix modifiers to the analyte modifier is thought to create oxidising conditions in the tube and so remove the organic component of the sample matrix during the ashing phase. There also exists the possibility that the delay in the atomisation of the sample may be due to occlusion of the analyte in the matrix modifier. The major advantage of the use of these two analyte modifiers is that they allow a delay in the atomisation of the analyte and so increase the chances of isothermal furnace conditions existing at this crucial stage of the analytical cycle. Although not as widely used as diammonium hydrogen phosphate, the use of palladium nitrate in combination with magnesium nitrate is becoming widely used for a variety of elements in a number of sample matrices.[5,14]

EXPERIMENTAL

Instrumentation

Analyses were made on an Instrumentation Laboratory (IL) S-12 spectrometer in the single beam mode of operation, using Smith–Hieftje background correction. The instrument was equipped with an IL 655 Controlled Temperature Furnace (CTF) atomiser, IL 254 auto-sampler and a FASTAC for aerosol sample deposition. Pyrolytically coated delayed atomisation cuvettes (DAC) were used throughout the experiment (Allied Analytical Systems and Ringsdorff). Visimax II hollow

cathode lamps were used as the radiation source. A linear dual-channel integrating chart recorder was used to record peak shapes. BOC high purity argon was used as a purge gas.

Reagents

The acid used in sample digestion and in the make-up of the standards was AristaR grade nitric acid, standards being made by the sequential dilution of Spectrosol cadmium standard solution (BDH Chemicals, Poole, UK). All water used in the analysis was initially glass distilled and then de-ionised using an Ionmiser 6C system.

Diammonium hydrogen phosphate modifier solution (2% w/v) was prepared from pro analysi grade reagent (Merck) and purified by passing it through a column of a H^+-substituted (10% AnalaR nitric acid) Chelex-100 cation-exchange resin (Bio-Rad Laboratories, Watford, UK) at a flow rate of 1 ml/min. The magnesium nitrate modifier solution (2% w/v) was prepared from AristaR grade reagent; no further purification was found to be necessary. The modifiers were added to sample and standard solutions to give 0.2% (w/v) diammonium hydrogen phosphate and 0.02% (w/v) magnesium nitrate in the solutions to be analysed.

Sample Preparation

All plant samples were taken from the field and thoroughly washed in distilled water to remove any soil. The sample was then shredded and left to dry at 65 °C in a forced-draught oven, until no further change in weight was observed. The dried material was finely ground in a Fritsch Pulverisette centrifugal ball mill; in order to minimise contamination, acid-washed polyamide pots and agate balls were used for this process. Samples were stored in acid-washed glass jars prior to analysis; the moisture content of the samples after storage was determined by the method described below.

Determination of Moisture Content of Prepared Samples

The moisture content of a sample was determined after drying the sample at 85 °C for 2 h and recording the change in weight. The sample aliquots used for these determinations were not digested for ETA-AAS analysis.

Sample Digestion

Samples (0.050 ± 0.001 g) were weighed into the PTFE liner of a Parr microwave acid digestion bomb (Scientific and Medical Products) using a Sartorius five-figure balance; the liner had previously been cleaned by the following process: ultrasonicated for 10 min in a 10% solution of Lipsol, rinsed with distilled water, soaked in 5% Lipsol, rinsed with distilled water, soaked in 5% AnalaR nitric acid and then rinsed in distilled de-ionised water. AristaR nitric acid (3.00 ml) was then added to each sample, and the liner was placed in the bomb. The bomb was then placed in a domestic microwave oven (Solavox T-2, 980 W) and heated at full power for

Table 1 Spectrometer and sample deposition parameters

Wavelength	228.80 nm	Bandwidth	1.00 nm
Lamp current	3.20 mA	Background current	0.45 mA
PMT voltage	700 mV		

Smith–Hieftje background correction.

Sample deposition: delay time, 7 sec; deposit time, 20 sec;
three repeats per sample.

Measurement: Peak height—2.00 sec integration time.
Peak area—5.00 sec integration time.
Peak shape—Linear dual-channel integrating chart recorder.

High-purity argon (BOC) used as the purge gas.

Table 2 Time/temperature programme for CTF atomiser

Step no.	*Step*	*Temperature (° C)*	*Ramp time (s)*	*Hold time (s)*
1	Injection/dry	135	—	5
2	Ash	650	15	5
3	Atomise	1550	5	5
4	Clean[a]	2500	Step	5

[a]Clean cycle not always necessary.

45 sec; this was sufficient to give a clear solution. Although discharges of fumes from the bomb are only occasional and slight, the inside of the oven was coated with a PTFE spray to mitigate their action. All samples were prepared in quadruplicate, two of the four samples were spiked with the quantity of cadmium necessary to double the concentration. Reagent blanks were carried through the entire procedure.

A refrigerated cooling period of 25 min was required before the bomb could be opened and the liner removed. Any acid which had condensed on the lid of the liner was then rinsed back into the liner with distilled de-ionised water. The liner, with the top removed, was then placed on a Techne dri-block and heated for ca. 90 min at 120 °C in order to reduce the volume of the sample to ca. 0.25 ml. The remaining solution was taken up in 5 ml of 4%(V/V) solution of AristaR nitric acid and then made up to 10 ml in a volumetric flask with distilled de-ionised water. Samples were usually stored in Sterilin bottles (30 ml) and not in the volumetric flask to avoid any adsorption of analyte onto the glass walls.

Instrumental Parameters

Analyses of the samples were made against standards of the following concentrations, 0.50, 1.00, 1.50, 2.00 and 2.50 ng Cd per ml. Each standard solution contained 2%(V/V) AristaR nitric acid, 0.2%(w/v) Merck diammonium hydrogen phosphate and 0.02%(w/v) AristaR magnesium nitrate.

The instrumental parameters are summarized in Tables 1 and 2.

RESULTS AND DISCUSSION

The complex nature of the ashing curves shown in Figures 1–3 for the modified standards are not easily explained, but it may be associated with reactions between the graphite tube wall and the modified analyte. Similar effects have been observed on molybdenum ashing curves when the sample was atomised from a pyrolytic platform or from the wall of a pyrolytically coated tube.[15] Another interaction between the tube material and the sample has been reported for lead analysis.[16] The matrix/analyte modifiers have clearly had an effect upon the analyte because ashing of the acidified standard does not show these marked changes with ashing temperature. However, Figs. 1–3 do show the significant benefit of the use of chemical modifiers in increasing the appearance temperature, in most cases to ca. 800 °C.

Atomisation studies showed the typical influence of atomisation temperature upon peak height and area; as expected, the peak height increases with temperature and then remains constant once a maximum has been reached. Peak area responds similarly but begins to decline at temperatures in excess of 1500 °C; this is due to the accelerated decay of the signal created by rapid diffusion of the atomised sample from the atomiser.[16,17]

The influence of matrix modifiers upon the atomisation of a sample can be seen in Figure 4, which shows the peak shapes produced by the atomisation of (a) acidified and (b) modified standards and samples. The acidified sample was ashed at 300 °C for 30 sec and then atomised at 1100 °C. For both acidified and modified solutions, the instrument was calibrated with five aqueous standards and the sample (a digest of NBS 1573 tomato leaves) was analysed against the resultant calibration. As can be seen from Figure 4a, the atomisation characteristics of sample and standard differ considerably in the absence of the modifiers, with the sample producing a two-phase atomisation. This is thought to represent the presence of two cadmium species of differing thermal stabilities within the sample. The results of the analysis of NBS 1573 against a calibration of acidified standards can be seen in Table 3. Although the quoted value for the sample used is not fully certified, it does represent the mean of several independent analyses. The atomisation of matrix/analyte modified samples and standards (Figure 3b) show marked differences from those of the acidified solutions. The forms of the peaks are very similar and more closely resemble those used in some theoretical models.[16] The analysis of matrix/analyte modified samples against aqueous standards can be seen to be a viable strategy; this is borne out by the data presented in Tables 3 and 4.

The final method using matrix/analyte modifiers was employed to analyse a variety of reference materials which had certified values for cadmium; summations of the results are shown in Table 4.

Each of the materials listed in Table 4 has been analysed in quadruplicate in three batches. Precision is assessed by the relative standard deviation between batches and is expressed as a percentage. Accuracy is calculated as the percentage difference between the certified and the observed value for a given material. The method was also used to analyse a large number of plant samples grown on soils contaminated with heavy metals due to the application of sewage sludges. The

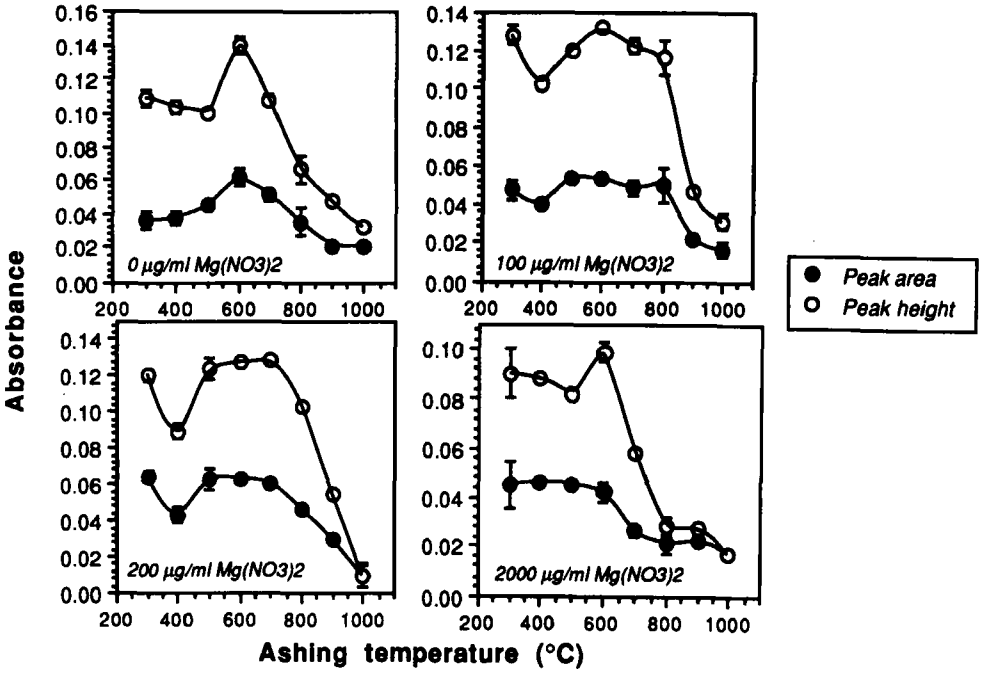

Figure 1 Ashing curves for a 1 ng Cd per ml standard modified with 200 µg/ml diammonium hydrogen phosphate and varying concentrations of magnesium nitrate.

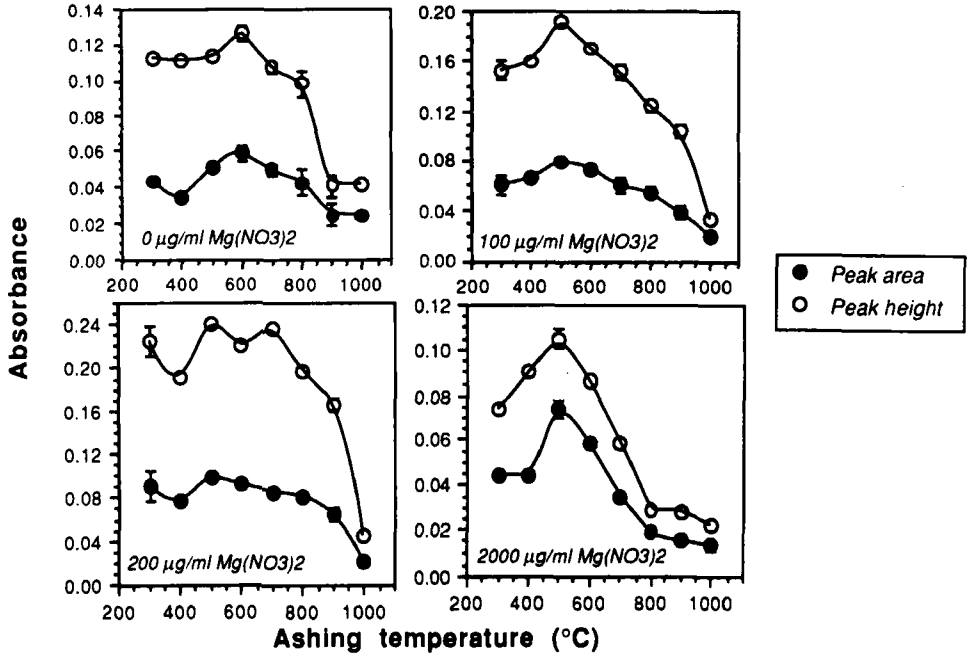

Figure 2 Ashing curves for a 1 ng Cd per ml standard modified with 500 µg/ml diammonium hydrogen phosphate and varying concentrations of magnesium nitrate.

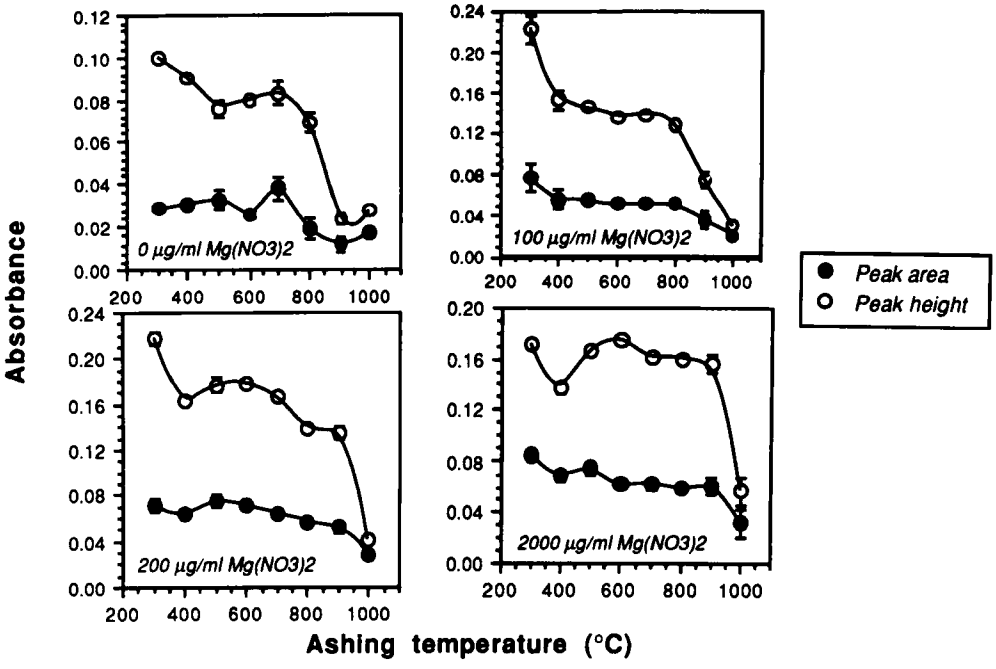

Figure 3 Ashing curves for a 1 ng Cd per ml standard modified with 2000 µg/ml diammonium hydrogen phosphate and varying concentrations of magnesium nitrate.

mean recovery of a spike sufficient to double the concentration of cadmium in the sample was $96.4 \pm 14.3\%$ ($n = 107$). In addition to the analysis of the certified reference materials, another check upon the precision of the analysis was made by the repeated analysis of an in-house quality control material supplied by the Food Science Division of the Ministry of Agriculture, Fisheries and Food. This material had been analysed by ETA-AAS and found to give a concentration of 4.43 µg Cd g^{-1} dwt; the method described above gave a value of 4.48 ± 0.31 µg Cd g^{-1} dwt ($n = 44$).

At an earlier stage of the development of the method described in the experimental section, a wide range of time/temperature parameters and concentrations of modifiers were used. Figures 1–3 show the effects of varying the concentrations of both analyte and matrix modifiers on ashing curves when peak areas were recorded. Initially, concentrations of 1%(w/v) diammonium hydrogen phosphate and 0.2%(w/v) magnesium nitrate were used and found to give good short-term accuracy (≤ 200 firings) and precision for a reference material (BCR 62). However, an accelerating decline in peak area absorbance values was observed, implying that the pyrocoating was being rapidly degraded (see Figure 5). In addition to this problem, the appearance of over-correction by the Smith–Hieftje background correction system was observed and seen to worsen with the number of firings. Although this problem could be eliminated by the inclusion of a high-temperature clean cycle, this was considered to be undesirable if tube life was

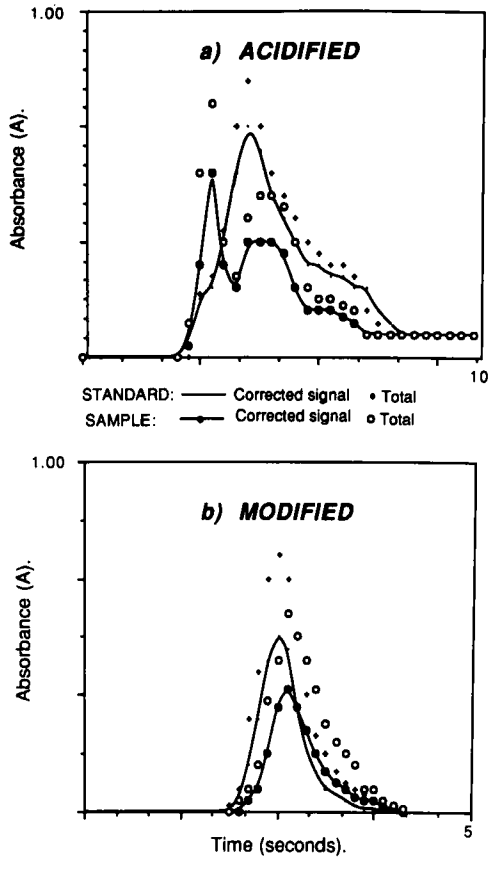

Figure 4 Peak shapes for acidified and modified standards and samples.

Table 3 Analysis of a reference material, NBS 1573 tomato leaves (reference value, 3.00 μg Cd/g dwt).[a]

Procedure	*Concentration of cadmium in NBS 1573 (μg/g dwt)*	
	Peak area (As)	*Peak height (A)*
Acidified	2.80 ± 0.25 (10)	3.40 ± 0.50 (10)
Modified	3.05 ± 0.24 (10)	3.08 ± 0.41 (10)

[a]Number of determinations shown in parentheses.

to be maximized and cycle times kept to the minimum. An order of magnitude reduction in the concentration of magnesium nitrate gave a more satisfactory performance, enabling both sensitivity and precision to be sustained over 400 firings. In order to more closely examine the problems of declining sensitivity and over-correction, a DAC tube was bisected along its longitudinal axis and analysed by scanning electron microscopy (SEM). A Hitachi S-450 SEM fitted with a Link

Table 4 Analysis of four reference materials for cadmium

Sample	*Certified* (μg/g dwt)	*Observed* (μg/g dwt)	*Precision* (%)	*Accuracy* (%)
BCR 60(*Lagarosiphon major*)	2.20±0.10	2.23±0.27	12.23	+1.36
BCR 62(*Olea europaea*)	0.10±0.02	0.097±0.004	4.20	−3.00
NBS 1567(Wheat flour)	0.032±0.007	0.032±0.005	15.60	0
NIES 1(Pepperbush)	6.70±0.50	7.17±0.13	1.80	+7.01

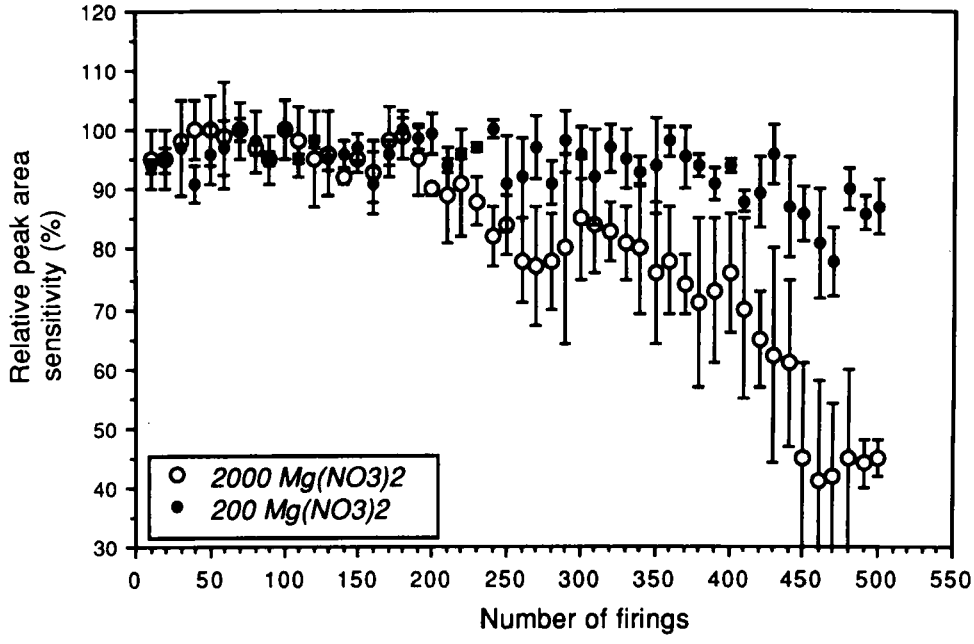

Figure 5 The effects of two concentrations of analyte modifier on tube life and analytical precision.

Analytical AN 10000 microanalysis system was used to make both a visual inspection and an energy dispersive X-ray chemical analysis. As can be seen in Plate 1, the oxidising conditions at the site from which the sample is atomised have completely removed the pyrocoating, leaving behind a porous and potentially reactive surface from which the subsequent samples have to be atomised. An area 12 mm from that in Plate 1 can be seen in Plate 2. At this point damage to the pyrocoating, such as that seen at the sample deposition area, is absent; however, there has been an accumulation of material on the surface. This material was analysed using the microanalysis system and found to be magnesium nitrate. At 13 mm from the area shown in Plate 1 the deposition of spheres of magnesium phosphate can be seen (Plate 3). This pattern may well be due to non-isothermal conditions in the tube after the atomisation of the sample, leading to the differential condensation of components of the sample modification compounds.

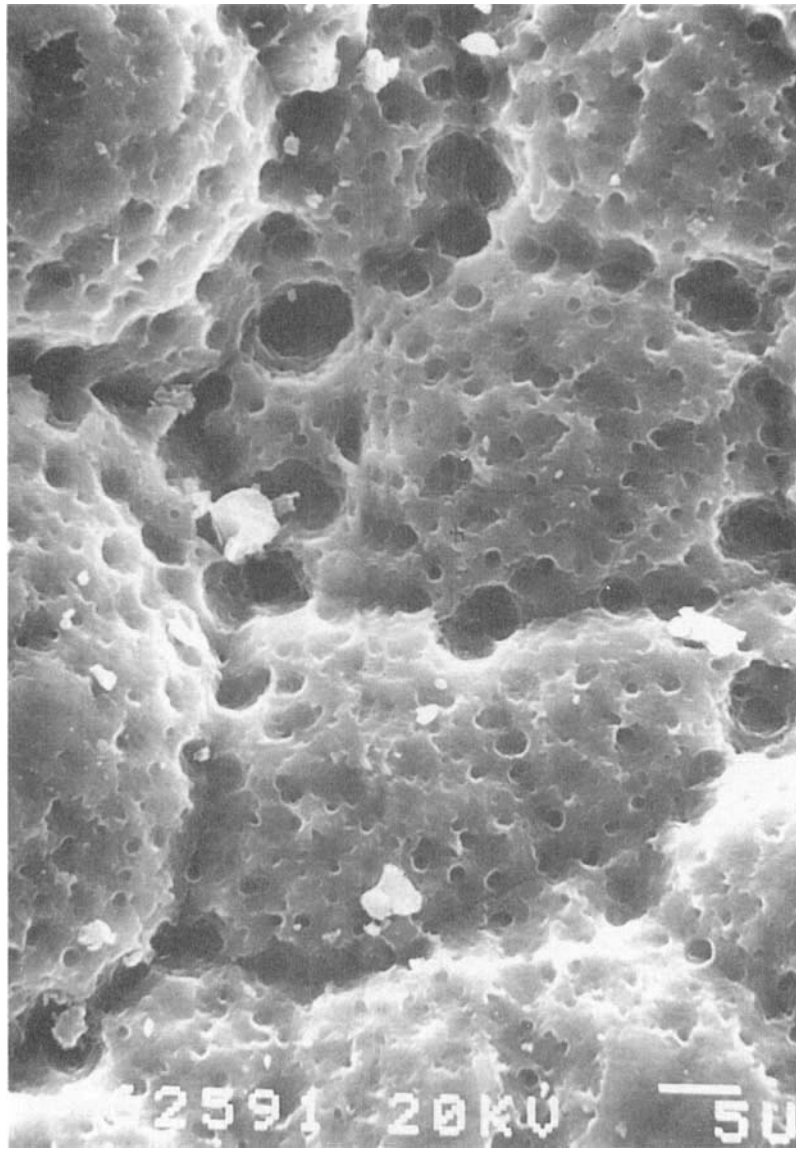

Plate 1 Degradation of pyrocoating at the site of sample deposition.

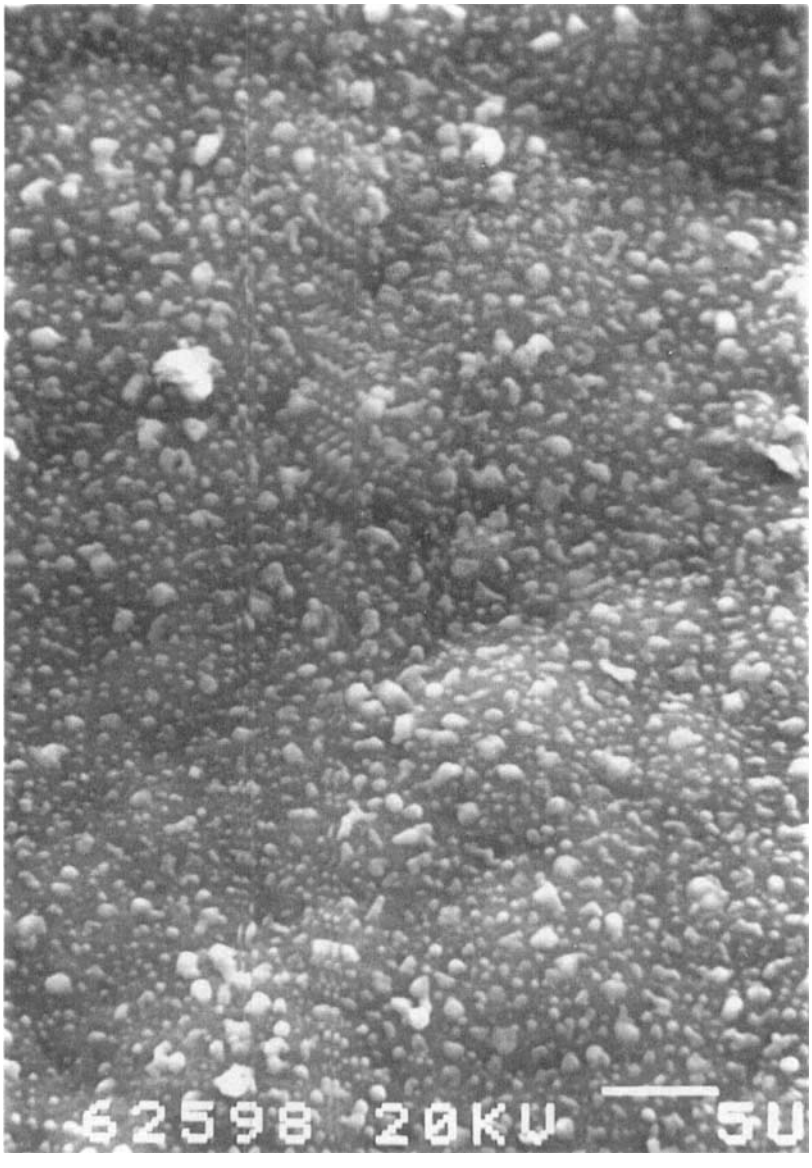

Plate 2 Deposits of magnesium nitrate 12 mm from the sample deposition zone.

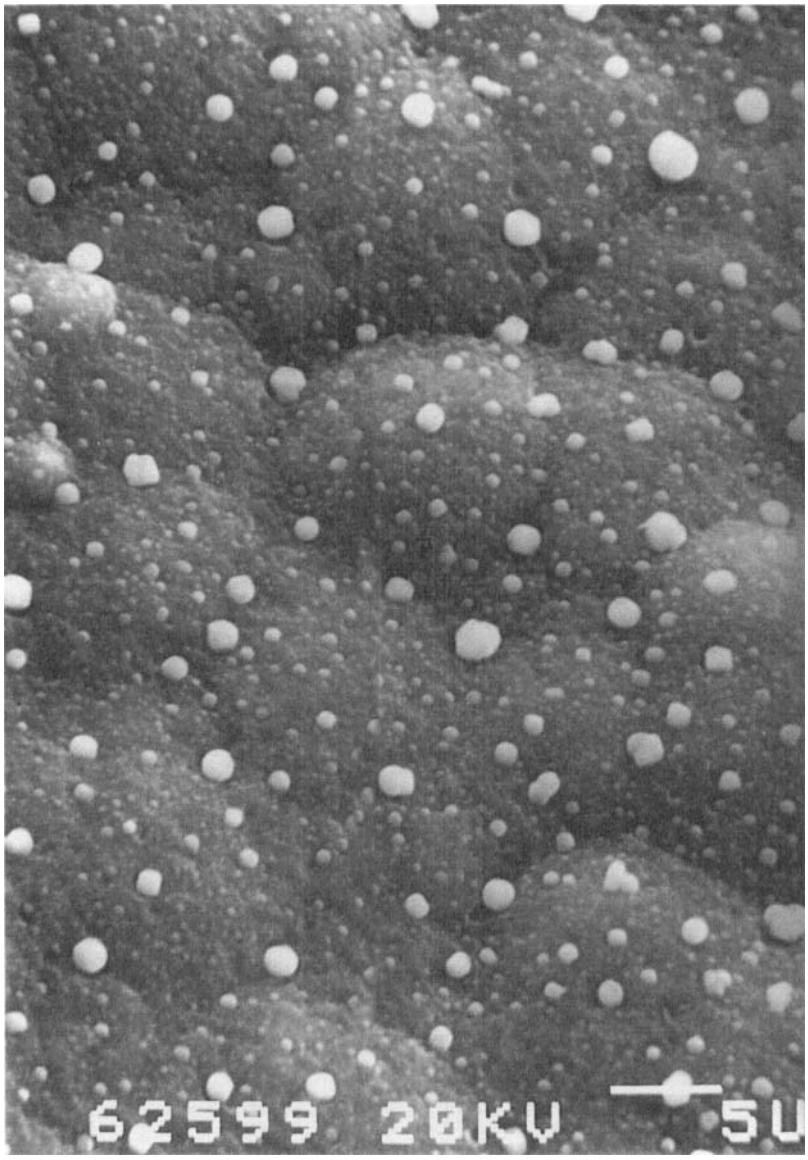

Plate 3 Deposits of magnesium phosphate 13 mm from the sample deposition zone.

As the tube cools down to the sample injection temperature, the areas adjacent to the thicker tube walls at the centre of the tube can be expected to lose heat more slowly and so lead to the spatial and temporal gradient which has caused the effects seen in Plates 1 to 3. The rapid losses in sensitivity are due mainly to the degradation of the pyrocoating at the sample deposition area; the loss of accurate background correction is probably due to the accumulation of magnesium phosphate 13 mm from the centre of the tube. The subsequent atomisation from these areas of secondary deposition will cause an increase in the background signal, eventually leading to the manifestation of over-correction. As a relatively low atomisation temperature was considered to be a desirable feature and the use of a clean cycle was thought to impair tube life, it was decided to use lower concentrations of both analyte and matrix modifier. The details of the developed method are in the experimental section.

CONCLUSION

The use of pressure decomposition with microwave heating has been shown to be a viable means for the preparation of plant materials for cadmium analysis by ETA-AAS. The use of delayed atomisation cuvettes, matrix/analyte modifiers and Smith–Hieftje background correction enabled accurate results to be obtained for four certified reference materials.

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