Palladium as a Chemical Modifier for the Determination of Lead in Food Slurries by Electrothermal Atomisation Atomic Absorption Spectrometry*

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Palladium is shown to be superior to ammonium dihydrogen phosphate as a modifier for lead in the analysis of food slurries by electrothermal atomisation atomic absorption spectrometry. A conventional autosampler was modified to permit magnetic stirring of the slurry samples in the autosampler cups. Stirred slurries can be accurately and precisely pipetted into a graphite furnace up to concentrations of 5% *m/V*. Above this, systematic errors occur. A method is described for the determination of lead in slurries up to a concentration of 4% *m/V*. The procedure involves calibration with aqueous standards, palladium matrix modification and platform atomisation.

Keywords: *Slurry sample introduction; electrothermal atomisation atomic absorption spectrometry; palladium matrix modification; lead determination; foodstuffs*

In recent years the direct analysis of solids[1–6] and slurries[7–24] by electrothermal atomisation atomic absorption spectrometry (ETAAS) has received much attention in an attempt to eliminate problems associated with conventional wet oxidation and dry-ashing sample preparation procedures. Advantages often provided by this approach include faster sample preparation with reduced sample contamination and dilution, thus achieving, in some instances, lower limits of detection.

Slurry analysis is perhaps more attractive compared with the direct analysis of solids as the procedure can be automated avoiding tedious, labour-intensive sample weighing and transfer routines. Addition of a chemical modifier to the slurry diluent can also result in greater contact between it and the analyte.

There are, however, several problems associated with the analysis of samples in the form of slurries. Firstly, calibration by the method of standard additions or using matrix matched standards is frequently a necessity as the elimination of interferences is difficult. High background levels and spectral interferences often associated with the atomisation of slurries necessitates the use of efficient background correction (*e.g.*, Zeeman effect) if accurate results are to be achieved. Additional problems are associated with the sampling of slurries. These include sampling errors related to sample inhomogeneity, sample concentration gradients in the bulk slurry, produced by particulate settling, and imprecise slurry volume introduction into the atomiser. A problem also associated with the introduction of large amounts of biological material into a furnace is the build-up of a carbonaceous residue which can impinge upon the optical path resulting in a drastic deterioration in the signal to noise ratio. Air - oxygen ashing[2,13,14,25,26] may be used to remove the residue, however, tube lifetimes are shortened as a consequence.

This paper considers the applicability of palladium as a chemical modifier for the stabilisation of analytes in food slurries. Although palladium on its own or in combination with other chemicals has been widely used for increasing the thermal stability of a variety of elements in solution[27–42] its use as an aid in the analysis of solid/slurry samples has received little attention. Recently Hinds *et al.*[43] showed that it stabilises lead in soil slurries effectively and Lindberg *et al.*[6] used it in the determination of selenium in solid biological samples.

In this work an ETAAS method was developed for the determination of lead in food slurries using palladium as a modifier, platform atomisation and direct calibration with aqueous standards. The suitability of palladium as a modifier for cadmium and tin is also demonstrated.

Experimental

Instrumentation

Almost all analytical measurements were made with a Perkin-Elmer Zeeman 5000 spectrometer equipped with an HGA-400 heated graphite furnace atomiser. For some preliminary optimisation studies, a Perkin-Elmer Model 3030 spectrometer, equipped with deuterium-arc background correction, and an HGA-500 graphite furnace was used. Absorbance measurements were obtained using lead, tin and cadmium hollow-cathode lamps (S. & J. Juniper, Harlow, Essex, Perkin-Elmer, Norwalk, CT, USA and Cathodeon, Cambridge, UK, respectively.) The instrumental conditions are given in Table 1. Standard non-grooved pyrolytic graphite coated electrographite tubes were used throughout, with pyrolytic graphite platforms placed inside them.

Reagents and Standards

Lead solutions. Prepared from AnalaR grade lead nitrate, BDH Chemicals, Poole, Dorset, UK.

Tin stock solution, 1000 mg l^{-1}. SpectrosoL grade, BDH.

Cadmium solutions. Prepared from AnalaR grade cadmium nitrate, BDH.

Ammonium dihydrogen phosphate. AnalaR grade, BDH.

Ammonium solution, 35% *V/V*. Aristar grade, BDH.

Palladium nitrate solution. Johnson Matthey Chemicals, Royston, Hertfordshire, UK.

Antifoam B emulsion. Sigma Chemicals, St Louis, MO, USA.

Preparation of Slurries

Freeze-dried food samples obtained from the MAFF Food Science Laboratory (Norwich, UK) were ground in an agate ball-mill for a time known to reduce similar samples to a particle size of <50 μm.[14] A mass of powdered sample was weighed, appropriate reagents added and the mixture diluted

* Presented at the Fourth Biennial National Atomic Spectroscopy Symposium (BNASS), York, UK, 29th June–1st July, 1988.

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to the final required volume. Chemical modifiers were added during this preparation, ensuring good mixing with the sample. The addition of antifoaming agent (final concentration of 0.5% *m/V*) prevented foaming when slurries were agitated. Better dispersion of animal tissue and fatty samples was produced by the addition of ammonia solution to a final concentration of 5% *V/V*.

To prevent settling out of material, slurries were either manually shaken before manual injection or magnetically stirred followed by sample introduction using an AS40 autosampler. A miniature magnetic stirring device was developed. It consisted of two 1.5-V d.c. motors (Mabuchi Motor FA 130) stuck on to an aluminium base plate with a small bar magnet fastened on to the axis of each motor. The speed of rotation of each motor was controlled by a variable resistor. Two identical motors were incorporated into this stirring device because the autosampler tray is composed of two concentric series of holes into which sample cups are placed. Minor alterations in the autosampler tray height and reduction of the sample cup depth by 3–4 mm allowed the stirring device to fit under the sample cup being sampled. Thus by switching the stirring device on, the slurry sample was stirred effectively by a small PTFE coated magnet placed in the sample cup. The autosampler capillary tube was positioned so as to withdraw an aliquot from a depth half-way down the cup when filled to near capacity with slurry.

Procedure

Accuracy and precision of slurry deposition

The accuracy and precision of slurry deposition into a graphite tube were determined as follows. The AS40 autosampler was programmed to deliver 20 μl of slurry. The mass of slurry actually introduced into the graphite furnace was determined by weighing the tube before and after sample deposition. The volume of slurry deposited was then calculated by dividing this mass by the slurry density. The mean and precision (RSD, %) were calculated for repeated slurry volume determinations (n = 7–10) with the accuracy of slurry deposition subsequently expressed as

$$\frac{\text{Mean slurry volume deposited}}{\text{programmed volume}} \times 100\%$$

Temperature measurements

Tube-wall temperature measurements were performed using an Ircon 1100 optical pyrometer. The HGA-400 power supply was observed to be slightly out of calibration. Set temperatures of 1100, 1200 and 1300 °C gave measured char temperatures of 885, 965 and 1050 °C, respectively. All temperatures quoted are measured values.

Optimisation of furnace conditions

Furnace conditions were optimised to achieve 100% recovery. Percentage recovery for a set of furnace conditions were calculated as follows:

Table 1. Instrumental conditions

	Element		
Parameter	Lead	Tin	Cadmium
Hollow-cathode lamp current/mA	7	15	8
Wavelength/nm	283.3	224.6	228.8
Spectral band width/nm	0.7	0.7	0.7
Measurement mode . .	Integrated absorbance		

Recovery of added lead (%) =

$$\frac{S\,(\text{slurry} + \text{solution}) - S\,(\text{slurry})}{S\,(\text{solution}) - S\,(\text{blank firing})} \times 100$$

where S (−) = peak area absorbance signal,

"slurry" = 20 μl of slurry

and "solution" = 20 μl of a 100 μg l^{-1} Pb solution.

Each individual determination was performed at least three times with the standard deviation of each recovery calculated to be approximately 5%.

Results and Discussion

Slurry Sample Introduction

Slurry samples have different physico-chemical properties (*e.g.*, viscosity and wettability of sample injector) compared with aqueous solutions. The degree to which these differences affect the accuracy and precision of sample deposition into a graphite tube must be determined before suitable furnace conditions for analysis can be developed and optimised.

The accuracy and precision of deposition of a kale slurry into a graphite furnace up to a concentration of 15% *m/V* is illustrated in Figs. 1 and 2, respectively. The precision of sample deposition is good (RSD <4%) for slurry concentrations of up to 10% *m/V*. The accuracy, however, significantly deviates from 100% at slurry concentrations greater than 5% *m/V* possibly due to incomplete deposition. This is, therefore, the highest slurry concentration that can be analysed using an ETAAS procedure incorporating this sample introduction method unless calibration is achieved by either standard additions or on an instrument which allows the use of an internal standard.

Stabilisation of Lead in Food Slurries

The effect of palladium on the thermal stability of lead in a kale slurry was studied and compared with the stability of lead

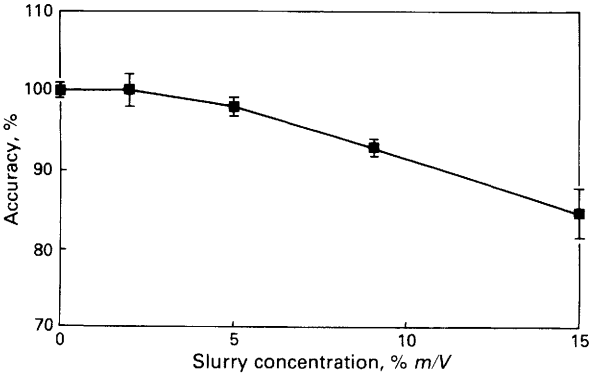

Fig. 1. Accuracy of slurry introduction into a graphite furnace. Error bars indicate 95% confidence intervals

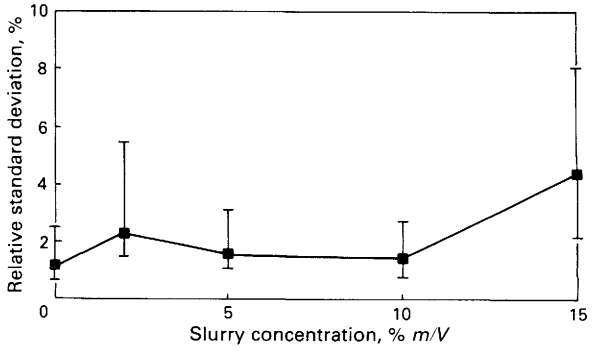

Fig. 2. Precision of slurry introduction into a graphite furnace. Error bars indicate 95% confidence intervals

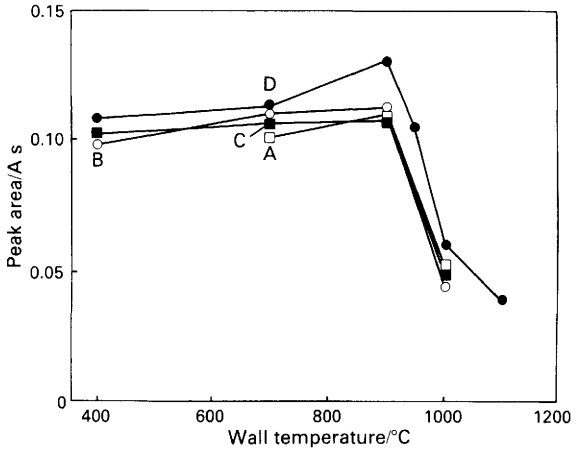

Fig. 3. Effect of grinding time on stabilisation of lead in a 4% *m/V* lettuce slurry by addition of 800 mg l^{-1} of palladium to the slurry. Duration of grinding: A, 15 min; B, 30 min; C, 1 h; and D, 3 h

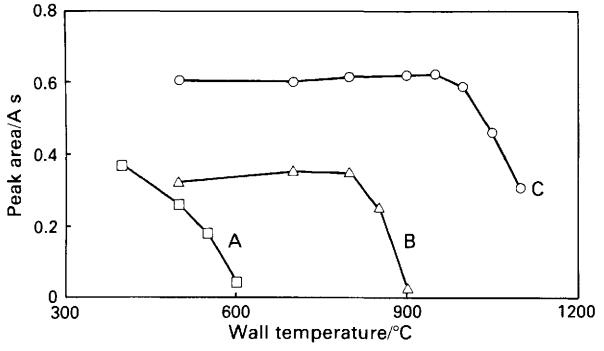

Fig. 4. Char curves for lead in a 4% *m/V* kale slurry with platform atomisation: A, no modifier; B, 0.5% *m/V* $NH_4H_2PO_4$; and C, 800 mg l^{-1} Pd

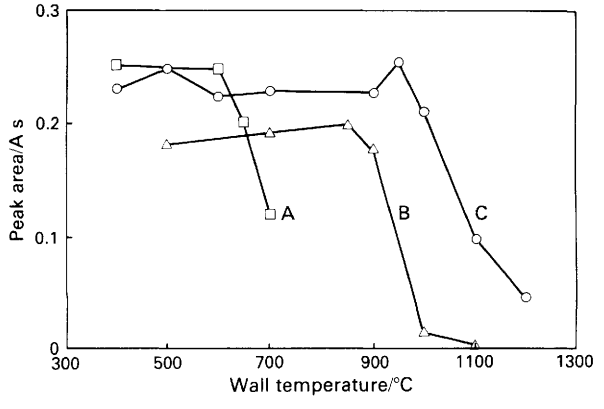

Fig. 5. Char curves for lead in a 4% *m/V* fish slurry with platform atomisation: A, no modifier; B, 0.5% *m/V* $NH_4H_2PO_4$; and C, 800 mg l^{-1} Pd

in aqueous solution. The maximum temperature at which lead in the slurry could be stabilised was approximately 900 °C, slightly lower than for lead in solution (950 °C). The concentration of palladium added to slurries and aqueous standards to give maximum stability of lead was 800 mg l^{-1} and this was used in all subsequent investigations and analyses.

The char curves for lettuce slurries prepared from samples ground for various lengths of time were found to be similar (Fig. 3). It is known that for similar samples[14] an increase in the grinding time reduces the percentage composition of large particles so it seems that the stabilisation of lead by palladium is not particularly sensitive to differences in the sample particle size distribution for grinding times of 15 min to 3 h.

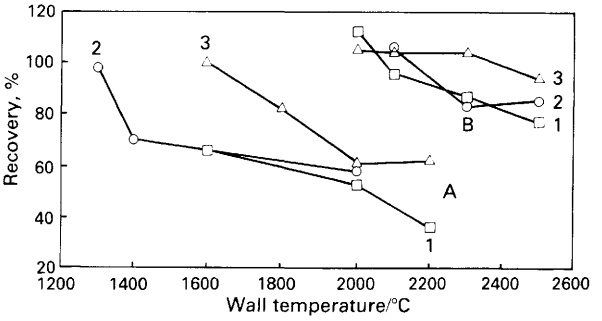

Fig. 6. Effect of varying atomisation temperature on percentage recovery of added lead (2 ng) using a pre-atomisation cooling step: A, 0.5% *m/V* $NH_4H_2PO_4$ and B, 800 mg l^{-1} Pd; 1, 4% *m/V* lettuce slurry; 2, 4% *m/V* fish slurry; and 3, 4% *m/V* bovine liver slurry

Table 2. Furnace programme for the determination of lead in samples. Nitrogen was used throughout the study

Step	Set temperature/ °C	Ramp time/ s	Hold time/ s	Gas flow-rate/ ml min^{-1}
Dry	300	5	40	300
Char	1100	30	20	300
Cool	20	5	20	300
Atomise . .	2100	0	10	0
Clean . .	2600	1	2	300

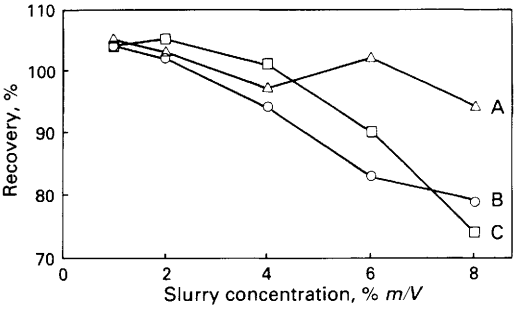

Fig. 7. Effect of varying slurry concentration on percentage recovery of added lead (2 ng) for some foodstuffs using 800 mg l^{-1} of Pd and platform atomisation with an atomisation temperature of 2100 °C: A, bovine liver; B, fish; and C, lettuce

Figs. 4 and 5 show char curves for a kale and a fish slurry, respectively, without addition of a modifier and with addition of either 0.5% *m/V* $NH_4H_2PO_4$ solution or 800 mg l^{-1} of Pd. The graphs clearly show that palladium permits the use of ashing temperatures approximately 150 °C higher than those obtained with 0.5% *m/V* $NH_4H_2PO_4$, while also avoiding the high background absorption that occurs when the latter is volatilised in a furnace. Without a modifier, the lead is stabilised to a higher temperature in the fish slurry, possibly due to its lower chloride concentration compared with the kale slurry.

Consideration of Stabilisation Mechanism

Several workers have considered the mechanism of increased thermal stability of various elements in a graphite furnace brought about by addition of palladium. Shan and Wang[44] from X-ray photoelectron spectra, suggested the formation of Pb–Pd and Bi–Pd bonds on the graphite surface. Electron-probe microanalysis by Teague-Nishimura *et al.*[37] has revealed that Se and Pd exist on the surface in a 1 : 1 mole ratio with no free Se being detected. Wendl and Müller-Vogt[45] identified the intermetallic compound Pd_3Pb using X-ray diffraction measurements.

Initially it was thought that the lead was extracted into the slurry diluent whereupon it came in contact with palladium permitting the formation of intermetallic species during the charring stage. This idea was rejected, however, because only 15% of the lead present in the kale sample was extracted into the diluent. Perhaps the palladium, dissolved in the slurry diluent, penetrated into the sample particles thus coming in close enough contact with the analyte to form an intermetallic compound. Reduction of Pd^{2+} to Pd^0 was probably assisted by the "active" carbon of the organic residue.

Stabilisation of Other Elements

Preliminary results indicated that palladium stabilises tin in food slurries to a temperature of approximately 1100 °C as compared with 800 °C with no modifier added.

The stabilising effect of palladium on cadmium has also been studied briefly. Palladium does not stabilise cadmium in an aqueous solution as well as a combination of $NH_4H_2PO_4$ and $Mg(NO_3)_2$ (stable to 800 and 900 °C, respectively). However, for food slurry samples stabilisation is achieved up to a temperature of 750 °C for both modifiers.

The performance of palladium as a modifier for cadmium, tin and other elements in food slurries is currently under investigation. Clearly, results so far suggest that palladium is a very useful modifier for the stabilisation of a range of elements in food slurries.

Optimisation of Atomisation Temperature

The rate of lead atom production differs markedly between food slurries and aqueous solutions. Therefore only peak-area measurements have the potential for allowing calibration by interpolation from a graph obtained from aqueous standards. To achieve this, atomisation must take place into a vapour which is approaching temporal isothermality. The mean residence time of analyte atoms in the vapour phase will therefore be independent of the sample matrix unless gas production results from the decomposition of the matrix remaining after sample ashing. The combination of chemical modifiers and platform atomisation with a pre-atomisation cooling step aims to delay atomisation until isothermality is approached.

For a specific tube wall heating rate, increasing the final atomisation temperature increases the rate of atom production from a platform and also the time taken to achieve a temporally isothermal vapour.[46] Therefore, above a specific final atomisation temperature volatilisation will no longer take place into a vapour approaching this ideal furnace condition. However, samples with a high halide content require a high vapour temperature to dissociate analyte halides. Clearly, careful optimisation of the atomisation temperature is necessary to achieve interference-free analysis.

Graphs of percentage recovery of added lead (2 ng) *versus* atomisation temperature are shown in Fig. 6 for 4% *m/V* food slurries using 0.5% *m/V* $NH_4H_2PO_4$ and 800 mg l^{-1} Pd as chemical modifiers. For the charring stage, set temperatures for lead of 900 °C with $NH_4H_2PO_4$ and 1100 °C with Pd were used. These corresponded to actual temperatures of approximately 700 and 900 °C, respectively. A pre-atomisation cooling step similar to that shown in Table 2 was also used. With $NH_4H_2PO_4$, quantitative recovery of lead was only achieved at an atomisation temperature of 1300 °C for a 4% *m/V* fish slurry and 1600 °C for a 4% *m/V* bovine liver slurry (MAFF Food Science Laboratory). Otherwise the recovery was 40–80% (Fig. 6). Conversely, Hoenig and Van Hoeyweghen[23] showed that when using $NH_4H_2PO_4$ as a modifier, it was possible to perform direct calibration for lead with an atomisation temperature of 2200 °C. The reason for this discrepancy is not clear, however, it may be due to the fact that they used a different graphite furnace and lower slurry concentrations. Also, it is possible that some temporal resolution of the analyte and interferent vaporisation may have occurred at the lower temperature settings, giving less interference.

Using palladium as a modifier enabled direct calibration to be performed when using higher atomisation temperatures (2000–2300 °C) and the signal was less sensitive to changes in atomisation temperature (Fig. 6). With the pre-atomisation step removed, poorer recoveries (60–80%) were obtained when atomising the fish sample using palladium as a modifier. This indicates that, for platform atomisation, the increased delay in vaporisation introduced by using the cooling step is of critical importance in achieving conditions suitable for direct calibration. Clearly, it could be suggested that the higher char temperature used with palladium (1100 °C compared with 900 °C for $NH_4H_2PO_4$) was responsible, at least in part, for the improved recoveries due to the removal of a greater proportion of interferents. This argument can be rejected as there was no significant deterioration in recoveries when palladium was used with a char temperature of 900 °C.

Fig. 7 shows that, using an atomisation temperature of 2100 °C (with palladium as modifier), direct calibration was only possible up to a slurry concentration of 4% *m/V* for fish and lettuce and 6% *m/V* for bovine liver. Above these concentrations the increase in mass of interferents resulted in systematic errors.

During this study recondensation of lead on to the cool ends of the graphite tube took place when platform atomisation occurred at temperatures of less than 2000 °C. This was discovered when atomisation of 20 µl of a 100 µg l^{-1} lead solution off a platform at ≤2000 °C was followed by a "blank firing" at 2500 °C which produced large signals. The same effect was observed when the platform was removed from the tube before the "blank firing" thus ruling out decreased atomisation efficiency from the platform as an explanation of the phenomenon.

Table 3. Ratio of slopes of standard additions to aqueous calibration graphs for lead in 4% *m/V* slurries of a variety of samples (± figures based on errors of two slopes)

Sample	Ratio ± 95% confidence interval
Lettuce	0.95 ± 0.06
Fish	0.99 ± 0.09
Pea	0.99 ± 0.15
Potato	0.99 ± 0.12
Liver	1.08 ± 0.08
Milk	1.08 ± 0.20

Table 4. Concentration of lead in foodstuffs (µg g^{-1}). A minimum of three determinations was performed on each sample with a slurry concentration of 4% *m/V*

Sample	Proposed method*	MAFF analysis*
Fish	1.10 ± 0.15	1.05 ± 0.2
Bovine liver	0.37 ± 0.20	0.21 ± 0.14
Kale	5.0 ± 0.5	4.5 ± 0.6
CRM 061 Aquatic plant material	60.0 ± 7.0	64.4 ± 3.5 (certified value)

* 95% confidence intervals included.
† Less sensitive lead wavelength, 368.3 nm.

Results of Analyses

The furnace programme used for the analysis of samples is shown in Table 2. For a variety of food slurries at a concentration of 4% *m/V*, the slopes of the standard additions and aqueous standard calibration graphs were shown to be similar with slope ratios being close to unity (Table 3). The

sensitivity of the proposed method is good. The lead characteristic mass of 19 pg per 0.0044 A s was within a factor of two of the 11 pg per 0.0044 A s value reported previously.[47] Analysis of several samples (Table 4) indicated that reasonably accurate results could be obtained using the slurry method. The slurry analyses results compare well with concentrations obtained at the Ministry of Agriculture, Fisheries and Food (MAFF) Food Science Laboratory, Norwich, UK, using a method based on acid digestion, chelation extraction, if necessary, and analysis by ETAAS.

The detection limit (2σ) of lead was estimated to be 200 ng g^{-1}. However, the limit of detection for an aqueous lead solution was 5–10 μg l^{-1}, at least five times higher than expected indicating poor instrumental stability. It is therefore considered that there is scope for improving the lead detection limit for slurry analysis, to <100 ng g^{-1}.

Conclusions

The slurry method of analysis described here, using palladium as a chemical modifier with platform atomisation, allowed direct calibration with aqueous standards for the determination of lead in slurries for up to 4% *m/V*. Above this, systematic errors in sample introduction and interferences necessitate the use of standard additions calibration. Measurements for cadmium and tin indicated that palladium shows promise as a general modifier for the analysis of slurries by ETAAS.

The authors thank the Ministry of Agriculture, Fisheries and Food (MAFF) for providing financial support for S. L.

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Paper 8/04059A
Received October 12th, 1988
Accepted December 22nd, 1988