

This article was downloaded by: [McGill University Library]
On: 01 November 2014, At: 04:05
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number:
1072954 Registered office: Mortimer House, 37-41 Mortimer Street,
London W1T 3JH, UK



Communications in Soil Science and Plant Analysis

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lcss20>

Analysis of indigenous zinc in alkaline sodic soil solutions by graphite furnace atomic absorption spectrometry

A. Fotovat^{a,c}, L. Smith^b, R. Naidu^b & J. M. Oades^a

^a Department of Soil Science, Waite Agricultural Research Institute, University of Adelaide, Waite Road, Urrbrae, Adelaide, SA, 5064, Australia

^b Division of Soils, CSIRO, PMB No. 2, Urrbrae, Adelaide, SA, 5064, Australia

^c Soil Science Department, College of Agriculture, University of Ferdowsi, Mashhad, Iran

Published online: 11 Nov 2008.

To cite this article: A. Fotovat, L. Smith, R. Naidu & J. M. Oades (1996) Analysis of indigenous zinc in alkaline sodic soil solutions by graphite furnace atomic absorption spectrometry, *Communications in Soil Science and Plant Analysis*, 27:18-20, 2997-3012, DOI: [10.1080/00103629609369757](https://doi.org/10.1080/00103629609369757)

To link to this article: <http://dx.doi.org/10.1080/00103629609369757>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Analysis of Indigenous Zinc in Alkaline Sodic Soil Solutions by Graphite Furnace Atomic Absorption Spectrometry

A. Fotovat,^{a,1} L. Smith,^b R. Naidu,^b and J. M. Oades^a

^a*Department of Soil Science, Waite Agricultural Research Institute, University of Adelaide, Waite Road, Urrbrae, Adelaide SA 5064, Australia*

^b*CSIRO Division of Soils, PMB No. 2, Urrbrae, Adelaide SA 5064, Australia*

ABSTRACT

Analytical determination of ultra low levels of micronutrients in soil solutions is one of the major problems limiting trace element studies in alkaline sodic soils. The low concentrations of trace metals in environmental samples are often measured by the graphite furnace atomic absorption spectrometry (GFAAS) technique. However, considerable difficulty was found with zinc (Zn) determination in alkaline sodic soil solutions. The effects of various chemical modifiers (phosphoric acid, ammonium phosphate, nitric acid, and palladium (Pd)) on GFAAS determination of ultra trace levels of Zn in soil solutions of four alkaline sodic soils were investigated in this study. The concentration of Zn in the soil solution was significantly ($P < 0.01$) higher in the presence of modifiers relative to that determined in the absence of modifiers. In addition, coefficient of variance [(CV) 21.5%] in the absence of chemical modifiers was up to three times higher than those determined with chemical modifiers (7 to 10.2%). Chemical modifiers also decreased

¹Corresponding author (permanent address: Soil Science Department, College of Agriculture, University of Ferdowsi, Mashhad, Iran).

the characteristic concentration (increased sensitivity). The decrease ranged from 22.1 to 34.6% for Pd and phosphoric acid, respectively, compared to that in the absence of chemical modifiers. The maximum ashing temperature for standard Zn solution increased from 300°C in the absence of modifiers to 800°C with phosphoric acid and ammonium phosphate, indicating increased stability of Zn at high temperatures. Based on the recovery test data, characteristic concentration, atomization temperature, and the shape of atomic signal peak, analysis of Zn in the presence of phosphoric acid was recommended for soil solution Zn.

INTRODUCTION

Micronutrient deficiency, in particular trace metals, is one of the major problems limiting crop production in sodic soils. The DTPA-extractable trace elements are commonly used as indicators of plant available micronutrients in soils. Such extractions generally provide an indication of the adsorbed and soluble trace metal concentrations in soils. However, for a detailed understanding of the chemistry of trace metals, information on their concentration in soil solution is required. Furthermore, plants derive nutrients from the soil solution. Numerous investigators (Bansal et al., 1980; Mahler et al., 1980; Mitchell et al., 1978) have shown that cadmium (Cd), copper (Cu), and Zn concentrations in the soil solution correlated with their contents in wheat and lettuce. Also, plant responses to the soil chemical changes can be predicted by understanding soil solution characteristics (Pearson, 1971). Lorenz et al. (1994) reported that soil solution data can give useful information on the dynamics of ions within the soil profile and over time, or the bioavailability of nutrients or toxic elements. In addition, soil solution composition is the result of the different physical, chemical, and biological reactions occurring in the soil (Sheppard et al., 1992). Therefore, an estimate of the concentration of elements in the soil solution will provide a better indication of plant available trace metals and their chemical forms that is active in transporting metals to the plant roots (Barak and Helmke, 1993; Naidu and Helmke, 1996) and into the ground waters.

The concentrations of trace elements including Zn in soil solutions are very low (Yamasaki et al., 1975). Usually, analytical determination of ultra low (<0.01 ppm) levels of micronutrients in soil solutions limit trace element studies in the soils (Yamasaki et al., 1975; Jeffery and Uren, 1983; Linehan et al., 1989; Helmke and Naidu, 1996). Presumably because of the analytical difficulties, data on trace elements in soil solution at indigenous levels are limited. Also, the concentration of Zn as a micronutrient is inversely related to the soil pH (Lindsay, 1972). This constraint is further compounded in sodic soils by the high pH that leads to lower solubility and even lower concentrations of trace metals in soil solutions.

Graphite furnace atomic absorption spectrometry (GFAAS) is commonly used for determination of trace elements in various environmental samples. While this technique provides excellent analytical sensitivity, is relatively convenient, rapid, accurate, requires a small sample volume, and is applicable to trace elements, ultra low concentrations of analyte in soil solutions can prove difficult to analyze due to matrix and/or chemical interference problems. Chemical interference is one of the major constraints to using GFAAS since it complicates the use of the method for the more volatile elements such as Zn (Voth-Beach, 1985). Such interferences are often overcome by including chemical modifiers (Burrell and Güner Wood, 1969) and by optimizing the furnace parameters. For example, Matousek and Brodie (1973), Czobik and Matousek (1977), and Brodie (1985) have shown that H_3PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ permit a higher ashing temperature and stabilize the absorbance signal in lead (Pb) determination by the graphite furnace. Furthermore, Pd has been used as the modifier in gallium (Ga) analysis (Shan et al., 1985). The use of Pd for samples having oxidizing components like HNO_3 , Na_2SO_4 , and H_2SO_4 requires a reducing agent such as ascorbic acid to be added (Beach, 1985).

Although there are numerous GFAAS methods of determining trace elements, this study found considerable difficulty with the analysis of Zn in alkaline sodic soil solution. Direct injection of soil solution led to broad analyte peaks and often large relative standard deviation (RSD) values. The objective of this paper is to present a comparative study of the effect of various chemical modifiers and furnace parameters on GFAAS analysis of Zn in alkaline sodic soil solution.

MATERIALS AND METHODS

Sample Preparation and Separation of Soil Solution

Four alkaline soils with pH ranging from 7.7 to 8.9 were used in this study (Table 1). Following drying, the soil samples were crushed gently by a plastic grinder to pass through a 2-mm stainless steel sieve and stored in polyethylene bags. Soil samples were then weighed into polyethylene bags, the appropriate volume of deionized water was added to reach field capacity (FC) soil water content (to matrix suction of 30 KPa) and mixed to aid redistribution of the water. The tops were then folded down and the bags placed in a single layer on a tray at 25°C to incubate for 24 h. A centrifugal method for obtaining soil solution as described by Gillman (1976) and Adams et al. (1980) with some modifications to minimize contamination was used for the isolation of the soil solution. Moist soil was packed into centrifuge tubes designed to allow flow of soil solutions into cups attached to the finely perforated bottom of the tubes and centrifuged at 9000 rpm (RCF, 10,800 g) for 1 h. After centrifuging, the soil solution was transferred to 2 mL polyethylene vials and filtered by centrifuging with a RCF of 15,800 g for 1 h to minimize colloidal contamination of the soil solution.

TABLE 1. Selected properties of the soils used in the experiment.

Soil	pH _{w(1:5)}	EC _{1:5} (dS m ⁻¹)	SAR* _{1:5}	Organic matter (%)
1	8.9	0.45	6.9	0.5
2	7.7	0.09	0.4	0.9
3	7.9	0.13	2.1	0.5
4	8.3	0.16	2.7	0.3

*Sodium adsorption ratio.

Apparatus

A SpectrAA-400 (Varian Australia Pty Ltd, Mulgrave, Victoria) spectrometer equipped with a GTA-96 graphite tube atomizer and DS-15 data station displaying atomization stage was used. Generally, the standard conditions given by the manufacturer were followed. Tubular furnaces coated with pyrolytic graphite were used. Hollow-cathode lamps were operated according to the manufacturer's recommended comments for all the measurements. Signals for Zn absorbance were obtained at 213.9 nm. Argon was employed as the protective inert gas at a 3 L min⁻¹ flow-rate. A deuterium background corrector was used for determination of Zn. Solutions were introduced into the furnace through the microliter pipette of the auto sampler which had disposable Teflon tips. Samples were then dried for 50 sec. In a preliminary test, this drying stage period was the minimum time required to dry the sample without boiling. The furnace temperature at the end of drying reached 240°C. The samples were ashed for 26 sec at appropriate temperature. The period of atomization was 2.8 sec at 1800°C with a ramp rate of 1750°C sec⁻¹. The height of peak absorption vs. time profile was measured as an indicator of absorbance.

The volume of the sample dispensed in the furnace tube was 5 µL and that of the modifier was 5 µL whenever it was applied. In this regard, 5 µL of the solution, 5 µL of deionized water as blank, and 5 µL of appropriate chemical modifier were dispensed into the partition tube. The volume of blank was 10 µL when no modifier was used. When Pd was used as modifier 5 µL of Pd solution and 5 µL of ascorbic acid as blank along with Zn standard or soil solution were applied.

The data were analyzed by randomized complete design with three replications. Standard errors were calculated and are demonstrated as error bars in the figures if the standard error was greater than the diameter of the data point.

Reagents

A Zn stock solution (1000 mg L⁻¹) was prepared by dissolving 4.57 g of high purity AR grade Zn(NO₃)₂·6H₂O in an adequate volume of dilute nitric acid (HNO₃)

and diluting to one L with deionized water. The final concentration of HNO_3 was 1%. All other working standards were prepared from this stock solution by serial dilution with deionized water. Monobasic ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) solution 0.1% (w/v), phosphoric acid (H_3PO_4), and nitric acid solutions 0.1% (v/v) were prepared with deionized water. A Pd solution was prepared by dissolving 2.41 g of Pd chloride dihydrate ($\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$) in deionized water. This solution contained 1200 mg Pd L^{-1} . A solution of Pd with concentration of 500 mg L^{-1} was then made from this stock solution. A 0.01% (w/v) solution of ascorbic acid [$\text{CH}(\text{OH})\text{-CH}_2\text{OH}$] as reducing agent was freshly prepared from analytical-reagent materials just before use.

Because the concentration of Zn was extremely low, precautions were taken during the extraction and analysis of the soil solutions to minimize contamination. Before use, all plastic, glassware, and soil solution extraction equipment were washed with Milli-Q deionized water, soaked overnight in 5M HCl solution, rinsed again with the deionized water, and dried. Milli-Q deionized water was also used for preparation of solutions. Zinc was not detected in the blank solutions analyzed prior to and during the analysis of all sample solutions, confirming no contamination.

Recovery Test

For the recovery test in each soil, an aliquot of a sample was diluted with equal parts of the zero Zn standard and another aliquot was diluted with equal parts of known Zn standard solution (4 replicates). The percent recovery (%) of the samples was calculated from the ratio of the concentration of the sample plus the standard minus the sample plus zero standard to half of the concentration of the standard added (Baker and Suhr, 1982).

Characteristic Concentration

Sensitivity, or more precisely characteristic concentration, is a valuable diagnostic property of the analysis in analytical chemistry in atomic absorption technique (Slavin et al., 1983). This value is approximately equal to the detection limit and shows the minimum concentration at which quantitative measurement for the interested element can be performed. The characteristic concentration for the graphite furnace for Zn determination was calculated as follows:

$$CC = \frac{CM}{V} \quad [1]$$

where,

CC = characteristic concentration $\mu\text{g L}^{-1}$ for a particular sample volume

CM = characteristic mass in picogram (pg)

V = sample volume in μL

The characteristic mass can be calculated after measuring the absorbance of a known volume of a known concentration as follows:

$$\text{Mass of sample in pg} = \text{volume in } \mu\text{L} \times \text{concentration in } \mu\text{g L}^{-1}$$

$$\text{Characteristic mass} = \frac{\text{mass of sample} \times 0.0044}{\text{absorbance of sample}} \quad [2]$$

The value 0.0044 is 1% absorption signal in absorbance unit (AU) (Irving et al., 1978).

Ashing Temperature

To study the effect of ashing temperature on the height of atomic absorption signal peak in the presence and absence of the chemical modifiers 0.02 ng Zn was used at ashing temperatures ranging from 300 to 800°C. The same temperature range was utilized to investigate the influence of ashing temperature on the Zn content of four soil solutions with and without use of the chemical modifiers.

RESULTS AND DISCUSSION

Analyte Peak and Ashing Temperature

The effect of modifiers on the atomization peak shape of Zn in the soils studied are shown in Figures 1a and 1b. Only the peaks for phosphoric and nitric acid are illustrated. Chemical modifiers had a marked effect on the width at half height

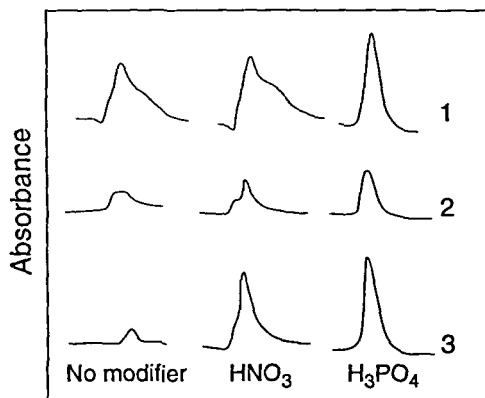


FIGURE 1a. The effect of modifiers on the atomization peak shape of Zn in soils 1, 2, and 3.

(WHH) and the size and shape of the analyte atomization peak. The atomization peaks in complex matrices can produce shifts in appearance time and multiple peak maxima, as well as peak height suppression (Voth-Beach, 1983). As can be seen from Figures 1a and 1b, the direct injection of soil solution resulted in a broad peak. The small analyte peak together with the large WHH indicate lower sensitivity, presumably due to incomplete atomization of the analyte species. Skoog and Leary (1992) emphasized that signal depression implies chemical interference. Chemical interference can be minimized by the inclusion of chemical modifiers. Czobik and Matousek (1977) examined the effect of anions on atomization temperature in furnace atomic absorption and concluded that high atomization temperatures and narrow peak-width indicate a faster rate of atom production. These investigators reported that a faster rate of atom production could also lead to a faster loss of atomic population, mainly because of increased diffusion at the higher temperature. However, the current investigation of the effect of various modifiers on ashing temperature suggests that of the four modifiers examined there was minimal loss of the analyte species in the presence of phosphate.

The effect of the presence of chemical modifiers on the ashing temperature and stability of Zn in the ashing stage in a standard solution (0.04 ng of Zn) is illustrated in Figure 2. Zinc showed maximum stability at 300°C in the absence of chemical modifiers. Above 300°C the atomization signal decreased rapidly to <0.1 AU (absorbance unit). Use of Pd and HNO₃ increased the stability of Zn up to 500°C, above which absorbance decreased to <0.1 AU. This indicates that addition of

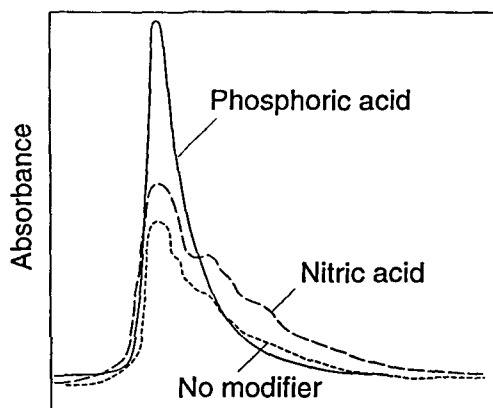


FIGURE 1b. A typical example of the effect of modifiers on the atomization peak shape of Zn (soil 4).

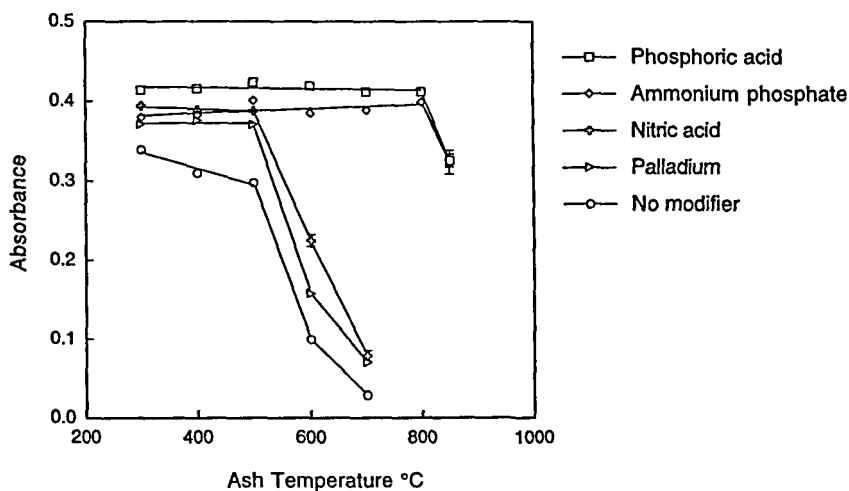
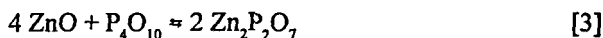


FIGURE 2. The effect of modifiers on the ashing temperature of Zn in standard solution.

either Pd or HNO₃ modifiers can enhance the stability of the analyte species up to 500°C. The lower stability of the analyte species above 500°C in the presence of nitric acid (Figure 2) may be attributed to the loss of the acid by evaporation during the drying and ashing stage or to the formation of compounds that decompose during the ashing stage or the very early stage of atomization.

In contrast to Pd and HNO₃, the presence of either NH₄H₂PO₄ or H₃PO₄ increased the stability of Zn species up to 800°C (Figure 2). This is consistent with the studies of Czobik and Matousek (1977), who found that PO₄ increased atomization temperature of Zn in the graphite furnace. They attributed the increased stability of the analyte species to the greater thermal stability of Zn pyrophosphate, which is formed in the presence of H₃PO₄ (Equation 3). Pyrophosphate formation is enhanced because H₃PO₄ persists in the graphite furnace up to relatively high temperatures (Czobik and Matousek, 1977).



The observed effect of chemical modifiers persisted when Zn in sodic soil solutions was analyzed using the graphite furnace (Figures 3 and 4). However, the maximum ashing temperature with direct injection varied between 300 and 600°C among the soil solutions examined, probably indicating chemical interference arising from the presence of both organic and inorganic ligands that can complex Zn. Indeed, recent studies by Naidu et al. (1995) suggest that

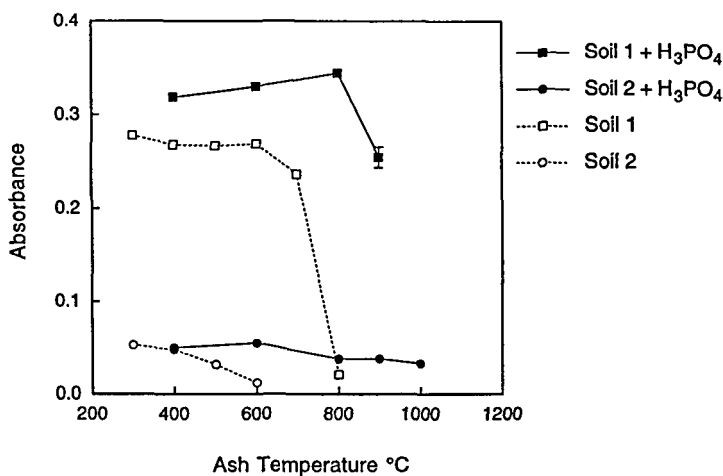


FIGURE 3. The effect of phosphoric acid on ash temperature of Zn in solutions of soils 1 and 2.

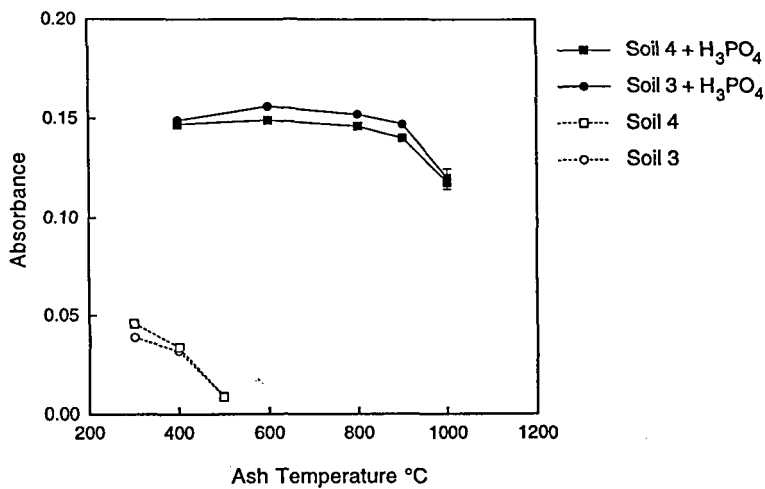


FIGURE 4. The effect of phosphoric acid on ash temperature of Zn in solutions of soils 3 and 4.

concentrations of dissolved organic carbon, sulphate, and phosphate in sodic soil solutions vary considerably. Such variations in ligand concentration can result in the presence of a wide range of Zn organic and inorganic ligand complexes. As with the standard solutions, inclusion of H_3PO_4 increased the stability of Zn species in soil solution during the ashing stage to temperatures exceeding 800°C . These results indicate that chemical interference in soil solution analysis of Zn may be overcome by using H_3PO_4 as the chemical modifier.

Although there are other methods of eliminating chemical interference, most of them are not applicable to solutions with elements present in trace amounts. For example, dilution of the sample solution can be used to reduce chemical interference. However, dilution can lead to concentrations below the detection limit of the instrument, especially in solutions with ultra trace levels of analyte species. Such a problem may be prevalent in alkaline sodic soil solutions, which are often low in trace elements with concentrations of Zn <1 to $2 \mu\text{g L}^{-1}$ but high in ligand ions; in such solutions ten times dilution will reduce the concentration to $<0.1 \mu\text{g L}^{-1}$. In $10 \mu\text{L}$ diluted soil solution, this dilution represents an absolute mass of 1 pg Zn , which produces an absorbance signal of about 0.015. Such a value is not acceptable for routine analysis where high precision is required (Hoenig, 1985). Additionally, another factor limiting the applicability of the other methods is the low volume of the soil solution. The volume of solution extracted from soil at field capacity (FC) soil moisture is often not enough to apply pre-concentration techniques (Yamasaki et al., 1975).

The Effect of Modifiers on Characteristic Concentration

The effect of chemical modifiers on sensitivity of Zn estimated by GFAAS was determined by characteristic concentration. Characteristic concentration is defined as the concentration of an element in solution that produces a 1% absorption signal (i.e., absorbance of 0.0044) (Irving et al., 1978). This concentration, which is usually expressed in $\mu\text{g L}^{-1}$, was previously defined as the sensitivity of the analytical technique. However, the term "sensitivity" which is conceptually the reciprocal of the International Union of Pure and Applied Chemistry (IUPAC) definition of the word (Slavin et al., 1983) is now considered unsuitable and characteristic concentration is preferred. Slavin et al. (1983) believed that characteristic concentration is an extremely significant diagnostic quantity for GFAAS. A lower characteristic concentration gives a steeper calibration curve, permitting the minimum concentration at which quantitative measurement can be accomplished to be lower. In other words, a smaller characteristic concentration indicates better accuracy.

Table 2 shows the decrease of characteristic concentration for 20 pg of Zn in the presence and absence of the chemical modifiers. The values shown in Table 2 are averages of six replications. In this table, the amount of decrease of

TABLE 2. The percentage of decrease in characteristic concentration by the use of the modifiers.

Modifier	Increase in characteristic concentration (%)	Standard error of mean
No modifier	-	-
Pd	22.1	±0.40
HNO ₃	26.5	±0.45
N ₂ NH ₄ PO ₄	29.3	±0.80
H ₃ PO ₄	34.6	±0.62

characteristic concentration (or increase of sensitivity) in the presence of the modifiers was compared with the characteristic concentration obtained in the absence of the modifiers. As can be seen from Table 2, the characteristic concentration decreased with the use of modifiers. Characteristic concentration was lowest in the presence of H₃PO₄ (highest sensitivity). The magnitude of decrease in characteristic concentration was 34.6% for H₃PO₄ relative to direct injection. However, this value was 29.3% for NH₄H₂PO₄, 26.5% for HNO₃, and 22.1% for Pd.

TABLE 3. The concentration of Zn in the soil solutions in the absence and presence of the chemical modifiers (numbers in brackets are standard error of mean).

Modifier	Soil 1	Soil 2	Soil 3	Soil 4
No modifier	3.44 (±0.03)	0.49 (±0.01)	0.35 (±0.01)	0.41 (±0.04)
Pd	3.27 (±0.03)	0.81 (±0.02)	2.01 (±0.03)	1.47 (±0.02)
H ₃ PO ₄	3.29 (±0.02)	0.63 (±0.02)	1.93 (±0.02)	1.70 (±0.03)
HNO ₃	3.43 (±0.04)	0.64 (±0.01)	2.14 (±0.02)	1.46 (±0.01)
N ₂ NH ₄ PO ₄	3.45 (±0.03)	0.79 (±0.01)	1.98 (±0.03)	1.43 (±0.01)
LSD _{0.01}	0.14	0.06	0.10	0.10

Zinc Concentration in the Soil Solutions and Recovery Test

Table 3 shows the concentration of Zn in the soil solution measured either with or without modifiers. The values shown are averages of measurements on solutions extracted from triplicate soil samples. The concentration of Zn in the solution of soils ranged from 0.4 to 3.5 $\mu\text{g L}^{-1}$ (0.01 to 0.05 μM). These values are consistent with those of Hodgson et al. (1966), who used pre-analysis concentration for Zn measurement by flame atomic absorption in calcareous soils. The concentration of Zn measured in the absence and presence of the chemical modifiers in all of the soils showed significant differences ($P < 0.01$). For example, the value in soil 3 measured in the presence of the chemical modifiers was about five times higher than in the absence of modifiers (Table 3). However, soil 1 showed little difference in the presence of chemical modifiers.

There was reasonable agreement between the amounts of Zn added to the soil solution and the amounts recovered (Table 4, mean values of four replications for each soil solution). Although recovery ranged from 92.3% in the samples analyzed directly to 95.9% with H_3PO_4 as the modifier, the coefficient of variance (CV) varied considerably (Table 4). The highest recovery with H_3PO_4 as the chemical modifier confirms the earlier observations for the characteristic concentration, illustrating the high sensitivity of this method.

The CV in the absence of a modifier was between two and three times higher than when samples were analyzed with modifier. These results indicate that the recovery is low in the absence of modifiers. For instance, very poor levels of recovery (30 to 40% correction) were observed in soils 2 and 4 when Zn was determined in the soil solution without the addition of modifiers (data not presented). From the results it is obvious that the use of modifiers, in particular H_3PO_4 , enhances Zn determination in alkaline sodic soil solutions. The modifiers

TABLE 4. The effect of modifier on the recovery and coefficient of variation (average of four soils) of Zn measurement.

Treatment	Recovery (%)	Coefficient of variance (CV) (%)
No modifier	92.3	21.5
Pd	94.6	10.2
HNO_3	92.3	9.9
$\text{N}_2\text{NH}_4\text{PO}_4$	94.3	8.9
H_3PO_4	95.9	7.0

reduce the volatility of the analyte to allow steady state thermal conditions to predominate before the analyte is vaporized (Slavin et al., 1983). No previous results about the effect of H_3PO_4 on Zn in alkaline sodic soil solution have been reported, although Ediger (1975) and Slavin et al. (1983) have successfully used ammonium phosphate for Cd and Pb analysis.

CONCLUSIONS

The use of all four modifiers improved measurement of ultra low concentrations of Zn in alkaline sodic soil solutions. Among the different modifiers applied, H_3PO_4 caused the greatest increase in ashing temperature. It allowed the use of higher ashing temperatures by decreasing the volatility of the Zn through the formation of more thermally stable species. The H_3PO_4 also gave lower characteristic concentration (better sensitivity). A lower CC produces a steeper calibration curve and yields better differentiation (or resolution) of lower levels of differences. In other words, H_3PO_4 improved analytical precision. Moreover, H_3PO_4 improved the analytical sensitivity by producing a sharp atomization peak, rather than the broad peaks resulting from the decomposition and atomization of a number of different molecular species present in a sample.

Phosphoric acid appears to be the most effective modifier, based on the recovery test results, characteristic concentration, gradient of the calibration curve, the reproducibility of the analyte species, ashing temperature, and atomic absorption peak shape analysis. Phosphoric acid, therefore, improves the precision of Zn measurement in soil solutions of alkaline sodic soils containing ultra low levels of this element.

Furthermore, this study shows that results obtained for Zn analysis using GFAAS in the absence of computer aided display of the atomization peak shape could be questionable. This is because measurements with incomplete atomization stages will nevertheless give absorbance, that do not reflect the true sample Zn concentrations. Additionally, the graphic display of the atomization signal peak is a benefit in diagnosing interference problems (Voth-Beach, 1983).

REFERENCES

- Adams, F., C. Burmester, N.V. Hue, and N.V. Long. 1980. A comparison of column-displacement and centrifuge method for obtaining soil solutions. *Soil Sci. Soc. Amer. J.* 44:733-735.
- Baker, D.E. and N.H. Suhr. 1982. Atomic absorption and flame emission spectrometry, pp.13-27. In: A.L. Page, R.H. Miller, and D.R. Heeney (eds.), *Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties*. Soil Science Society of America, Madison, WI.

- Bansal R.L., P.N. Takkar, N.S. Sanota, and M.S. Mann. 1980. Evaluation of soil procedures for predicting Zn availability to wheat under calcareous alkaline field conditions. *Field Crops Res.* 3:43-51.
- Barak, P. and P.A. Helmke. 1993. The chemistry of zinc, pp. 1-13. In: A.D. Robson (ed.), *Zinc in Soils and Plants*. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Beach, K. 1985. Chemical modification using reduced palladium, pp. 157-168. In: E. Rothery (ed.), *Analytical Methods for Graphite Tube Atomizers*. Varian, Mulgrave, Australia.
- Brodie, K. 1985. The measurement of lead in food products by graphite furnace AA and Spectra 40. *Varian Instruments at Work*, No. 52, Mulgrave, Australia.
- Burrell, D.C. and G. Güner Wood. 1969. Direct determination of zinc in sea water by atomic absorption spectrophotometry. *Anal. Chim. Acta* 48:45-49.
- Czobik, E.J. and J.P. Matousek. 1977. Effect of anions on atomisation temperatures in furnace atomic absorption. *Talanta* 24:573-577.
- Ediger, R.D. 1975. Atomic absorption analysis with the graphite furnace using matrix modification. *Atomic Absorpt. Nwsl.* 14:127-130.
- Gillman, G.P. 1976. A centrifuge method for obtaining soil solution. CSIRO Australia Division of Soils, Div. Rep. No. 16.
- Helmke, P.A. and R. Naidu. 1996. Fate of contaminants in the soil environment: metal contaminants, pp. 69-93. In: R. Naidu, R.S. Kookuna, D.P. Oliver, S. Rogers, and M.J. McLaughlin (eds.), *Contaminants and the Soil Environment in the Australasia-Pacific Region*. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Hodgson, J.F., W.L. Lindsay, and J.F. Trierweiler. 1966. Micronutrient cation completing in soil solution: II. Complexing of zinc and copper in displaced solution from calcareous soils. *Soil Sci. Soc. Amer. J.* 30:723-726.
- Hoening, M. 1985. The direct determination of cadmium in blood by electrothermal atomisation with the graphite platform. *Varian Instruments at Work*, No. AA-49, Mulgrave, Australia.
- Irving, H.M.N.H., H. Freiser, and T.S. West. 1978. *Compendium of Analytical Nomenclature*. Pergamon Press, London, UK.
- Jeffery, J.J. and N.C. Uren. 1983. Copper and zinc species in the soil solution and the effect of soil pH. *Aust. J. Soil Res.* 21:479-488.

- Lindsay, W.L. 1972. Zinc in soils and plant nutrition. *Advan. Agron.* 24:147-186.
- Linehan, D.J., A.H. Sinclair, and M.C. Mitchell. 1989. Seasonal changes in Cu, Mn, Zn, and Co concentrations in soil in the root-zone of barley (*Hordeum vulgare* L.). *J. Soil Sci.* 40:103-115.
- Lorenz, S.E., R.E. Hamon, and S.P. McGrath. 1994. Differences between soil solutions obtained from rhizosphere and non-rhizosphere soils by water displacement and soil centrifugation. *European J. Soil Sci.* 45:431-438.
- Mahler, R.J., F.T. Bingham, G. Sposito, and A.L. Page. 1980. Cadmium-enriched sewage sludge application to acid and calcareous soils: Relation between treatment, cadmium in saturation extracts, and cadmium uptake. *J. Environ. Qual.* 9:359-364.
- Matousek, J.P. and K.G. Brodie. 1973. Direct determination of lead airborne particulates by nonflame atomic absorption. *Anal. Chem.* 45:1606-9.
- Mitchell, G.A., F.T. Bingham, and A.L. Page. 1978. Yield and metal composition of lettuce and wheat grown on soils amended with sewage sludge enriched with cadmium, copper, nickel, and zinc. *J. Environ. Qual.* 7:165-171.
- Naidu, R. and P.A. Helmke. 1996. Donnan equilibrium speciation of soil solution cadmium, copper and zinc in wheat soils from South Australia. *Aust. J. Soil Res.* (submitted).
- Naidu, R., P. Rengasamy, N.J. Delacy, and B.A. Zarcinas. 1995. Soil solution composition of some sodic soils, pp. 155-161. In: R. Naidu, M.E. Sumner, and P. Rengasamy (eds.), *Australian Sodic Soils: Distribution, Properties, and Management*. CSIRO, Melbourne, Australia.
- Pearson, R.W. 1971. Introduction to symposium: The soil solution. *Soil Sci. Soc. Amer. J.* 35:417-420.
- Shan, X.Q., Z. Yan, and Z.M. Ni. 1985. Determination of gallium in sediment, coal fly ash and botanical samples by graphite furnace AAS using nickel matrix modification. *Anal. Chem.* 57:857-861.
- Sheppard, M.I., D.H. Thibault, and P.A. Smith. 1992. Effect of extraction techniques on soil pore water chemistry. *Commun. Soil Sci. Plant Anal.* 23:1643-1662.
- Skoog, D.D. and J.J. Leary. 1992. *Principles of Instrumental Analysis*. Saunders College, New York, NY.
- Slavin, W., G.R. Carnrick, D.C. Manning, and E. Pruszkowska. 1983. Recent experience with the stabilised temperature platform furnace and Zeeman background correction. *Atomic Spect.* 4:69-86.

- Voth-Beach, L.M. 1983. Dealing with matrix interferences in the determination of the priority pollutant metals by furnace AA. *Varian Instruments at Work*, No. AA-34, Mulgrave, Australia.
- Voth-Beach, L.M. 1985. The reduction of matrix interferences utilizing the platform in graphite furnace AAS. *Varian Instruments at Work*, No. AA-54, Mulgrave, Australia.
- Yamasaki, S., A. Yoshino, and A. Kishita. 1975. The determination of submicrogram amounts of elements in soil solution by flameless atomic absorption spectrophotometry with a heated graphite atomiser. *Soil Sci. Plant Nutr.* 21:63-72.