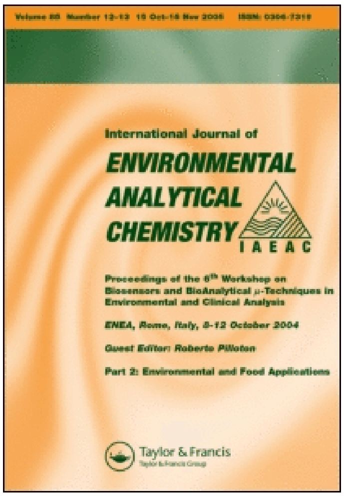

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Ure, M. , Thomas, R. and Littlejohn, D.(1993) 'Ammonium Acetate Extracts and Their Analysis for the Speciation of Metal Ions in Soils and Sediments', International Journal of Environmental Analytical Chemistry, 51: 1, 65 — 84

To link to this Article: DOI: 10.1080/03067319308027612
URL: http://dx.doi.org/10.1080/03067319308027612

Intern. J. Environ. Anal. Chem., Vol 51, pp. 65–84
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AMMONIUM ACETATE EXTRACTS AND THEIR ANALYSIS FOR THE SPECIATION OF METAL IONS IN SOILS AND SEDIMENTS

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(Received in final form, 17 July 1992)

The use of ammonium acetate (1 mol/1 at pH 7) extraction of soils and sediments for the speciation of metal ions is briefly discussed. Because the sensitivity of flame atomic absorption spectrometry (FAAS) is insufficiently sensitive for the determination of many of the heavy metals in ammonium acetate extracts of unpolluted, and even in some polluted soils, the use of electrothermal atomic absorption spectrometry (ETAAS) was studied. A general procedure, using graphite furnace atomisation and the "universal" matrix modifier, palladiun, was developed, that was sufficiently sensitive for the determination of Cd, Cr, Cu, Ni, Pb and Zn even in unpolluted soils. The concentration of zinc, however, will almost always be high enough for determination of FAAS and this method is to be preferred to ETAAS for this element.

While, for Cr, Cu, Ni and Pb, direct calibration with external standard solutions is practicable, it is necessary to use the standard additions calibration method for cadmium, to avoid matrix interference effects. The standard additions technique is recommended, however, because it compensates for real differences in the operating parameters of different instruments set to the same nominal values. This is particularly important for interlaboratory comparisons or for certification analyses in the preparation of reference materials.

KEY WORDS: Ammonium acetate extraction, soils, sediments, electrothermal atomic absorption, palladium matrix modifier, reference material.

INTRODUCTION

In unpolluted soils and sediments the trace metals, including those essential to life as well as those with toxic properties, exist mainly as relatively immobile species in silicates and primary minerals. As the result of weathering, a fraction of the trace element content is gradually mobilized to forms accessible to plants. In polluted soils the metal pollution input in nearly all cases is in non-silicate bound forms and contributes to the pool of potentially available metals. The situation in sediments is in principle very similar. The metal species arising from these mobilization or pollution processes can exist in several different soil or sediment phases. These include:

1) in solution, ionic or colloidal
2) in organic or inorganic exchange complexes as readily exchangeable ions
3) in complexes in which they are strongly bound

4) in insoluble mineral/organic phases
5) in precipitated major metal (Fe, Mn, Al) oxides and insoluble salts
6) in resistant secondary minerals.

In phase 1), above, the metals are available for uptake by plant or primitive biological forms and can be removed from the soil or sediment as the soil solution or sediment pore water by displacement, centrifugation or extrusion. Phase 2), above, containing the "readily exchangeable" ions, together with the Phase 1 water-soluble species, constitute the pool of trace metals that is most easily taken up by plants and other living matter into the food chain. From the point of view of assessing the likelihood of plant or animal deficiency or toxicity in agriculture or of metal induced toxicity from sediments used, for example as land-fill, these two phases are the most important, at least in the short term. This paper will be concerned with the use of ammonium acetate extraction as a method of quantifying the readily exchangeable fraction, and, in the process, also measuring the water soluble species.

The interest in choosing ammonium acetate as an extractant stems largely from its widespread use for the assessment in soils of cation exchange capacity, exchangeable bases and plant-available nutrients including manganese as well as (animal) toxicants such as molybdenum.

THE ION EXCHANGE PROCESS

The principal processes involved in the transfer of trace metals from the soil to the plant root are shown in Figure 1. (reproduced from Ref. [1] by kind permission of The Macaulay Land Use Research Institute) and illustrate the complexity of the soil chemistry. The reactions shown will also occur in the sediment situation. The figure shows the release of electrostatically bound cations, E^+, by hydrogen or calcium ions. This active displacement of metal ions by cations such as Ca^{2+}, K^+, Mg^{2+}, Na^+, and NH_4^+ can be represented by the equation

$$R\text{-}M^{2+} + Ca^{2+} \rightarrow R\text{-}Ca^{2+} + M^{2+}$$

where M^{2+} is the cation released by the ion exchange reaction.

While divalent cations are likely to be more effective in these displacement reactions, K^+ and NH_4^+ are often used because of their ability to replace ions in interlayer sites in some clay minerals [2]. A wide range of neutral solutions of salts, including ammonium acetate [3,4], ammonium nitrate [5], calcium chloride [6, 7], magnesium chloride [8], sodium nitrate [9], and potassium nitrate [10] have been used to assess exchangeable metal contents in soils, sediments and sewage sludges using both single and sequential extraction procedures. With ammonium salts of strong acids a lowering of the pH of the extraction can occur with the promotion of preferential attack by hydrogen ions on exchange sites and some hydrolysis of clay minerals. Salts of strong acids and alkali and alkaline earth elements have no effect on the pH of extraction but salts of weak acids, such as acetic acid, and strong bases may elevate the pH with the danger of precipitation of some metal hydroxides. In the case of ammonium acetate the complexation of released metal ions by acetate helps to retain them in solution and

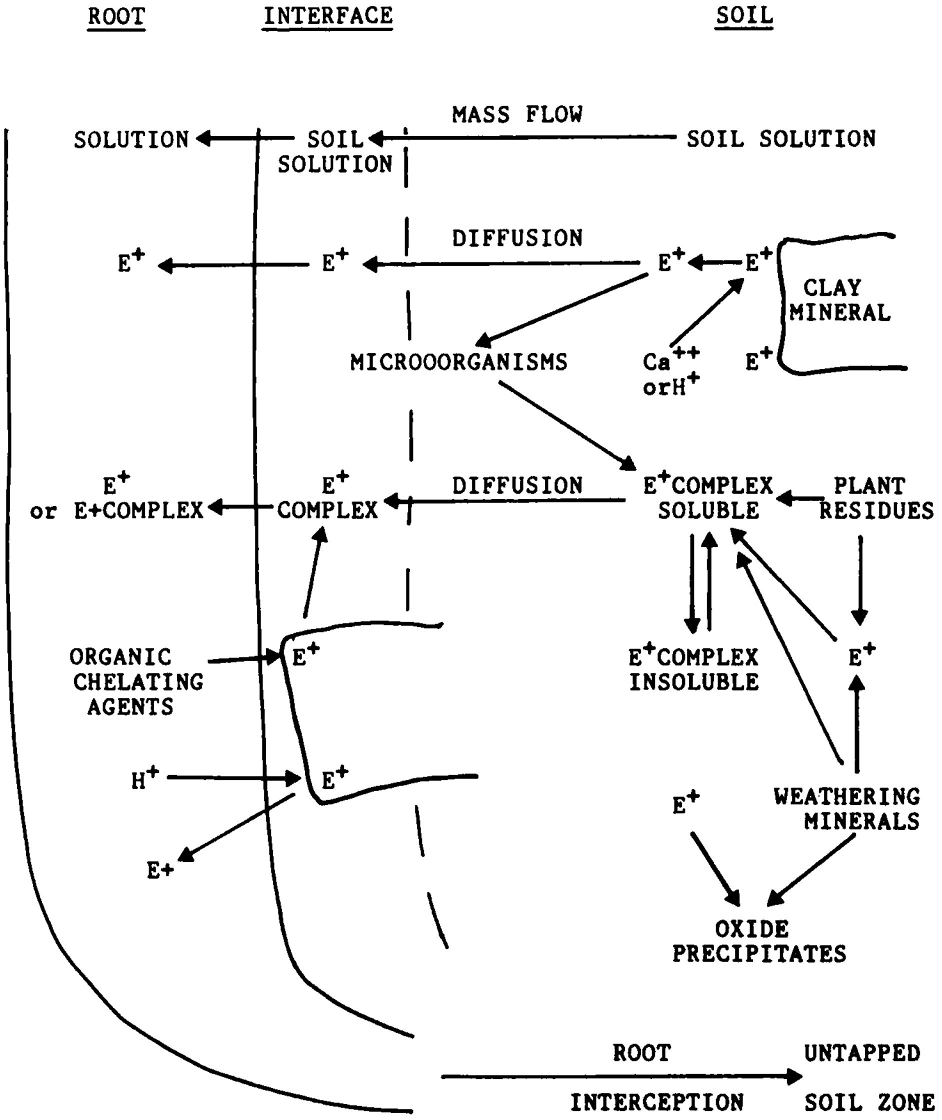


Figure 1 An illustration of the complex chemistry of the transport of metal ions from soil components into solution and interactions at the soil-root interface. Reproduced by permission of The Macaulay Land Use Research Institute, Aberdeen from reference 1.

minimizes the danger of precipitation. The concentration extracted will depend generally on the concentration of the neutral salt in the extracting solution. The salt concentration commonly used is around 1 mol/l but attempts to simulate conditions more likely to occur naturally have encouraged the use of lower concentrations e.g. 0.05 mol/l $caCl_2$ [6] and 0.05 mol/l $NaNO_3$ [9].

The principal advantage of solutions of ammonium salts over alkali and alkaline earth salts lies in the potential spectral, including background and scattered light, interference effects that can result from the use of relatively strong solutions of alkali and alkali metals in both flame atomic absorption and inductively coupled plasma emission spectrometric analysis. That ammonium acetate is the salt most commonly used is mainly due to the acetate complexation of liberated metal ions, which nullifies any potential problems of pH change in the extraction. The most commonly used concentration of ammonium acetate extracting solution at pH 7 is 1 mol/1.

RANGE OF AMMONIUM ACETATE EXTRACTABLE CONTENTS IN SOILS and ANALYTICAL SENSITIVITY

The ranges of the ammonium acetate extractable contents for the elements Cd, Ni, Pb and Zn in a range of 12 typical Scottish agricultural soils is shown in Table 1 [11]. These ranges were determined by direct current arc emission spectrometry following preconcentration by a co-precipitation procedure [12]. Notional limits of determination, based on approximately 10 times the detection limit, are also given in Table 1. It can be seen that only zinc is likely to be determinable in normal soils by flame atomic absorption (FAAS) or by inductively coupled plasma emission spectrometry (ICPOES). In a sewage sludge treated soils, such as the Great Billings soil used in the BCR interlaboratory study in 1989/1990 [13], the comcentrations found in the extract were as shown in Table 2. The concentration of zinc of about 1000 ug/1, or more, likely to be found in extracts of such polluted soils can readily be determined by FAAS and could only successfully be determined by ETAAS after dilution by a factor of about 100. In the remainder of this paper the application of ETAAS methods of analysis for ammonium acetate extracts of soils and sediments is discussed with respect to the heavy metals Cd, Cr, Cu, Ni, and Pb. This method of analysis is not considered suitable for the element zinc because of the relatively high concentrations likely to occur in such extracts and only marginal reference will be made to it in these discussions.

Table 1 Ammonium acetate extractable contents for 12 typical Scottish agricultural soils; ranges in extract and soil. 50g soil extracted with 800 ml of 1 mol/l ammonium acetate, pH7. Determination by direct current arc emission spectrometry following preconcentration by co-precipitation with 8-quinolinol [12].

Element	Extract range (mg/l extract)	Soil range (mg/kg dry soil)	Determination limit (mg/l solution)		
			FAAS	ICPOES	ETAAS
Cd	0.0025-0.0125	0.04 - 0.2	0.01	0.03	0.0001
Ni	0.0006-0.0125	0.009-0.2	0.1	0.1	0.001
Pb	0.0044-0.019	0.07 - 0.3	0.2	0.4	0.0005
Zn	0.0125-0.0625	0.2 - 1.0	0.01	0.2	0.0001

Table 2 Mean ammonium acetate concentrations extracted from the Great Billings sewage sludge treated soil (ug/l in soil extract) together with standard deviations and CVs.

	Cd	Cr	Cu	Ni	Pb	Zn
Mean	200	87	350	89	138	1150
Std. Dev.	23	35	81	20	37	260
CV %	10.9	40.6	23.4	22.5	26.8	22

ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY (ETAAS)

The objective of this study was to examine the method of ETAAS for the analysis of ammonium acetate extracts with particular reference to the elements Cd, Cr, Cu, Ni, and Pb. It was hoped that as far as possible a common procedure for all these elements could be developed and to this end the use of a so-called "universal modifier", viz. palladium nitrate, [14] was studied. This modifier requires an additional conditioning step in the furnace programme[15].

Extraction procedure

The extraction procedure followed that used in an earlier interlaboratory trial held under the auspices of the Bureau of Reference (BCR) of the Commission of the European Communities [13].

A 5g sample of dry <2 mm soil is extracted with 80 ml of 1 mol/1 ammonium actetate solution at pH 7 for 16 hours on an end-over-end mechanical shaker rotating at about 40 rpm. The filtrate is used for analysis. All apparatus was acid and distilled water washed and reagents were checked for purity.

Apparatus

Most of the experimental work was carried out using a Perkin Elmer 3030 atomic absorption spectrometer with a HGA 500 graphite furnace atomizer and an automatic sampling attachment. In order to verify the universality of the procedures and conditions established with this instrumentation analyses were carried out using the same furnace programme on this instrument and on a Unicam PU 9400 atomic absorption spectrometer fitted with a new model graphite furnace atomiser, type GF 90. Pyrolytically coated graphite tubes were used throughout.

Reagents

Ammonium acetate solutions prepared from Analar grade acetic acid and ammonia and Aristar ammonium acetate were analysed for their contents of the 6 analytes. Distilled water from two stills were also examined. In addition the 200 mg/l solution of palladium nitrate,

Table 3 Significant reagent blank concentrations (ug/l)

Element	Reagent	Concentration
Cd	Dist. Water	<0.2
	Amm. acetate, Analar	0.75
	Amm. acetate, Aristar	0.75
	Palladium nitrate (200ug/l)	0.7
Cr	Palladium nitrate (200ug/l)	1.0
Cu	Dist. Water "A"	1.4
	Dist. Water "B"	1.2
	Amm. acetate, Analar	4.4
	Amm. acetate, Aristar	1.9
	Palladium nitrate (200ug/l)	3.8
Ni	Palladium nitrate (200ug/l)	2.0
Pb	Palladium nitrate (200ug/l)	2.0
Zn	Dist. Water "A"	1.2
	Dist. Water "B"	0.5
	Amm. acetate, Analar	5.0
	Amm. acetate, Aristar	4.5
	Palladium nitrate (200ug/l)	>20

$Pd(NO_3)_2$, to be used as the matrix modifier was analysed for these analytes. The results in Table 3 show the significant blank concentrations found.

Aristar ammonium acetate had lower blank concentrations for copper and zinc but was not superior for cadmium to the Analar reagent. Significant but low concentrations of copper and zinc were also found. Palladium nitrate contributed significant but small (0.7 to 2 ug/l) blanks for Cd, Cr, Ni and Pb, somewhat higher (3.8 ug/l) for copper and very high (>20 ug/1) for Zn. This last high zinc blank reinforced the decision not to consider ETAAS as a suitable method of analysis forthis element. In the light of these findings Aristar ammonium acetate was used throughout for extraction and for the preparation of standard solutions.

Wavelengths

The wavelengths used were 228.8 nm for Cd, 357.8 nm for Cr, 324.8 nm for Cu , 232.0 nm for Ni, 283.3 nm for Pb and 213.9 nm for Zn. The 5000 times less sensitive, alternative 307.6 nm line was used for Zn determinations in polluted soils.

Optimization of char temperature

The optimization of char temperatures for Cd, Cr, Cu, Ni, and Pb in the presence of palladium modifier and for Zn without modifier are shown in Fig. 2 A, B and C. A common "dry" temperature, 130 C, and time, 40 s, were used and 10 ul injections of sample solution and of palladium nitrate solution (200 mg/l) were made. The final optimised furnace programme is shown in Table 4 and was used thereafter.

The effect of the ammonium acetate matrix compared with an aqueous matrix on Cd, Cr, Cu, Ni, and Pb is shown in Fig. 3 A, B, C, D and E, and summarised in Table 5. Although there is a demonstrable effect on all the elements except cadmium when peak height

Table 4 Optimized ETAAS furnace programme.
Injection: 10 ul sample + 10 ul matrix modifier
Matrix modifier, 200 mg/l palladium nitrate used for all elements except Zn

step	temp °C	time (s)
DRY	130	40
CONDITION	500	10
CHAR (Cr, Cu, Ni, Pb)	1200	10
CHAR (Cd)	800	10
CHAR (Zn)	500	10
ATOMIZE (Cd, Cu, Pb)	2500	2
ATOMIZE (Cr, Ni)	2600	3
Atomize (Zn)	1600	2
CLEAN (All except Zn)	2700	2
CLEAN (Zn)	2000	2

measurement is used the effect is virtually non-existant, when peak area measurement is used, for all the elements except lead. For lead the ammonium acetate matrix effect remains considerable whether or not peak height or peak area measurement is used. All standard solutions were matrix matched with respect to ammonium acetate concentration and dilutions, where required, were made with 1 mol/l ammonium acetate.

Analysis of normal, unpolluted soils

Ammonium acetate extracts of a series of arable topsoils, untreated with sewage sludge, were analysed for Cd, Cr, Ni or Pb. At the low concentrations of copper and zinc extracted from these unpolluted soils the blank levels were too high for reliable analysis and these elements were excluded. These analyses were carried out directly using external standard solutions in ammonium acetate for calibration and also by the standard additions technique. Peak area measurements were used throughout. The results are presented graphically in Fig. 4, A and B, and in Table 6. These show that for Cr, Ni and Pb the standard addition graph is essentially parallel to the normal calibration graph and this can be interpreted as the absence of any systematic effect of the soil matrix on the sensitivity of the measurement. Thus minimal interference effects are likely on these three elements and direct calibration with external standard solutions can be used. For Cd, however, there is some indication of a slightly lower slope for the standard additions graph, Fig. 4A, which would suggest a small depressive effect of the soil matrix. Although background correction with a deuterium lamp was used, the possibility of errors due to the the effects of a structured background, only correctable by Zeeman or Smith-Hieftje background correction methods, should be borne in mind in interpreting the differences for cadmium in Tables 6 and 8 obtained by the two calibration procedures. When it is considered that the concentrations in these extracts are within 1 order of magnitude of the measured detection limits, for the elements in 1 mol/l

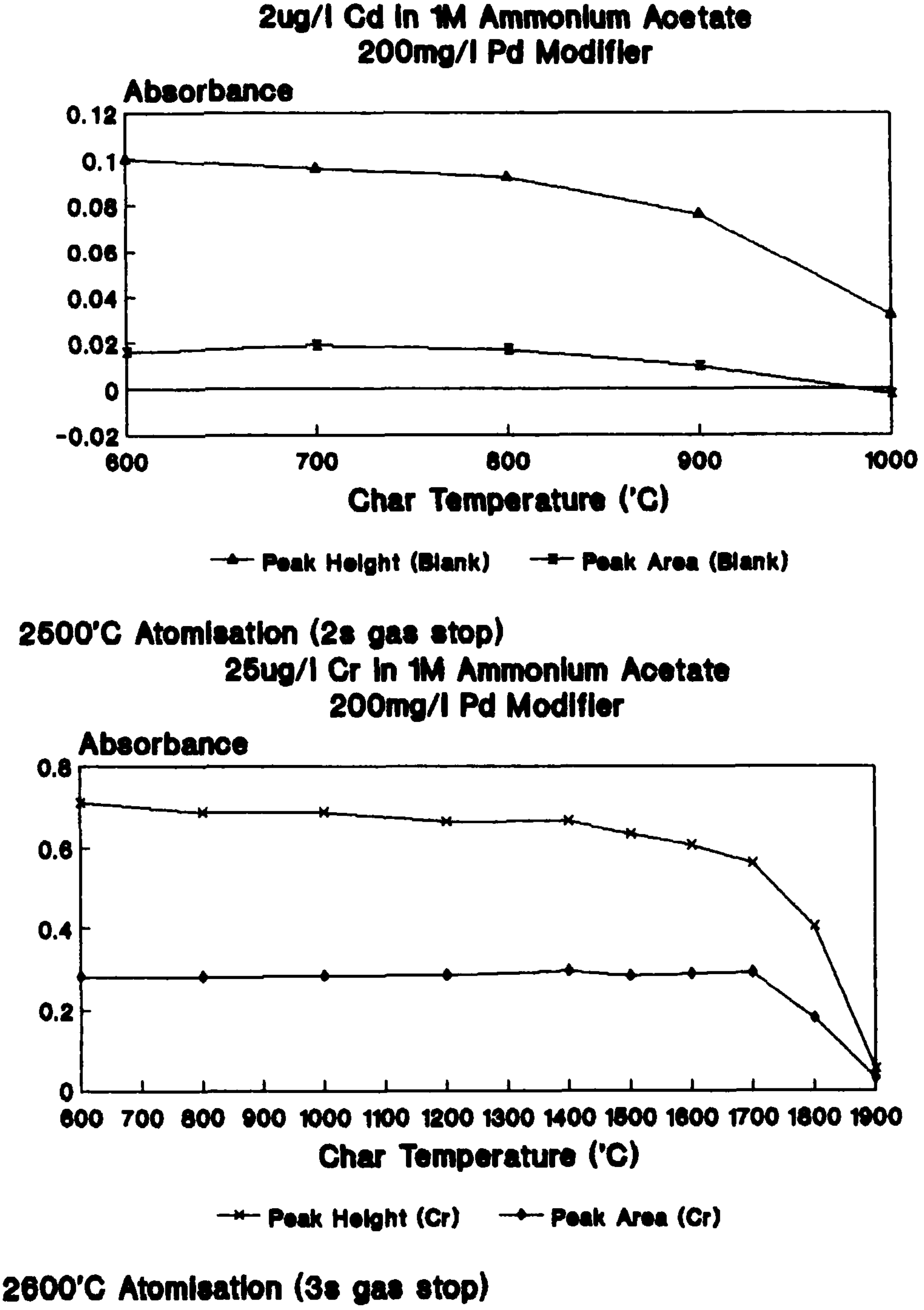
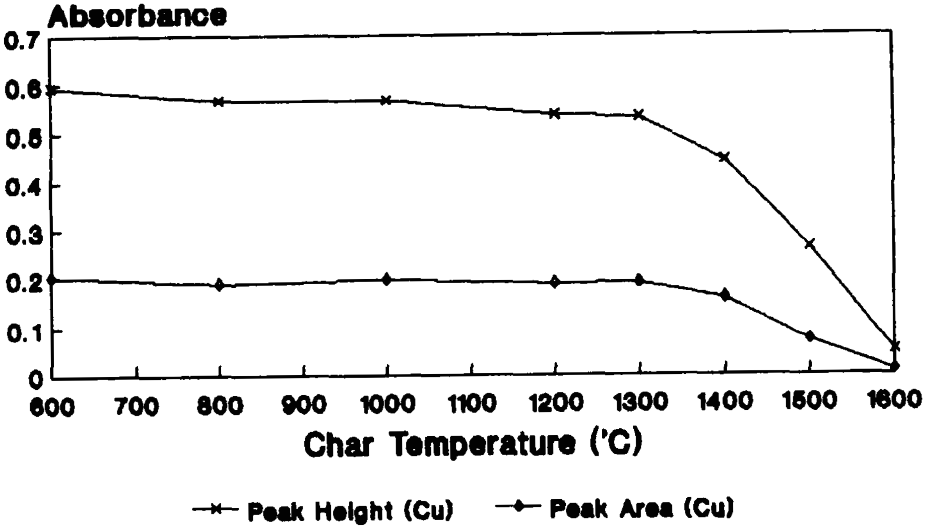
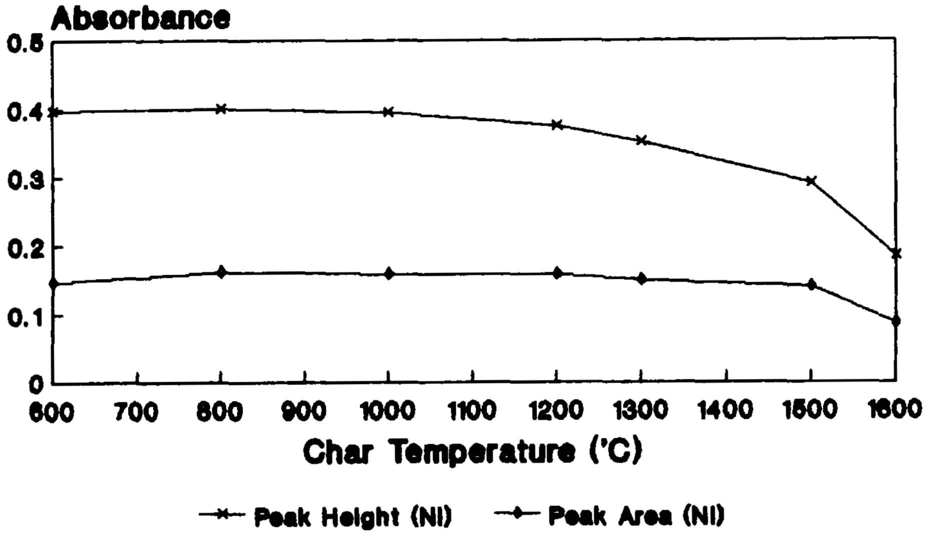


Figure 2 A, B, C, D, E, F. Char Temperature optimisation; Graphs of absorbance versus char temperature for A) Cd, B) Cr, C)Cu, D) Ni, E) Pb and F) Zn.



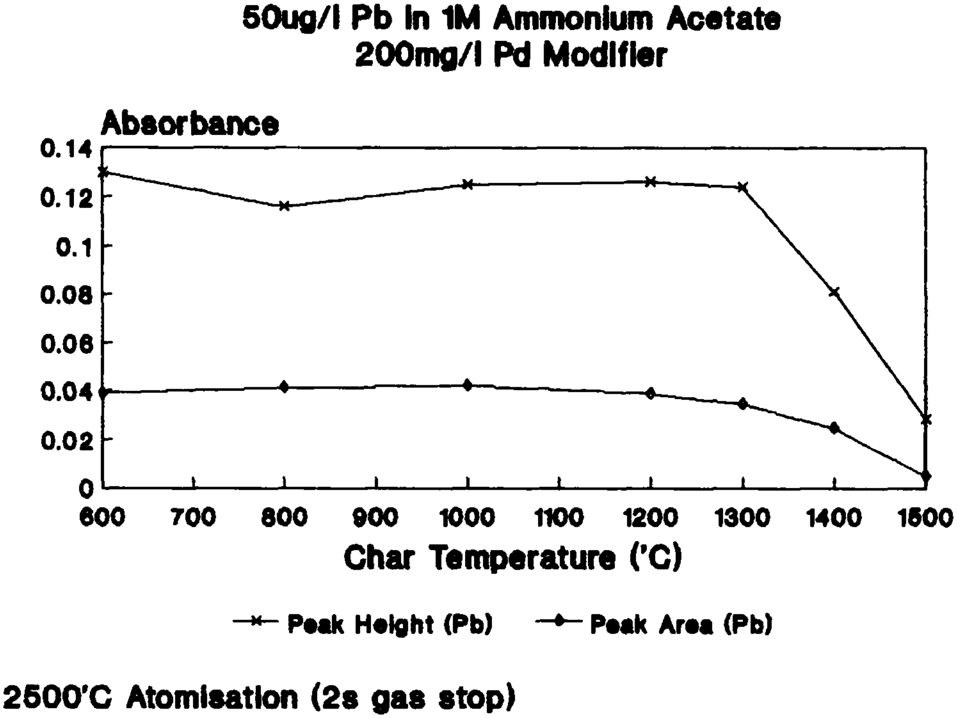
50ug/l Cu in 1M Ammonium Acetate
200mg/l Pd Modifier

2500'C Atomisation (2s gas stop)



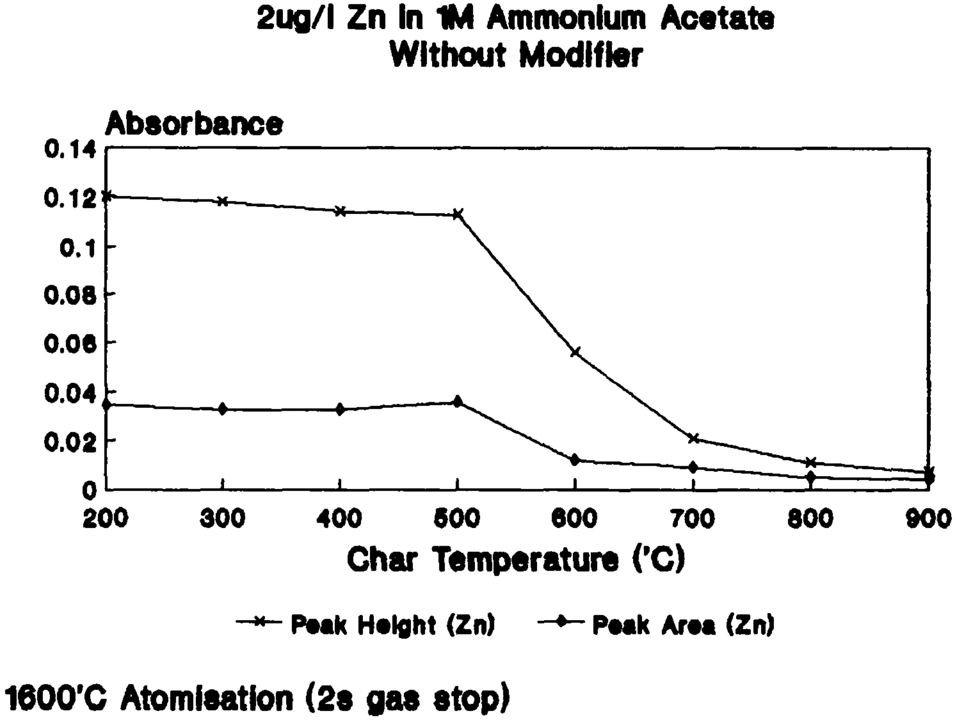
50ug/l Ni in 1M Ammonium Acetate
200mg/l Pd Modifier

2600'C Atomisation (3s gas stop)



50ug/l Pb in 1M Ammonium Acetate
200mg/l Pd Modifier

2500'C Atomisation (2s gas stop)



2ug/l Zn in 1M Ammonium Acetate
Without Modifier

1600'C Atomisation (2s gas stop)

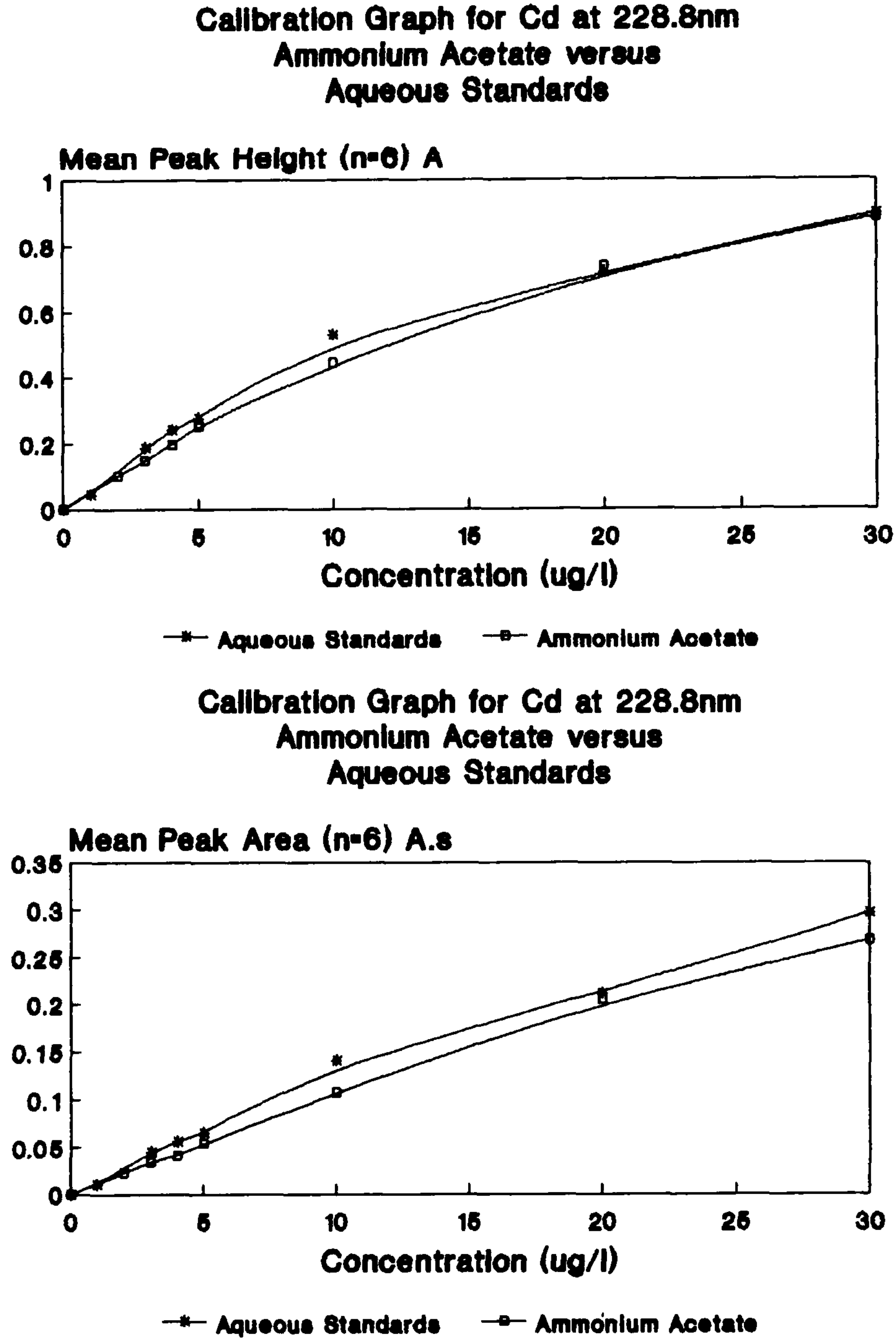
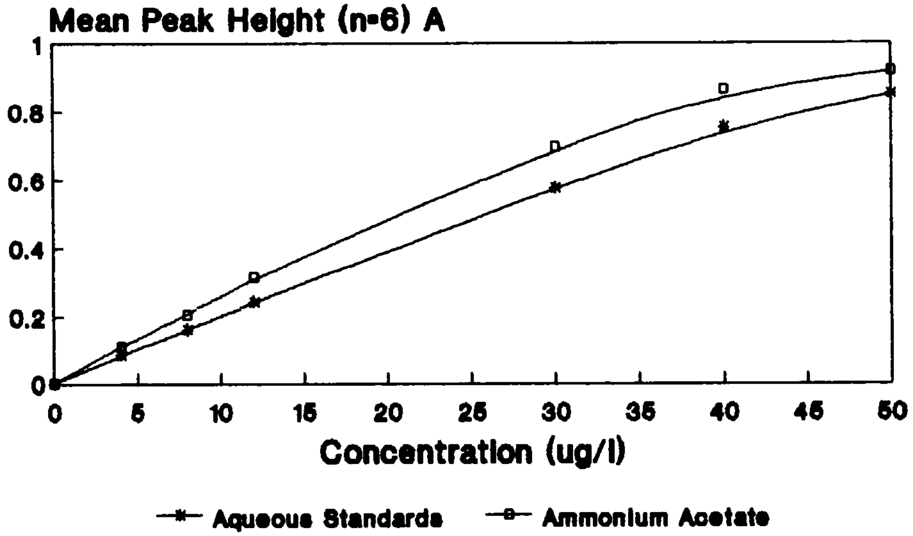
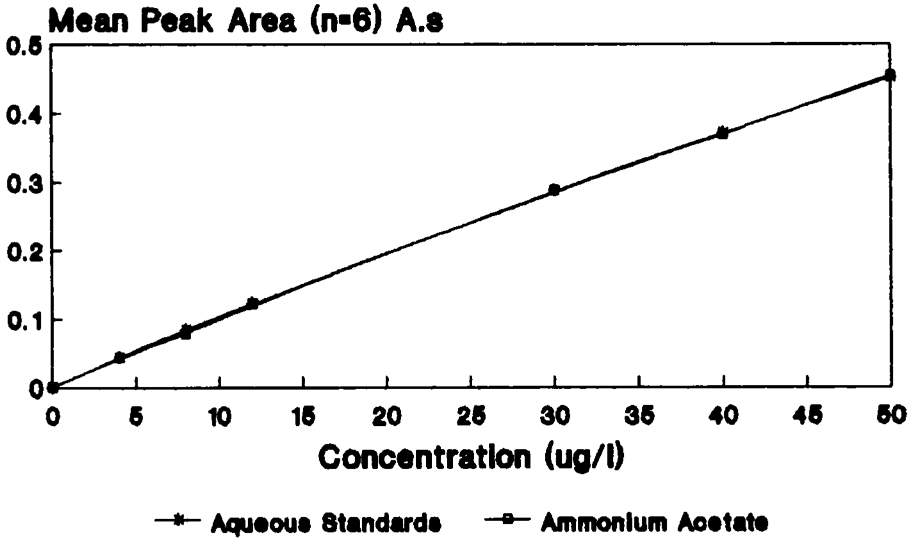


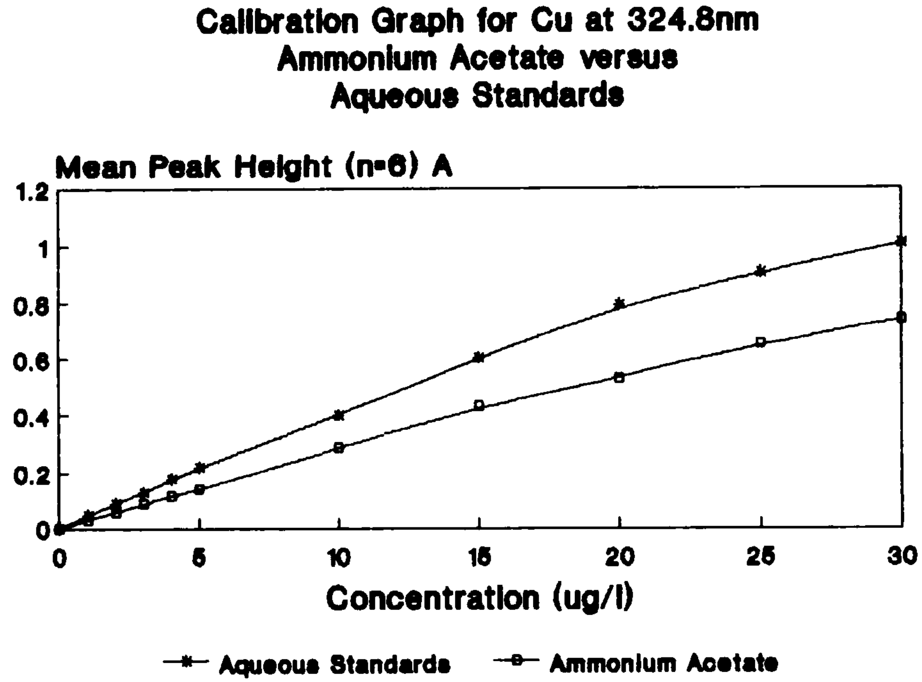
Figure 3 A, B, C, D, E, F. Comparison of aqueous and 1 mol./l anmmonium acetate calibration graphs for A) Cd, B) Cr, C) Cu, D) Ni, E) Pb.



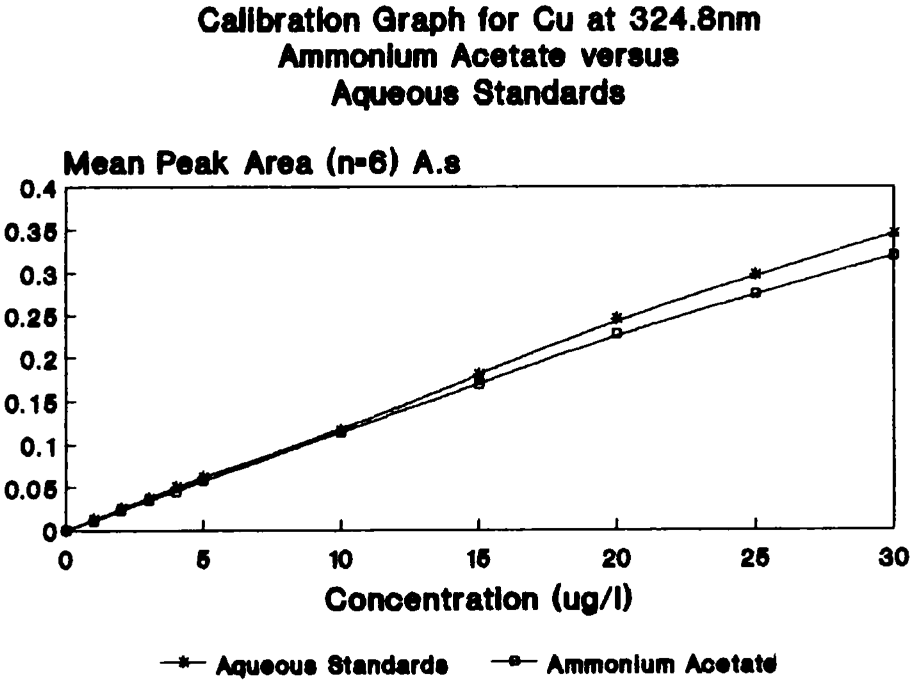
Calibration Graph for Cr at 357.9nm Ammonium Acetate versus Aqueous Standards



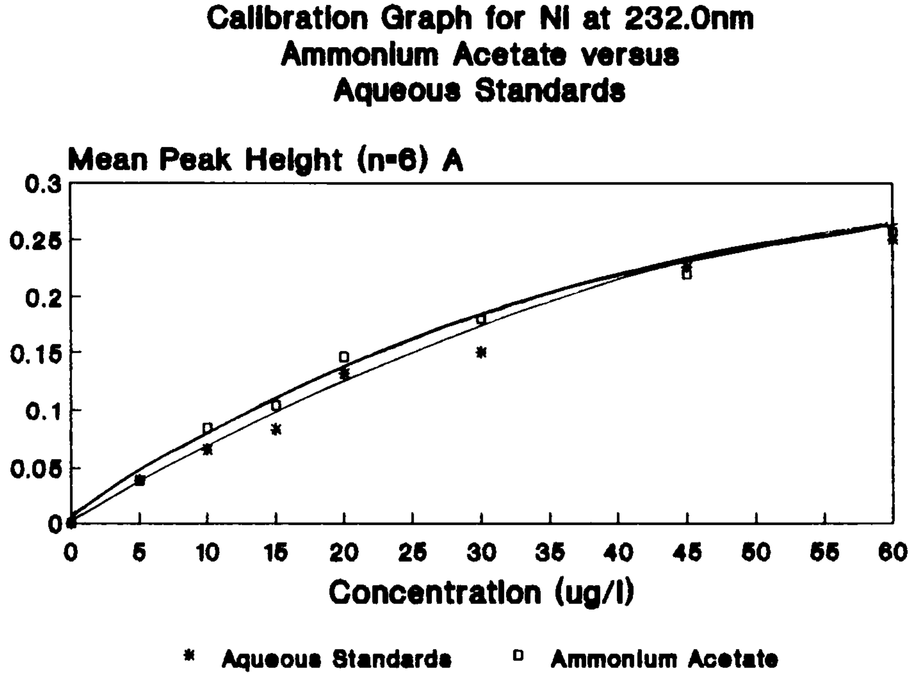
Calibration Graph for Cr at 357.9nm Ammonium Acetate versus Aqueous Standards

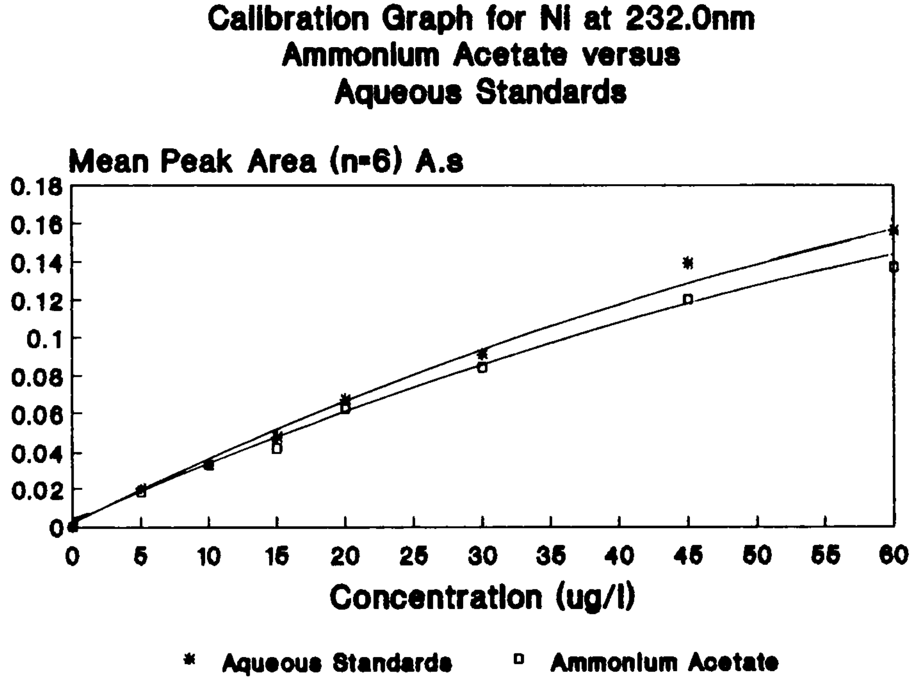


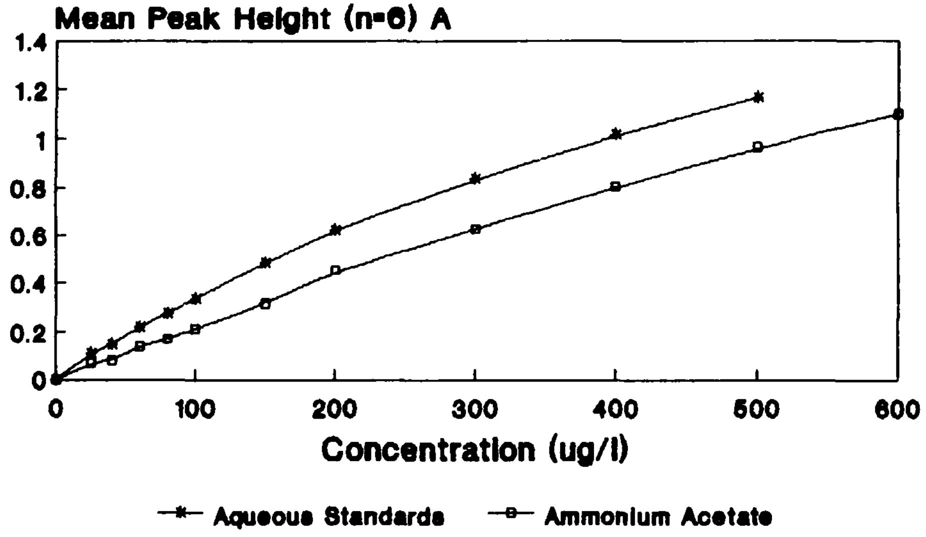
Calibration Graph for Cu at 324.8nm
Ammonium Acetate versus
Aqueous Standards



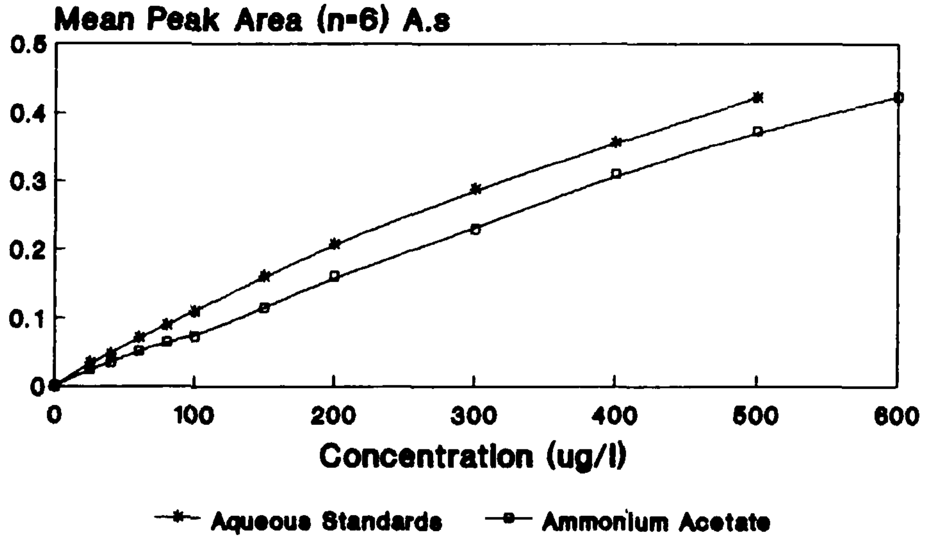
Calibration Graph for Cu at 324.8nm
Ammonium Acetate versus
Aqueous Standards


Calibration Graph for Ni at 232.0nm
Ammonium Acetate versus
Aqueous Standards
Mean Peak Height (n=6) A
0.3
0.25
0.2
0.15
0.1
0.05
0
0
5
10
15
20
25
30
35
40
45
50
55
60
Concentration (ug/l)
* Aqueous Standards
□ Ammonium Acetate


Calibration Graph for Ni at 232.0nm
Ammonium Acetate versus
Aqueous Standards
Mean Peak Area (n=6) A.s
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
5
10
15
20
25
30
35
40
45
50
55
60
Concentration (ug/l)
* Aqueous Standards
□ Ammonium Acetate



Calibration Graph for Pb at 283.3nm Ammonium Acetate versus Aqueous Standards



Calibration Graph for Pb at 283.3nm Ammonium Acetate versus Aqueous Standards

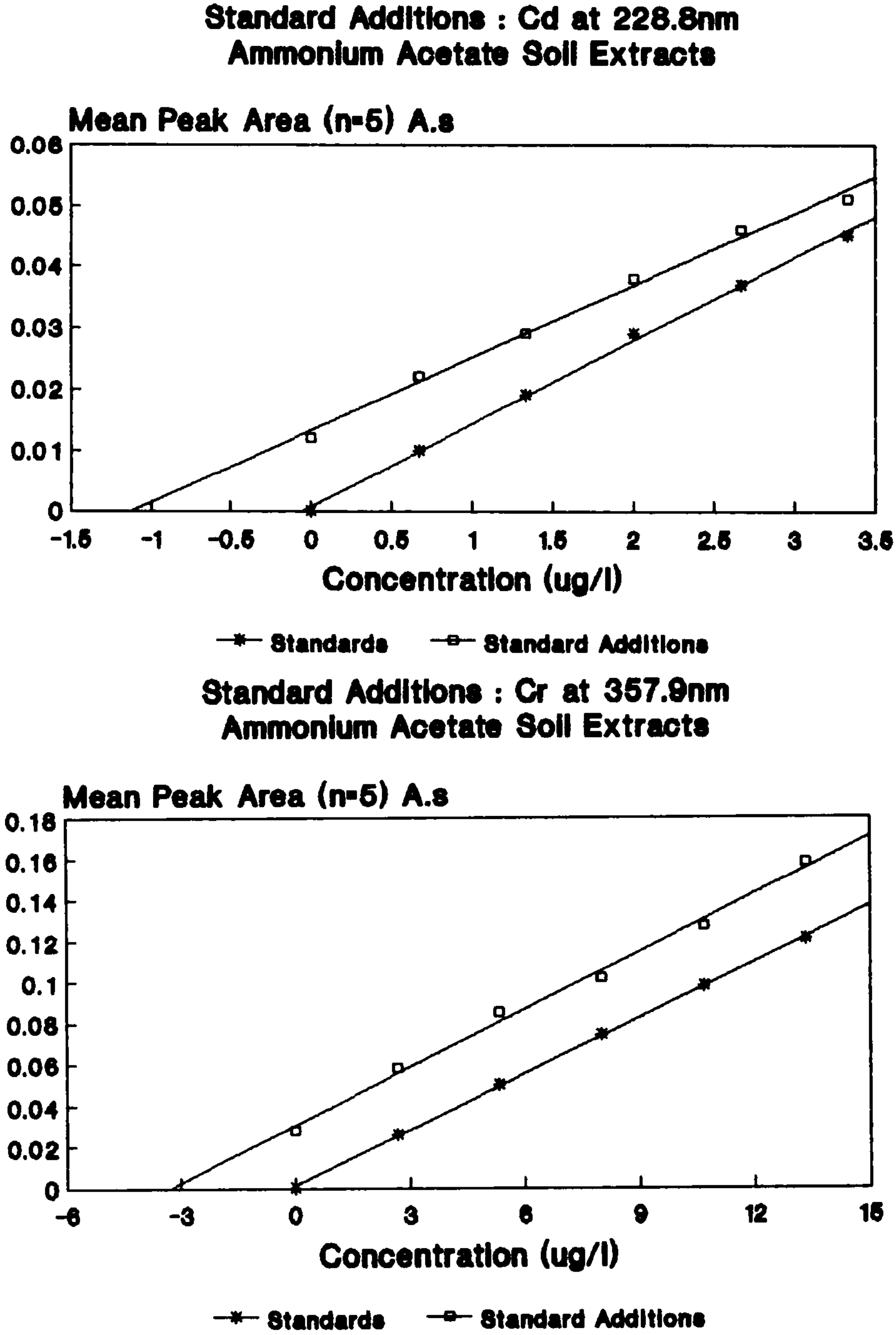
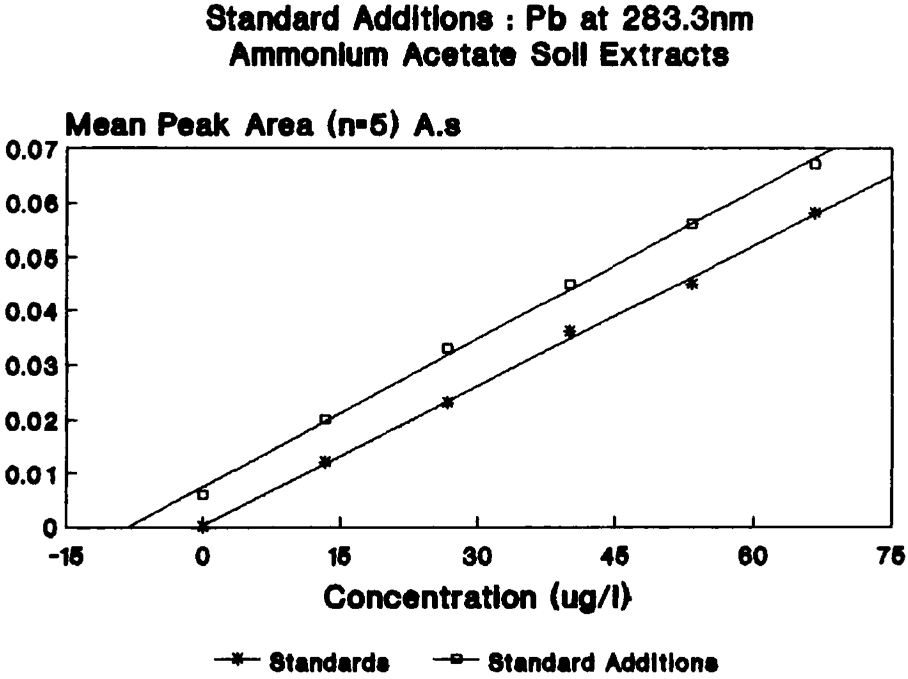


Figure 4 A, B, C, D. Comparison of direct calibration graphs with standard addition calibration graphs for A) Cd, B) Cr, C) Ni and D) Pb.


Standard Additions : Pb at 283.3nm
Ammonium Acetate Soil Extracts
Mean Peak Area (n=5) A.s
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
-15
0
15
30
45
60
75
Concentration (ug/l)
Standards
Standard Additions

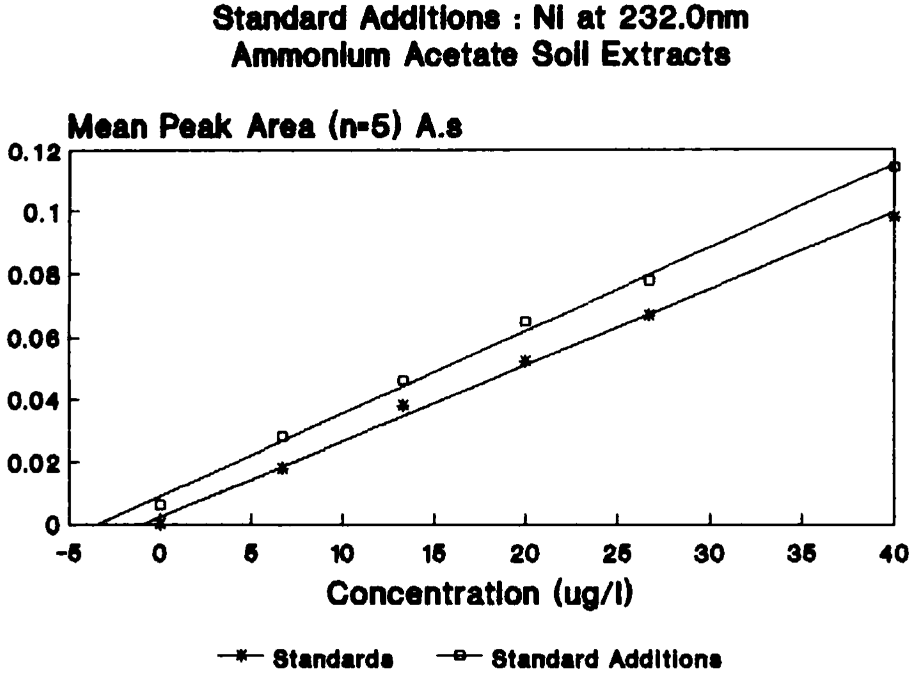

Standard Additions : Ni at 232.0nm
Ammonium Acetate Soil Extracts
Mean Peak Area (n=5) A.s
0.12
0.1
0.08
0.06
0.04
0.02
0
-5
0
5
10
15
20
25
30
35
40
Concentration (ug/l)
Standards
Standard Additions

Table 5 Effect of 1 mol/l ammonium acetate matrix, relative to aqueous matrix on Standard calibration graphs.

element	effect with peak ht measurement	effect with peak area measurement
Cd	None	None
Cr	+22%	None
Cu	-21%	-7%
Ni	+30%	-7%
Pb	-25%	-20%

Table 6 Analysis of unpolluted Scottish soils using Table 4 Programme. Perkin Elmer 3030 / HGA 500. Concentrations (ug/l) in extract

element	concentration by "additions"	concentration "direct" standardisation
Cd	0.60+/- 0.5	0.41
Cr	3.2 +/- 0.5	3.0
Ni	3.6 +/- 1.2	3.7
Pb	7.0 +/- 0.1	7.1

Cu and Zn not determined because of high blanks

ammonium acetate, listed in Table 7, the agreement between direct and standard addition results are remarkably close.

Analysis of a polluted soil

A fresh, field sample of the sludge amended, Great Billings Sewage Farm soil used in the recent BCR interlaboratory trial [13] was extracted and analysed by ETAAS using both the Perkin Elmer 3030 / HGA 500 and the Unicam PU9400 / GF 90 with the same operating programme for each instrument's atomizer, viz. that of Table 4. Direct and standard additions methods were used and the results compared in Table 8 with indicative values obtained by FAAS and with those obtained on a different sample from the same Great Billings site in the course of the BCR interlaboratory trial mentioned above. Because of the polluted nature of this soil it was necessary to dilute the ammonium acetate extract with 1 mol/1 ammonium acetate as indicated in Table 8.

It is clear that, while the direct analyses with the two instruments are similar, there are significant differences that are probably related to the different instrumental parameters and particularly to differences in actual as distinct from nominal furnace temperatures. Despite these differences the use of the standard additions procedure not only minimized interference effects but in fact compensated for instrumental differences as shown by the very close agreement of the two instruments when standard additions calibration was used. As expected there is only limited qualitative agreement with FAAS results and with the earlier BCR interlaboratory "Trial" results for a different sample from the same site.

Table 7 Detection limits determined with Perkin Elmer 3030 / HGA 500 and pyro-coated graphite furnace tubes for elements in 1 mol/l ammonium acetate solution.

element	detection limit ug/l	detection limit pg
Cd	0.4	5
Cr	0.5	5
Cu	0.9	5
Ni	0.5	15
Pb	6.2	55

TABLE 8 Analysis of sewage sludge amended soil sampled (in 1991) from Great Billings Sewage Farm by ETAAS using Pd matrix modifier and furnace programme of Table 4. Ammonium acetate extract contents (ug/l) from ETAAS determinations using direct and standard additions calibration are presented for 2 instruments, Perkin Elmer 3030 / HGA 500 and Unicam PU 9400 / GF 90. FAAS contents are also shown, but, as the concentrations are near the detection limits they can only be regarded as indicative. Direct comparison with the BCR interlaboratory 'Trial' results can also only be indicative as, although the present sample was from the same field site, it was taken some 5 years later.

	PE 3030		PU 9400			
Element	ETAAS direct	ETAAS std.add.	ETAAS direct	ETAAS std.add	FAAS	trial
Cd	154	133	97	125	[190]	[200]
Cr	23	22	25	22	[89]	[87]
Cu	381	305	352	320	[336]	[350]
Ni	53	43	55	40	<	[89]
Pb	32	32	29	30	[79]	[138]

Dilution Factors:-

Cd	Cr	Cu	Ni	Pb
1:25	1:5	1:10	1:5	1:5

CONCLUSIONS

While further work is no doubt required some reasonable conclusions can be drawn from this study.

1. The determination of zinc by ETAAS is neither necessary or desirable since FAAS is in general sufficiently sensitive and precise. The use of ETAAS for zinc in extracts of polluted soils would require dilutions of the extract by factors of perhaps 100 or more. Furthermore the use of palladium nitrate, at least, as a matrix modifier is not feasible because of the high zinc blank found.
2. In the analysis of ammonium acetate extracts of unpolluted soils there is a considerable possibility of contamination in the case of copper.
3. ETAAS, using commercial instrumentation and graphite furnaces, is sufficiently sensitive for extracts of most unpolluted soils, but for many polluted soils dilution of the extracts with ammonium acetate will be required to fit the effective working

ranges of ETAAS of about 3 to 50 ug/l for Cd, Cr, Cu, and Ni, and about 30 to 500 ug/l for Pb.

4. While direct calibration with external standard solutions is practicable for most of the elements except Cd, which does require the use of standard additions for calibration, the use of standard additions for calibration makes the technique much more robust and insensitive to differences in parameters in instruments from different manufacturers and probably in instruments of the same type in different laboratories. The use, therefore, of calibration by the method of standard additions is an essential requirement for the harmonization of analyses across different laboratories and national boundaries.
5. The analytical feasibility of using ammonium acetate as an extractant has been demonstrated and this, together with the diagnostic importance of this extractant, should justify its inclusion in further studies.

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