

## Determination of Copper, Chromium, Iron and Lead in Pine Needles by Electrothermal Atomisation Atomic Absorption Spectrometry With Slurry Sample Introduction

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An investigation has been carried out to establish a rapid method for the determination of copper, chromium, iron and lead in pine needle samples by electrothermal atomisation atomic absorption spectrometry with slurry sampling. In order to determine the accuracy of the proposed method, certified pine needle samples (National Bureau of Standards Standard Reference Material 1575) were analysed according to the proposed method and the results obtained compared with those obtained using a standard wet-ashing procedure. The results obtained by the proposed slurry procedure have sensitivities, reproducibilities and detection limits similar to those observed when solutions of the same samples are analysed.

**Keywords:** Slurry sample introduction; electrothermal atomisation atomic absorption spectrometry; pine needle samples

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The determination of trace elements in plants is important because their concentrations may be indicative of deficiencies in the soil composition or the result of metabolic changes which usually lead to low productivity and poor quality crops. It is therefore necessary to develop fast, precise and accurate methods of analysis which allow the determination of trace elements in any part of the plant.

The advent of graphite furnace atomic absorption spectrometry (GFAAS) for analysing solutions of plant material has lowered the limit of detection for metallic trace elements to 0.1–1  $\mu\text{g g}^{-1}$ , but even these limits of detection are not good enough in some instances. Also, as the limit of detection becomes lower, the problems of blanks from reagents can become more severe, and it would be particularly useful to develop methods of analysis which can be applied directly to these samples without a dissolution step.

For many AAS determinations, sample dissolution is the limiting step in determining the speed of analysis. For other determinations, sample dissolution restricts the detection limit owing to the dilution. In an effort to overcome these limitations, investigations have been carried out using GFAAS for the direct analysis of a great variety of samples.

Kerber *et al.*<sup>1</sup> determined trace amounts of metallic elements in fibres, plastics, paper products and fingernail clippings by direct analysis of solid samples using GFAAS. It was found that although GFAAS can be applied directly to the analysis of many solid samples, there are limitations to the types of samples which can be analysed. For example, if the distribution of the element of interest in the sample is not homogeneous, the determined concentration may have a substantial degree of error.

Brady *et al.*<sup>2</sup> used electrothermal atomisation atomic absorption spectrometry (ETA-AAS) for the direct determination of zinc in sediments using slurry introduction and compared the results obtained with those from the analysis of the solutions by flame AAS (FAAS). It was found that the

ETA-AAS method gave more accurate results than FAAS and experimental data which confirmed the homogeneity of the mixed solid sample were reported. Brady *et al.*<sup>2</sup> concluded that the proposed procedure should also be applicable to other metals in sediments, soils and possibly in biological samples.

The direct analysis of solid samples by AAS has been reviewed by Langmyhr,<sup>3</sup> who concluded that the most useful and extensively employed atomisation cell for solids is the cylindrical graphite tube, and that solid sampling AAS has considerable potential in trace analysis, especially where only small amounts of samples are available.

Frech *et al.*<sup>4</sup> investigated the determination of trace elements in steels and graphite by solid sampling AAS using a modified system. The samples were introduced under isothermal conditions. They suggested the use of suitable standard alloys for standardisation because calibration using aqueous solutions gives inaccurate results for solid samples.

The successful direct determination of Pb, Cd and Zn in plant materials<sup>5,6</sup> by GFAAS shows the effectiveness of slurry sampling for the determination of volatile elements. The findings reported by Nichols *et al.*,<sup>6</sup> using a different constant-temperature furnace to that used by Frech *et al.*,<sup>4</sup> appear to contradict the view that calibration can be carried out with simple aqueous standards, without the need for running similar solid calibration standards.<sup>4</sup>

Grobenski *et al.*,<sup>7</sup> in an attempt to improve microanalysis in solid sampling GFAAS, developed a specialised sampling tool to introduce powders and finely ground materials into the furnace. Accurate and precise results were obtained for the determination of trace elements in various National Bureau of Standards Standard Reference Materials (NBS SRMs). Direct calibration against acid standards was possible.

Many workers have made progress in developing the technique of solid sampling to induction and graphite furnaces.<sup>8–29</sup> These methods have been shown to be accurate and precise, particularly in analysing metal alloys, however, the lack of good standards for calibration is a major drawback.

Fuller *et al.*,<sup>30</sup> in a comparison study of the techniques used for the direct analysis of slurries, concluded that the problem

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of standardisation with electrothermal atomisation is not as critical as with nebuliser-based systems, where the variation in signal response with particle size and matrix make it necessary to use matched standards. Fuller *et al.*<sup>30</sup> proposed the use of aqueous standards for ETA-AAS, provided that the samples have been ground to a particle size of less than 25  $\mu\text{m}$ .

Olayinka *et al.*<sup>31</sup> have recently described a slurry technique for the determination of cadmium in foodstuffs by ETA-AAS with *in situ* ashing of samples. Their results show that the slurry method is accurate and comparable in precision to traditional wet- and dry-ashing procedures.

Stephen *et al.*<sup>32</sup> reported an evaluation of the slurry technique for the determination of lead in spinach by ETA-AAS. They used a thixotropic thickening agent to suspend the powdered spinach, and oxygen was introduced during the ashing stage to allow the use of higher ash temperatures and to avoid the build-up of carbonaceous residues in the tube. Good agreement was found between results obtained by the standard additions procedure and by direct calibration with aqueous standards and also by a wet-digestion procedure. Lead and cadmium were determined<sup>33</sup> directly in sandy soils and in high clay content soils by pipetting an aqueous slurry into two different graphite furnaces with platforms and the result were compared with those obtained by ETA-AAS and FAAS. It was also shown that insufficient grinding of the sample leads to poor recovery from larger particles. Good agreement for both lead and cadmium over a wide concentration range was found and complete recovery by the slurry sampling ETA-AAS procedure when aqueous calibration standards and finely ground samples were used was confirmed.

Hoenig *et al.*<sup>34</sup> determined lead and cadmium in three different types of solid sample: plant and animal tissue and ground marine sediment by ETA-AAS using platform atomisation. Dispersing agents were used in order to avoid particle agglomeration, and matrix modifiers to allow the use of higher ashing temperatures. The described procedure permits the use of direct calibration with simple standard solutions.

Karwowska *et al.*<sup>35</sup> conducted studies of the atomisation behaviour of lead introduced into an electrothermal atomiser using a platform and two types of graphite surface in a slurry of  $\text{Al}_2\text{O}_3$  and in a solution of  $\text{Al}(\text{NO}_3)_3$ . Their comparative studies of slurry atomisation provide information on the feasibility of the determination of trace amounts of lead, and on the mechanism of the release of lead when it is adsorbed on and/or occluded in the slurry particles; a similar study has been carried out on low-temperature alumina.<sup>36</sup> These studies have shown that trace amounts of metals such as lead in soils are chemisorbed on to the active surfaces of clay particles, and have provided an insight into the probable behaviour of lead in soil.

Ebdon and Lechotycky<sup>37</sup> have determined lead in three certified reference materials: aquatic plant, olive leaves and mussel tissue by slurry sampling ETA-AAS. Using aqueous calibration standards and matrix modifiers, excellent agreement with certified values was found.

Fagioli *et al.*<sup>38</sup> extended their carbonaceous slurry method using GFAAS to the determination of cadmium and lead in five NBS SRMs. Good precision and accuracy for both elements were found, the determination for lead being slightly better than that for cadmium.

Ebdon and co-workers<sup>39-41</sup> have recently determined trace amounts of metals in coal, a difficult matrix to bring into solution by ETA-AAS and ICP-AES using slurry sampling.

Ebdon and Evans<sup>42</sup> have also used ETA-AAS for the determination of copper in biological reference materials and real samples using direct slurry atomisation from both the tube wall and direct platform atomisation. They found that both sampling techniques are reasonably accurate and precise for the determination of copper in animal and botanical samples.

A method for the determination of cadmium in soil slurries

by FAAS using a micro-sampling cup has been described by Rygh and Jackson<sup>43</sup> and has been compared with slurry ETA-AAS. The proposed method shows good correlation with slurry ETA-AAS and FAAS with acid digestion, however, its precision was comparatively poor. Provided that this poorer precision is acceptable, the micro-sampling cup procedure could be used as an alternative to slurry sampling ETA-AAS for the determination of cadmium in soil, mainly because it is relatively inexpensive.

We have investigated the injection of slurries of pine needle samples into a graphite furnace for the determination of copper, chromium, iron and lead by AAS. Aspects of sample drying and grinding, particle size distribution and the ratio between the suspended solid - solvent have been reported previously.<sup>44</sup> The optimum furnace conditions for the determination of these elements by standard dissolution and slurry methods are given, together with the sensitivity, reproducibility and detection limits. Ten samples of pine needles from different locations were analysed.

## Experimental

### Apparatus

A Varian Techtron Model AA6 atomic absorption spectrometer and a Jarrel Ash Model 83000 atomic absorption spectrometer coupled with a Perkin-Elmer HGA-2100 graphite furnace and a CRA-90 were used for all measurements. The same absorption line, spectral band pass and lamp current were used for both suspension and solution measurements and single element hollow-cathode lamps were used. The suspensions and solutions were injected into the graphite tube (5  $\mu\text{l}$  for the CRA-90 and 20  $\mu\text{l}$  for the HGA-2100) with Eppendorf micropipettes and the absorbance was read in the peak-area mode.

### Optimisation of Heating Conditions

The atomisation conditions were optimised for the analysis of slurries and were not significantly different from those found for aqueous solutions. These conditions were optimised using an aqueous standard solution containing 50  $\mu\text{g l}^{-1}$  of the element in question. Optimum charring conditions for solution analysis were determined using sample solutions containing 20  $\mu\text{g l}^{-1}$  of Cu, 20  $\mu\text{g l}^{-1}$  of Cr and 25  $\mu\text{g l}^{-1}$  of Pb, respectively. The charring conditions for slurry analysis were carried out using sample slurries containing 50  $\mu\text{g l}^{-1}$  of the analyte element. The atomisation profile for each element was obtained from a data acquisition system developed in our laboratory, which was connected to a Hewlett-Packard Model HP-85 microcomputer using an impedance modifier installed on the photomultiplier. Further, power supplies were constructed for the hollow-cathode lamp and for the photomultiplier and programmes were developed to measure the absorbance signal at 10-ms intervals. Once the atomisation cycle had finished, the data were processed and the absorbance *versus* time plot (atomisation profile) was displayed on the screen. With this system, additional information such as maximum appearance time of the peak, peak-area and peak-height readings can be obtained.

A particle size distribution was obtained by using nylon standard sieves. Grinding of the samples was carried out using a vibrational type Spex mixer mill with a porcelain cylinder and tungsten carbide balls. In order to check possible sample contamination from this commercial grinding unit and from the cleaning procedure, measurements of the certified compositions of the NBS reference material were carried out by grinding samples and reference materials alternately. No variations were observed in the certified values. Homogenisation of the slurries was carried out using a Blackstone Model ST-2D ultrasonic device.

**Reagents**

All chemicals used were of analytical-reagent grade and de-ionised water (Milli-Q) was used throughout. Stock solutions (100 mg l<sup>-1</sup>, BDH) were prepared, and working standards prepared by dilution of these. Calibration of the slurries was carried out using NBS SRM 1575 Pine Needles.

**Sample Preparation**

The sample treatment used to prepare the slurries was the same as that reported previously.<sup>44</sup> Pine needle samples were washed repeatedly with doubly distilled water and oven-dried at 100 °C for 12 h then ground and homogenised in a mixer mill

for 15 min. For the determination of iron, the samples were sieved and only particles of less than 160 µm were used to prepare the slurries. These analyses were carried out by suspending the sample without thermica treatment (not calcined).

For the determination of chromium, copper and lead, the original sample (without sieving) was calcined in a sample furnace for 4 h, increasing the temperature gradually from 100 to 400 °C at 1-h intervals. Slurries of 1 mg ml<sup>-1</sup> prepared in 0.1% HNO<sub>3</sub> were analysed directly, stirring for 1 min before each measurement. Slurries of the NBS SRM were used for calibration. Working standard slurries were prepared by dilution of a stock slurry and were processed in the same way as the samples.

**Table 1.** Optimum furnace conditions for the determination of Cr, Cu, Pb and Fe

Element	Instrument	T <sub>at</sub> /°C	t <sub>at</sub> /s	T <sub>char</sub> /°C	t <sub>char</sub> /s	T <sub>dry</sub> /°C	t <sub>dry</sub> /s	Gas flow-rate/ml min <sup>-1</sup>
Cr	CRA-90	2300	3	500	30	120	30	3000
Cu	CRA-90	2000	2.5	500	30*	120	30	3000
Pb	HGA-2100	1800	4.8	500	20	120	30	20†
Fe‡	CRA-90	2200	2.5	500	40	120	30	3000

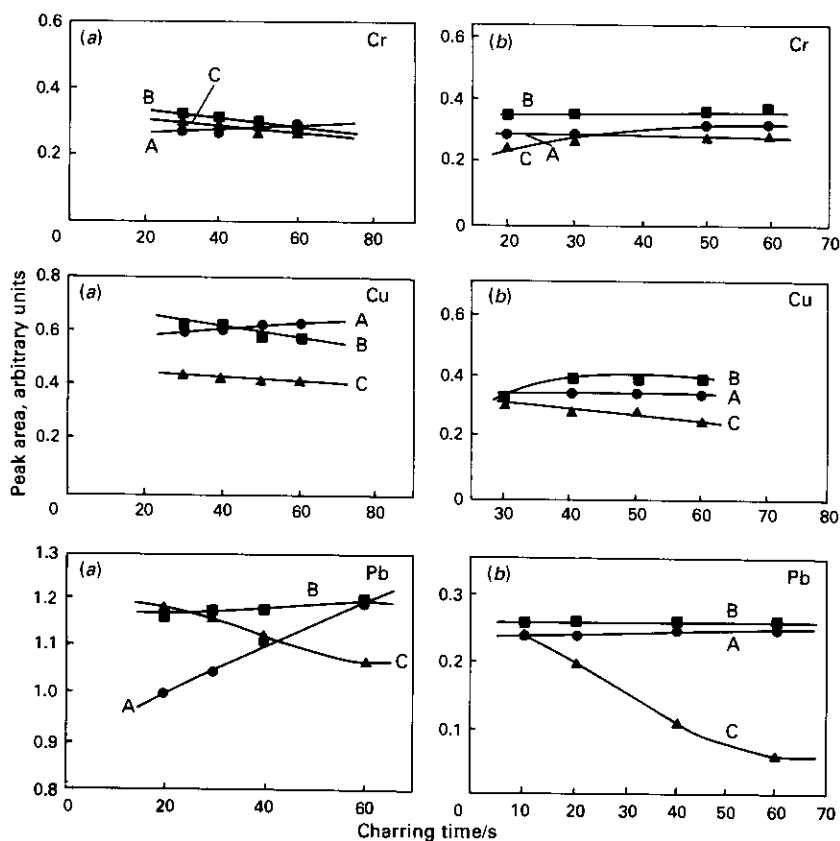
\* Charring time for slurry analysis was 40 s.

† Interrupt.

‡ The furnace conditions given for iron are only for slurry analysis. Conditions for other elements are the same for both acid solutions and slurry analysis.

**Table 2.** NBS SRM 1575 Pine Needle solution analysis

Sample content	Cr/ mg kg <sup>-1</sup>	RSD, %	Cu/ mg kg <sup>-1</sup>	RSD, %	Pb/ mg kg <sup>-1</sup>	RSD, %	Fe/ mg kg <sup>-1</sup>	RSD, %
Found	2.6 ± 0.3	11	3.1 ± 0.2	7	10.7 ± 0.7	7	205 ± 8	4
Certified	2.6 ± 0.2		3.0 ± 0.3		10.8 ± 0.5		200 ± 10	



**Fig. 1.** Peak area versus charring time at different temperatures for (a) solution and (b) suspension. (A) 300; (B) 500; and (C) 700 °C

### Wet-acid Digestion of Sample

A representative pine needle sample and the pine needle reference material were digested by the following procedure. An 8-ml volume of H<sub>2</sub>SO<sub>4</sub> - HNO<sub>3</sub> - H<sub>2</sub>O<sub>2</sub> (2 + 1 + 1) was used to digest the samples (0.1000 g) for the determination of copper, chromium and iron. Sample digestion for the determination of lead was carried out using 4 ml of HNO<sub>3</sub> - HClO<sub>4</sub> (2 + 1) for 0.2000 g of sample. This acid mixture was used for lead because of the reported interference of sulphate on the atomic absorption signal of lead.<sup>45</sup> The determination of iron was carried out by FAAS owing to its concentration in the samples, and aqueous standard solutions were used for calibration.

Copper, chromium and lead were determined in the digested samples by GFAAS. Matrix-matched calibration standards were used for the determination of copper, whereas the method of standard additions was used for chromium. Lead was determined using a platform and calibration standards with NH<sub>4</sub>NO<sub>3</sub> (2%) added to samples and standards as a matrix modifier.

## Results and Discussion

### Optimum Furnace Heating Conditions

The optimum furnace heating conditions for chromium, copper, lead and iron in acid solutions are shown in Table 1. The optimum heating conditions for slurry analysis did not differ significantly from those obtained for the acid solutions except that the charring time for copper, which was 40 s. As the charring step is one of the most important parameters when dealing with different sample media, plots of peak area

versus charring time at different temperatures are shown in Fig. 1 for both solution and slurry samples. The charring time and temperature for the determination of chromium and copper are the same for both solutions and slurries. However, lead behaves differently, e.g., at 300 °C the volatilities are considerably different. At 700 °C the loss of lead is faster in a slurry than in solution, perhaps indicating that different chemical species are formed. At 500 °C, however, the charring time and temperature for lead in both solutions and slurries are similar.

### Results of Determinations

In order to test the accuracy of the dissolution and slurry methods, the NBS SRM 1575 Pine Needles were analysed by the acid dissolution method. Table 2 shows the results obtained for five replicate analyses of this sample. Excellent agreement with the certified values was obtained with acceptable precision.

A comparison study by both methods was carried out on pine needle samples (Table 3) and good agreement between the two methods was obtained. The Student *t*-test and the *F*-test were applied<sup>46</sup> to the results and for a confidence level of 95% the results show that there is no statistically significant difference between the mean of both populations.

### Sensitivity Studies

The sensitivities were determined for copper, chromium, iron and lead in solutions and compared with those obtained from the analysis of the slurry sample. The slope of the calibration graph was taken as a measurement of the sensitivity and the results obtained are presented in Table 4. The results of this study showed that for iron and copper, the sensitivities are higher for the slurry method than for the solution method. However, chromium and lead show lower sensitivities for the slurry method than for the dissolution method.

### Detection Limit

In order to evaluate the proposed method further, the detection limit was determined experimentally<sup>46</sup> for each element for both methods. Table 4 shows these results for a 5- $\mu$ l aliquot of copper, chromium and iron solutions and slurries and a 20- $\mu$ l aliquot of a lead solution and slurry. The detection limits (DL) for chromium and copper are similar for

Table 3. Results of the analyses of pine needle samples by dissolution and slurry methods

Element	Concentration/ mg kg <sup>-1</sup>		Concentration/ mg kg <sup>-1</sup>	
	(dissolution)	RSD, %	(slurry)	RSD, %
Fe	76 ± 3	4	81 ± 5	6
Cr	12.5 ± 0.6	5	13.3 ± 0.4	3
Cu	14 ± 1	7	14.2 ± 0.4	3
Pb	5.3 ± 0.4	7	4.8 ± 0.2	4

Table 4. Comparison of the determination of iron, chromium, copper and lead in solutions and slurries

Element	Concentration range/ $\mu$ g <sup>-1</sup>		Regression line ( $A = mc + b$ )		Correlation coefficient ( $r^2$ )		Detection limit/ $\mu$ g	
	Solution	Slurry	Solution	Slurry	Solution	Slurry	Solution	Slurry
	Fe	20-100	20-100	0.010c + 0.069	0.018C + 0.044	0.989	0.994	20
Cr	20-100	20-100	0.013c + 0.035	0.011C + 0.002	0.992	0.996	20	20
Cu	20-100	20-100	0.008c + 0.008	0.013C + 0.037	0.992	0.995	13	10
Pb	20-100	20-100	0.009c + 0.013	0.007C + 0.016	0.985	0.987	84	100

Table 5. Analysis of pine needle samples with the slurry introduction method

Sample	Fe/ mg kg <sup>-1</sup>	RSD, %	Cr/ mg kg <sup>-1</sup>	RSD, %	Cu/ mg kg <sup>-1</sup>	RSD, %	Pb/ mg kg <sup>-1</sup>	RSD, %
1	102	7	13.7	4	12.3	3	15	6
2	52	7	12.8	2	10.0	3	7.6	6
3	71	7	14.0	2	10.1	4	2.3	4
4	220	6	13.5	4	9.7	4	1.2	8
5	134	8	9.5	6	9.5	4	1.0	8
6	100	9	10.5	6	8.6	3	1.0	7
7	88	6	10.3	2	7.7	3	1.2	8
8	166	6	11.2	3	8.4	4	1.3	7
9	65	7	9.6	4	6.5	4	0.77	5
10	37	7	8.1	3	7.8	5	0.75	4

both methods whereas for iron the DLs in solution are twice those obtained using slurries. The DL of lead in the slurry is slightly superior to that obtained in solution.

#### Analysis of Pine Needle Samples

To show the applicability of the proposed method, ten samples from different locations were analysed for iron, chromium, copper and lead following the proposed method. The results in Table 5 show that the concentrations of these metals are very variable. The relative standard deviation varies between 2 and 9%. When a precision of this order is acceptable, the direct analysis of slurries is useful as it avoids the time-consuming acid digestion currently used in the preparation of plant material for analysis by AAS.

#### Conclusions

The reproducibility of the proposed method is similar and in some instances better than that observed when solutions of the same solid are used. The results of the analyses of the standard reference material obtained by the two methods fall within the same concentration range. No significant difference between the results obtained with the standard wet-ashing and the slurry procedures is apparent, showing the accuracy of the slurry method. The element sensitivities are also very similar. Although the sensitivities for chromium and lead obtained by dissolution are better than those obtained with the slurry method, in instances where the sensitivity is not a factor which limits a particular analysis, this difference is not considered to be very significant.

Generally, the use of slurries with GFAAS has some utility which should be considered. Various samples may be analysed by this technique and it is especially useful for those samples which would otherwise require dissolution procedures.

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