Comparison of open microwave digestion and digestion by conventional heating for the determination of Cd, Cr, Cu and Pb in algae using transverse heated electrothermal atomic absorption spectrometry

Introduction

Plants such as algae and organisms such as yeast, mosses have been used as bio-indicators for monitoring the environment [1]. Algae have excellent potential for absorbing trace metals from their surroundings, with high selectivity for various elements and their different oxidation states [2, 3].

In recent years the introduction of microwave heating has made sample preparation much simpler and rapid for ETAAS determination [4–6]. For determination of toxic metals at ultra trace levels, large quantities of sample need to be processed. Such digestions can be done in a closed microwave system, after prior ashing of samples in a muffle furnace. This requires 6–8 h of sample preparation [7, 8], and the chances of contamination are greater and the process tedious. Open focused microwave digestion is more suitable for digesting large quantities of sample and is used for a variety of matrices [9, 10], digestion being completed within 45–50 min.

In the present work the suitability of a focused open microwave digestion system has been examined for the algae matrix. The results have been compared with conventional digestion using a hot plate. Algae samples along with SRM GBW 08504 cabbage were analysed for Cd, Cr, Cu, and Pb.

Abstract

A comparison between open microwave digestion and digestion by conventional heating was carried out for the determination of Cd, Cr, Cu, and Pb in two algae matrices using transverse heated electrothermal atomic absorption spectrometry (ETAAS). A SRM GBW 08504 cabbage was also analysed. These matrices were digested with HNO₃, using a quartz vessel for microwave digestion and PFA vessel for digestion by conventional heating. Cd, Cu and Cr were determined without any modifier, while magnesium nitrate and ammonium phosphate mixed modifier was used for Pb. Results obtained by both the procedures were in good agreement with each other at 95% confidence level, and for SRM GBW 08504 cabbage the values agree well with the certified values. The limits of detection obtained were 0.0004, 0.060, 0.065 and 0.054 mg/kg for Cd, Cr, Cu, and Pb, respectively, using the microwave digestion process. The RSD for Cd was 10–15% and for the other elements 5–10%.

Experimental

Instrumentation. A Perkin-Elmer (Uberlingen, Germany) spectrometer, Model 4100 ZL, equipped with a transverse heated graphite atomizer (THGA), and an AS-70 autosampler, and pyrolytic coated graphite tubes with an integrated platform and longitudinal inverse Zeeman effect background correction were used. The analytical signals were measured in integration mode.

Samples and working standards were prepared inside a class 10 laminar flow clean bench having vertical laminar flow in a class 100 clean room. Microdigest 401 (Prolabo, Paris, France) was used for open microwave digestion.

Reagents and standard solutions. Ultrapure water (> 18W M) was obtained by passing the de-ionized water through a Millipore water purification system. Nitric acid used was purified by quartz sub-boiling distillation. Stock standards of Cd, Cr, Cu and Pb were prepared by dissolving 99.99% pure metals in nitric acid. Working standard at ng/mL level was prepared daily by subsequent dilution. Micropipettes and PTFE/PFA containers were used. These were cleaned by soaking in 10% (v/v) nitric acid for a week and then washed with ultrapure water.

Decomposition of sample by conventional heating. About 0.5 g of samples were taken in 10 mL PFA containers and 3 mL of HNO₃ was added. Once the initial reaction ceased, the screw cap was tightened and the sample was digested on the hot plate for 1 h at 80–90°C. The sample solution was evaporated near to dryness and made up to 3–4 mL using ultrapure water. The time required was about 2 h.

Decomposition of sample by open microwave digestion. About 0.5 g of powdered material and 2 mL of HNO₃ were taken into a quartz sample digester (250 mL) using an on-line reagent addition facility. The microprocessor was programmed for 10, 30, and 40% focused microwave power of about 5 min, respectively, in reflux mode. It was further refluxed for 10 min at 40% power after a further addition of 2 mL HNO₃. The solution was found to be clear. Excess acid was evaporated near to dryness using microwave heating. The final solution was made up to 3–4 mL using ultrapure water. The total time required was 25 min. The optimized THETAAS temperature programme and instrumental parameters used are given in Table 1. In both cases quantification was carried out using a standard addition calibration graph.

Results and discussion

Optimization of the temperature programme

The temperature programme of the THETAAS instrument was optimized (Table 1). Cd was found to be retained up to 600°C.

Table 1 Optimized operating parameters for THETAAS

<table>
<thead>
<tr>
<th>Element</th>
<th>Wave-length nm</th>
<th>Spectral band pass nm</th>
<th>Ashing temp. °C</th>
<th>Ramp/hold s</th>
<th>Atomization temp. °C</th>
<th>Ramp/hold s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>228.8</td>
<td>0.7</td>
<td>500</td>
<td>10/10</td>
<td>1200</td>
<td>0/3</td>
</tr>
<tr>
<td>Cr</td>
<td>357.9</td>
<td>0.7</td>
<td>1200</td>
<td>10/10</td>
<td>2300</td>
<td>0/3</td>
</tr>
<tr>
<td>Cu</td>
<td>324.8</td>
<td>0.7</td>
<td>1000</td>
<td>10/10</td>
<td>1900</td>
<td>0/3</td>
</tr>
<tr>
<td>Pb</td>
<td>283.3</td>
<td>0.7</td>
<td>900</td>
<td>10/10</td>
<td>1600</td>
<td>0/3</td>
</tr>
</tbody>
</table>
Table 2 Recovery of Cd, Cr, Cu, and Pb in algae matrix dissolved by using conventional heating and open-microwave digestion procedures

<table>
<thead>
<tr>
<th>Element</th>
<th>Amount of element added (pg)</th>
<th>Recovery (%) in conventional heating</th>
<th>Recovery (%) in open microwave heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>22</td>
<td>98a</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>44</td>
<td>94a</td>
<td>95</td>
</tr>
<tr>
<td>Cr</td>
<td>100</td>
<td>75</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>75</td>
<td>85</td>
</tr>
<tr>
<td>Cu</td>
<td>200</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>95</td>
<td>100</td>
</tr>
<tr>
<td>Pb</td>
<td>400</td>
<td>80</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>75</td>
<td>94</td>
</tr>
</tbody>
</table>

*aMg(NO₃)₂ + PO₄³⁻ modifier

Matrix interference

The recoveries of Cd, Cr, Cu, and Pb at 20–800 pg in both conventional and open microwave digestion procedures are shown in Table 2. It is seen that the analyte recovery in the case of conventional sample dissolution procedure is slightly lower for Pb and Cr when compared to microwave digestion. In the case of Pb, without any modifier, only 25 and 50% of the 400 pg of element added were recovered, respectively, by conventional and microwave digestion procedure. This shows loss of Pb, therefore magnesium nitrate and ammonium phosphate mixed modifier was used. In the presence of the mixed modifier the recoveries improved to 80% and 92%, respectively, for conventional and open microwave digestion. In the case of Cr, in both cases 75–85% recoveries were obtained. This indicates that nitric acid alone is not suitable for digestion and a combination of acids such as HF, HClO₄/H₂SO₄ are necessary as reported [10–12]. However, to avoid contamination and reduce loss of Pb in H₂SO₄, only nitric acid was used for digestion.

For Cd 94–98% recovery was obtained in the case of conventional digestion using magnesium nitrate and ammonium phosphate mixed modifier, which compares well with 95–98% recovery obtained in the case of microwave digestion without any modifier. Similarly for Cu the recovery was 95–100% by both digestion procedures.

Process blank, characteristic mass (mₒ) and limit of detection (LOD)

Even though the amount of nitric acid used in the conventional digestion was 3 mL as compared to 4 mL in microwave digestion, the process blank was lower in the latter case. The process blanks for 20 μL aliquot of the sample solution in conventional and microwave digestion were about 12, 70, 76 and 3, 33, 35, 40 pg, respectively, for Cd, Cu, Pb and Cr. It appears that small sample preparation times and automatic addition of the reagents results in a low process blank, because all other sources of contaminations such as containers, acid and water were found to be free from these elements.

The characteristic mass is defined as the mass of analyte corresponding to 0.0044 A.s. The mₒ values were 1.8, 8.0, 15 and 25 pg for Cd, Cr, Cu and Pb, respectively. The limit of detection obtained were 0.0004, 0.060, 0.065 and 0.054 mg/kg for Cd, Cr, Cu, and Pb, respectively, in the microwave digestion procedure.

Analytical performance

The slopes of the normal and standard additions calibration graphs obtained from open microwave dissolved algae samples are compared in Table 3. It is observed that for Cu and Pb, the slopes of the two calibration graphs are the same, and normal calibration graphs can be used for quantification. In the case of Cd and Cr, the two slopes are different; therefore standard addition calibration should be used for quantification.

The results of the determination of Cd, Cr, Cu, and Pb in algae samples and SRM GBW 08504 cabbage using conventional and microwave digestion are given in Table 4. The student’s t-test (t₀.⁹⁷⁵ = 2.31, N₁ + N₂ − 2 = 8) applied at the 95% confidence level shows there is no significant difference, except Cd and Pb in algae1. The difference in Cd and Pb values in algae1 may be due to the sample inhomogeneity.

Conclusion

The open microwave digestion procedure is rapid and suitable for routine analysis of large numbers of samples required for environmental monitoring. The matrix dissolution is efficient, leading to less matrix interference and decomposed species acting as self-modifier using THETAAS. The process blank is low compared to conventional digestion because of automatic addition of the reagents and less time for digestion.

Acknowledgements

The authors are grateful to Dr. S. Gangadharan, Chief Executive, BRIT/CCCM and Dr. J. Arunachalam, Officer-in-Charge, UTAL for their keen interest and encouragement during the course of the work.