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Electrothermal Atomic Absorption Spectrometry to Determine As, Cd, Cr, Cu, Hg, and Pb in Soils and Sediments: A Review and Perspectives

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2Departamento de Ciencias Analíticas, Facultad de Ciencias, Universidad Nacional de Educación a Distancia, Madrid, Spain

Environmental pollution from trace elements has been increasing in recent decades and has become an important concern for environmental agencies. The trace elements arsenic, cadmium, chromium, copper, mercury, and lead are among the elements that cause the greatest environmental impact and carry the highest risk to human health. Electrothermal atomic absorption spectrometry (ETAAS) has long been employed in trace element determination. In the last few years the main constraints of spectroscopy absorption methods have been overcome. These advances have increased the possibilities and the utility of ETAAS for trace element determination at \( \mu \text{gL}^{-1} \) levels in difficult matrices such as soils and sediments, giving greater accuracy and precision, lower economic cost, and easier sample pretreatment than other methods. The main advances come from sample manipulation for matrix destruction and preconcentration, the use of new lab-on-valve FIA systems, the solid sampling, the use of new, more efficient modifiers and in situ trapping methods for analyte stabilization and pre-concentration, and the progress in the capacity to control the atomization temperature and to correct background spectral interferences. All of them have permitted an improvement in the sensitivity, decreasing the detection limits and manipulation process, and increasing the accuracy and precision of the analyses.

Moreover, the new technology in the optic and detector systems have given rise to high-resolution continuum source ETAAS (HR-CS ETAAS) spectrometers that solve most of the constraints presented by the more conventional line source ETAAS (LS ETAAS) spectrometers. HR-CS ETAAS enables a rapid detection of several elements at once, facilitates direct determination from solid sampling, and reduces the matrix interferences and background noise. Here we give an overview of the recent advances and the different possibilities of using ETAAS, drawing on studies from the last decade on methods to analyze As, Cd, Cu, Hg, and Pb in soils and sediments.

Keywords As, Cd, Cu, environment, ETAAS, FIA, GFAAS, Hg, HR-CS-ETAAS, Pb

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Introduction

The great impact of trace elements on natural resources and environment quality justifies the increasing interest in monitoring them through chemical analysis. Several human activities release trace elements into the environment in chemical forms that may increase their bioavailability. Soils are the water and nutrient reservoir of terrestrial ecosystems and an irreplaceable source for food production. Soil trace element pollution is a problem arising from different causes in several areas of the world. In Europe there are 40,000 km² of soils polluted with heavy metals. Among the soil trace elements, arsenic, cadmium, chromium, copper, mercury, and lead are those most studied (López-García et al., 1997a; Shotyk et al., 1998; Tüzên, 2003; Walker et al., 2003; Chirenje et al., 2004; Sardans and Peñuelas, 2005; Sardans et al., 2008; Polizzotto et al., 2008) and generate the greatest concern for the general public and therefore also for the environmental agencies in most states.

Trace elements affect living organisms in several ways, both due to the behavior of specific elements and due to the general effects that most trace elements display. For instance, by the capacity of heavy metals to form chelates with organic molecules, such as proteins and nucleic acids, which then interfere with and inhibit metabolic pathways.

Studies which monitor bioaccumulation in soils and sediments are essential to investigate the actual impact of trace elements on environmental pollution. Adequate analytical methods are essential to study the trace element contents of soils and sediments of large areas (Chen et al., 2001; Chirenje et al., 2001; Billon et al., 2002; Komarnicki, 2005; Cuong and Obbard, 2006; Figuereido et al., 2007), in order to find out the sources of trace element pollutants (Massadeh and Snook, 2002; Fytianos and Lourantou, 2004; Sardans and Peñuelas, 2005, 2006; Hjortenkrans et al., 2006; Salonen and Korkka-Niemi, 2007), and to evaluate the risk of soil use for agriculture (Palumbo et al., 2000; Linden et al., 2001; Kashem and Singh, 2002) or forestry (Kuang et al., 2007; Sardans and Peñuelas, 2007; Sardans et al., 2008), and the general risk for human health (Gebel et al., 1998; Yaman and Dilgin, 2002). A plant’s capacity to absorb trace elements depends on the trace element concentration in soil, the water mass flow, the capacity of plant-soil cationic exchange, and the chelating processes between macromolecules and trace elements.

The adequate monitoring and control of trace elements in the environment and particularly in soil and sediments require processing a large amount of samples to characterize the presence and abundance of trace elements and to reach significant conclusions. The techniques most widely used for these analyses have been ICPOES (inductively coupled plasma with optic emission spectrometry), ICPMS (inductively coupled plasma with mass spectrometry), FAAS (flame atomic absorption spectrometry) and ETAAS (electrothermal atomic absorption spectrometry), mainly using graphite furnaces (GF) as the atomizer.

ETAAS is a widely used technique to determine the total trace element concentration in soils and sediments. In the past, trace element determination in an unknown sample was often very disrupted by multiple physical and/or chemical reactions and effects in the atomizer that limited its use. For example, the sample matrix can lead the analyte to form volatile or stable molecules and can cause a greater loss of free analyte atoms in comparison to the reference solution. Moreover, the sample matrix can also influence the absorption signal in the analytical line making it difficult to reach adequate detection limits. Nevertheless, over the last decades these constraints have been partially or totally solved by progressively incorporating improvements that have enhanced the capacity of ETAAS to compete with ICP-MS in terms of sensitivity, while maintaining the advantages of absorption techniques such as the easy possibility of performing analytical determination using solid samples.
In this study, we present the main constraints that ETAAS techniques had in past decades to determine As, Cd, Cr, Cu, Hg, and Pb in soils and sediments. After this, we discuss the progressive improvements that have been introduced to solve these problems. Among these advances, we highlight the following: the use of adequate methods of sample pre-treatment, the direct solid sampling, the correct use of modifiers, the use of the graphite furnace to improve the atomization efficiency, the emergence of new optical systems for radiation sources and array detectors, the advances in the methods for spectral corrections, and the improvements in the use of an atomizer for pre-concentration. Finally, we focus on the high resolution continuum source ETAAS (HR-CS ETAAS) that combines the use of a more intense spectral continuum radiation source with modern spectrometers equipped with new detector systems and more modern furnaces and software. These advances, together with an adequate use of modifiers and modern atomizers such as the graphite filter atomizer (GFA), enable reaching a high sensitivity and low detection limits, provide an easy sample preparation, and open the future possibility of simultaneous multi-element determination.

In addition to these advances, we also discuss progress that is complementary to the analytical process, such as the connection of sample introduction in the graphite furnace to FIA systems, where sample pre-treatments can be automated. This is an additional improvement that, together with a reasonably low cost and relatively short time consumption, makes ETAAS a very useful tool for As, Cd, Cr, Cu, Hg, and Pb determination in soils and sediments.

Our aim is to review the different possibilities offered by the analytical methods based on ETAAS for the determination of As, Cd, Cr, Cu, Hg, and Pb in soils and sediments. In this way we hope to provide an easy and updated understanding of this method for scientists coming from all disciplines in environmental science, agriculture, forestry, and human health who frequently need to analyze these 5 elements or any combination of them in soils and sediments.

Sample Pretreatments

Due to the heterogeneity of the different soil and sediment samples analyzed and the specific purpose of the study in the different reports we examined (Table 1), there is no unique pretreatment prior to sample introduction in the graphite furnace. The pretreatment chosen depends on the possibilities of the laboratory and the study objectives (Table 1). The matrix can hinder complete analyte atomization and may interfere in the determination. Because of this, several methods involve pretreatments to separate the analyte from the matrix without any significant analyte loss. On the other hand, recent advances in spectrometers have resulted in easier direct solid sampling analyses that reduce the necessity for sample preparation.

Since the introduction of ETAAS, detection limits have dropped significantly and some of the advances introduced in this analytical method have solved problems linked to the interferences that matrix components can have on AAS determination. Some of these improvements consist of pretreatments that partially or completely destroy the matrix prior to sample introduction in the GF. These methods minimize the matrix effects by optimizing the atomization process and by minimizing the spectral interferences.

Acid Digestion

The most widely used method to destroy the sampling matrix in soils and sediments is acid digestion (Table 1). This method is especially useful when we aim to determine the total
Table 1
Different analytes, sample matrix types, sample pre-treatments, standards, recovery, modifiers, background correction used, GFAAS spectrometer and detection limits in the determination of As, Cd, Cu, Hg, and Pb by GFAAS in soils and sediments

<table>
<thead>
<tr>
<th>Elements</th>
<th>Sample matrix</th>
<th>Sample pretreatment</th>
<th>Standards(^1)</th>
<th>Recovery</th>
<th>Modifiers</th>
<th>Back.cor. system</th>
<th>Spectrometer characteristics(^2)</th>
<th>Detection limits</th>
<th>Ref.</th>
<th>N°</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>Soils</td>
<td>USEPA 3051a</td>
<td>S</td>
<td></td>
<td></td>
<td>LS.</td>
<td></td>
<td></td>
<td>Chirenje et al. (2001)</td>
<td>1</td>
</tr>
<tr>
<td>As</td>
<td>Soils</td>
<td>USEPA 3051a</td>
<td>S</td>
<td></td>
<td></td>
<td>LS. USEPA 7060A.</td>
<td></td>
<td></td>
<td>Chirenje et al. (2003)</td>
<td>2</td>
</tr>
<tr>
<td>As, Cd, Pb</td>
<td>Soils</td>
<td>USEPA 3051a</td>
<td>NH(_4)N(_2)PO(_4) + Mg(_2)O(_3) \rightarrow) Cd, Pb, Pd(NO(_3))(_2) \rightarrow) As S 97.3%. Pd + Mg(NO(_3))(_2)</td>
<td></td>
<td></td>
<td>LS.</td>
<td></td>
<td></td>
<td>Coskun et al. (2006)</td>
<td>3</td>
</tr>
<tr>
<td>As</td>
<td>Lake sediments</td>
<td>USEPA 3051a</td>
<td>Leaching with acid water</td>
<td></td>
<td></td>
<td>LS. At 2000°C. LHA.</td>
<td></td>
<td></td>
<td>Arain et al. (2009)</td>
<td>4</td>
</tr>
<tr>
<td>As, Cd</td>
<td>Soils and Sediments</td>
<td>USEPA 3051a</td>
<td></td>
<td></td>
<td></td>
<td>LS.</td>
<td></td>
<td></td>
<td>Salonen and Korkka-Niemi (2007)</td>
<td>5</td>
</tr>
<tr>
<td>As</td>
<td>Soils</td>
<td>Acid digestion (HNO(_3) + H(_2)SO(_4)) and CV Generation</td>
<td>S</td>
<td></td>
<td></td>
<td>D(_2) lamp</td>
<td>LS. 0.5 (\mu)g L(^{-1}) in acid digests</td>
<td></td>
<td>Gebel et al. (1998)</td>
<td>6</td>
</tr>
<tr>
<td>As</td>
<td>Soils</td>
<td>USEPA 3051a</td>
<td></td>
<td>Pd + Mg(NO(_3))(_2)</td>
<td>Zeeman</td>
<td>LS. At. 2100°C. THA.</td>
<td></td>
<td></td>
<td>Bissen et al. (2000)</td>
<td>7</td>
</tr>
<tr>
<td>As, Cd, Cr, Pb</td>
<td>Soils and sediments</td>
<td>USEPA 3051a</td>
<td>S</td>
<td></td>
<td></td>
<td>Zeeman</td>
<td>LS. THA. 9.5 (\mu)g L(^{-1}) As, 0.18 (\mu)g L(^{-1}) Cd, 2.5 (\mu)g L(^{-1}) Pb in acid digests</td>
<td></td>
<td>Myöhänen et al. (2002)</td>
<td>8</td>
</tr>
<tr>
<td>Substance</td>
<td>Location</td>
<td>Method</td>
<td>Recoveries</td>
<td>Detection Limit</td>
<td>Notes</td>
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<tr>
<td>As, Cd, Cr, Cu, Pb</td>
<td>Soils</td>
<td>USEPA 3052 USEPA 3051a and (HNO3 + HF + H3BO3)</td>
<td>S 94% using HF</td>
<td>L.S.</td>
<td>Chen and Ma (2001)</td>
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</tr>
<tr>
<td>As</td>
<td>Soil humus</td>
<td>Acid digestions: (HNO3 + HF + H2O2 + H3BO3) and (HNO3 + H2O2).</td>
<td>S (95–109%)</td>
<td>Pd + Mg (NO3)2</td>
<td>Zeeman</td>
<td>L.S. <em>In situ</em> trapping. At. 2200°C.</td>
<td>Perämäki et al. (2000)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As, Cd, Cu</td>
<td>Soils</td>
<td>Extraction with aqua Regia. Acid digestion with HNO3</td>
<td>S near 100%. No differences among different pretreatments</td>
<td>NH4N2PO4 + Mg (NO3)2 for Cd, and Pd + Mg (NO3)2 for Cu</td>
<td>Zeeman</td>
<td>L.S. THA. At 1400°C Cd and 2000°C As and Cu</td>
<td>Väisänen and Suontamo (2002)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>As</td>
<td>Soils</td>
<td>Acid digestion HNO3 + HCl</td>
<td>S</td>
<td>Zeeman and D2 lamp.</td>
<td>L.S.</td>
<td>Beccaloni et al. (2002)</td>
<td></td>
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</tr>
<tr>
<td>As, Cd, Pb.</td>
<td>Soil and sediments</td>
<td>USEPA 3051a</td>
<td>S 95–104%</td>
<td>W, Rh, Ir, Ru, W + Rh, W + Ru, W + Ir</td>
<td>L.S. THA.</td>
<td>0.32, 0.01, 0.15 µg g⁻¹ for As, Cd, Pb in samples</td>
<td>Lima et al. (2002)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>Sediments</td>
<td>USEPA 3051a. CV in FIA</td>
<td>S 100%</td>
<td>Ir coated</td>
<td>Zeeman</td>
<td>L.S. <em>In situ</em> trapping. THA</td>
<td>Ringmann et al. (2002)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>Soils</td>
<td>USEPA 3052</td>
<td></td>
<td></td>
<td></td>
<td>Chen et al. (2001)</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

*Continued on next page*
<table>
<thead>
<tr>
<th>Elements</th>
<th>Sample matrix</th>
<th>Sample pretreatment</th>
<th>Standards¹</th>
<th>Recovery</th>
<th>Modifiers</th>
<th>Back.cor. system</th>
<th>Spectrometer characteristics²</th>
<th>Detection limits</th>
<th>Ref.</th>
<th>N°</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>Soils</td>
<td>Leaching in FIA and USEPA 3052</td>
<td>S</td>
<td>97–115%</td>
<td>Pd</td>
<td>D₂ lamp</td>
<td>LS. At. 2200°C. LHA.</td>
<td></td>
<td>Shiowatana et al. (2001b)</td>
<td>16</td>
</tr>
<tr>
<td>As</td>
<td>Soils and marine sediments</td>
<td>USEPA 3052 and slurry with triton X 100 and hydride generation by FIA system</td>
<td>S</td>
<td></td>
<td>Ir coated</td>
<td>D₂ lamp</td>
<td>LS. In situ trapping. THA. 0.005 µg g⁻¹</td>
<td></td>
<td>Matusiewicz and Mroczkowska (2003)</td>
<td>17</td>
</tr>
<tr>
<td>As</td>
<td>Soils</td>
<td>USEPA 3052 and acid digestion HNO₃ + HClO₄ Slurry (HNO₃ + H₂O₂).</td>
<td>S</td>
<td>40–90% in USEPA 3052 and 95–124% in slurry</td>
<td>Ir + Mg (coated)</td>
<td>Zeeman</td>
<td>LS. At. 2500°C.</td>
<td></td>
<td>Vassileva et al. (2001a)</td>
<td>18</td>
</tr>
<tr>
<td>As</td>
<td>Soils</td>
<td>USEPA 3052</td>
<td>S</td>
<td>96–102%</td>
<td>Rh, Ir, Ru, W + Rh, W + Ir, W + Ru coated.</td>
<td>D₂ lamp</td>
<td>LS. At 2300°C. THA.</td>
<td></td>
<td>Lima et al. (2003)</td>
<td>19</td>
</tr>
<tr>
<td>As</td>
<td>Estuarine, river sediments</td>
<td>Solid leaching and with final acid digestion (HNO₃ + HF) of residue and solid sampling.</td>
<td>S</td>
<td>103–175%</td>
<td>Pd + Mg (NO₃)₂</td>
<td>D₂ lamp</td>
<td>LS. At 2150°C. 0.44 µg g⁻¹ in acid digests</td>
<td></td>
<td>Sahuquillo et al. (2003)</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 1
Different analytes, sample matrix types, sample pre-treatments, standards, recovery, modifiers, background correction used, GFAAS spectrometer and detection limits in the determination of As, Cd, Cu, Hg, and Pb by GFAAS in soils and sediments (Continued)
<table>
<thead>
<tr>
<th>Elemental Compositions</th>
<th>Sample Types</th>
<th>Preparation Methods</th>
<th>Detection Methods</th>
<th>Detection Limits</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>As, Cd, Pb</td>
<td>Sediments</td>
<td>USEPA 3052</td>
<td>Pd + Mg(NO₃)₂</td>
<td>0.25, 0.05, 0.25 μg g⁻¹</td>
<td>Murko et al. (2002)</td>
</tr>
<tr>
<td>As</td>
<td>Soils</td>
<td>(NO₃)₃ + HF</td>
<td>Zeeman and D₂ lamp</td>
<td>1 μg g⁻¹ using 4 mg of solid in 1 mL slurry</td>
<td>López-García et al. (1997a)</td>
</tr>
<tr>
<td>As</td>
<td>Sediments</td>
<td>Slurry in ultrasonic bath</td>
<td>Zeeman</td>
<td>0.7 μg g⁻¹ using 1 mg of solid in 1 mL of slurry</td>
<td>Vieira et al. (2002)</td>
</tr>
<tr>
<td>As, Cd</td>
<td>Soils</td>
<td>Leaching with HNO₃ 7 M</td>
<td>LS.</td>
<td>3 μg g⁻¹</td>
<td>Tijhuis et al. (2002)</td>
</tr>
<tr>
<td>As, Cd, Cu, Pb</td>
<td>Standards</td>
<td></td>
<td>HR-CS ETAAS.</td>
<td></td>
<td>Heitmann et al. (2006)</td>
</tr>
<tr>
<td>As</td>
<td>Soils</td>
<td>Solid sampling</td>
<td>Pd(NO₃)₂, Mo(NO₃)₂, Ni(NO₃)₂, Ni + triton</td>
<td></td>
<td>Akdeniz and Yaman (2005)</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Elements</th>
<th>Sample matrix</th>
<th>Sample pretreatment</th>
<th>Standards</th>
<th>Recovery</th>
<th>Modifiers</th>
<th>Back.cor. system</th>
<th>Spectrometer characteristics</th>
<th>Detection limits</th>
<th>Ref.</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>Flters with Trapped particles</td>
<td>Solid sampling. CV in FIA</td>
<td>S</td>
<td>98%</td>
<td>Ir coated</td>
<td>L.S. In situ trapping. At 2000 °C.</td>
<td>0.02 µg L⁻¹ in acid digests</td>
<td>Moreda-Piñeiro et al. (2007).</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>Water solutions</td>
<td>As(III) coprecipitation Specification of As(III) and of As(V)</td>
<td></td>
<td></td>
<td></td>
<td>Zeeman</td>
<td>L.S.</td>
<td>0.02 µg L⁻¹ in acid digests</td>
<td>Zhang et al. (2004)</td>
<td>29</td>
</tr>
<tr>
<td>As</td>
<td>Water solutions</td>
<td>As(III) coprecipitation Specification of As(III) and As(V)</td>
<td></td>
<td></td>
<td></td>
<td>D₂ lamp.</td>
<td>L.S. LHA.</td>
<td>0.05 µg L⁻¹ in acid digests</td>
<td>Elçi et al. (2008)</td>
<td>30</td>
</tr>
<tr>
<td>Cd, Pb</td>
<td>Soils</td>
<td>USEPA 3051a</td>
<td>S</td>
<td></td>
<td></td>
<td>Zeeman</td>
<td>L.S.</td>
<td></td>
<td>Komamicki (2005)</td>
<td>31</td>
</tr>
<tr>
<td>Cd, Cr, Pb</td>
<td>Soils and Sediments</td>
<td>Acid dig. HNO₃ + HF, HNO₃ + HClO₄, HNO₃, HNO₃ + H₂O₂</td>
<td>S</td>
<td>96–102%</td>
<td></td>
<td>Zeeman</td>
<td>L.S.</td>
<td>At 1650 °C Cd, 1800 °C Pb At 2500 °C Cr</td>
<td>Kazi et al. (2009)</td>
<td>32</td>
</tr>
<tr>
<td>Cd</td>
<td>Soils</td>
<td>USEPA 3051a</td>
<td>S</td>
<td></td>
<td></td>
<td>Zeeman</td>
<td>L.S.</td>
<td></td>
<td>Beccaloni et al. (2005)</td>
<td>33</td>
</tr>
<tr>
<td>Element(s)</td>
<td>Sample Type</td>
<td>Digestion Method</td>
<td>Recovery (%)</td>
<td>Detection Method</td>
<td>Temperature (°C)</td>
<td>Authors</td>
<td>Year</td>
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<td>Cd, Pb</td>
<td>Road dust</td>
<td>USEPA 3051a Slurry with HNO₃</td>
<td>S</td>
<td>96–98% Cd, 98–102% Pb</td>
<td>NH₄N₂PO₄ + Mg₂O₃ for Cd</td>
<td>D₂ Lamp</td>
<td>LS.</td>
<td>At 1600°C Cd, 1800°C Pb</td>
<td>Massadeh and Smook (2002)</td>
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<td>Cd, Cu, Pb</td>
<td>Soils</td>
<td>Acid digestion (HNO₃)</td>
<td>S</td>
<td>Cd 45–95%, Cu 78–104%, Pb 55–67%, Cr 47–90%</td>
<td>LS.</td>
<td>Walker et al. (2003)</td>
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<td>Cd, Cr, Cu, Pb</td>
<td>Soils</td>
<td>Acid digestion (micro-wave) (HNO₃ + HCl + HClO₄)</td>
<td>S</td>
<td>Zeeman</td>
<td>Palumbo et al. (2000)</td>
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<td>Cd</td>
<td>Soils</td>
<td>Acid digestion (HNO₃ + H₂O₂) and sequential extraction</td>
<td>S</td>
<td>LS.</td>
<td>THA.</td>
<td>Yaman and Dilgin (2002)</td>
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<td>Cd, Cu, Pb</td>
<td>Soils and sediments</td>
<td>Leaching by FIA with HNO₃ or HNO₃ + HClO₄.</td>
<td>S</td>
<td>Zeeman</td>
<td>LS.</td>
<td>Mosbaek et al. (2003)</td>
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<tr>
<td>Cd</td>
<td>Soil and sediments</td>
<td>(HNO₃ + H₂O₂) hydride generation in FIA</td>
<td>S</td>
<td>80–110%</td>
<td>Zeeman and D₂ lamp</td>
<td>LS.</td>
<td>In situ trapping.</td>
<td>0.01 µg g⁻¹ in solid sample</td>
<td>Matusiewicz et al. (1997)</td>
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(Continued on next page)
Table 1
Different analytes, sample matrix types, sample pre-treatments, standards, recovery, modifiers, background correction used, GFAAS spectrometer and detection limits in the determination of As, Cd, Cu, Hg, and Pb by GFAAS in soils and sediments (Continued)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Sample matrix</th>
<th>Sample pretreatment</th>
<th>Standards</th>
<th>Recovery</th>
<th>Modifiers</th>
<th>Back.cor. system</th>
<th>Spectrometer characteristics</th>
<th>Detection limits</th>
<th>Ref.</th>
<th>N°</th>
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<tbody>
<tr>
<td>Cd, Cr, Cu, Pb</td>
<td>Soils and sediments</td>
<td>USEPA 3052, USEPA 3051a</td>
<td>S</td>
<td>100% using HF</td>
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<tr>
<td>Cd, Cr, Pb</td>
<td>Soils</td>
<td>USEPA 3052 and acid digestion with NHO₃ + H₂SO₄ + H₂O₂</td>
<td>S</td>
<td>NH₄₂N₂PO₄ + Mg(NO₃)₂ → Pb Pd + Pb LHA.</td>
<td>L.S. At 1650°C Cd, 1800°C Pb LHA.</td>
<td>0.13 μg L⁻¹ in extracts</td>
<td>Rucandio and Petit (1999)</td>
<td>43</td>
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<tr>
<td>Cd</td>
<td>Soils</td>
<td>USEPA 3052.</td>
<td>S</td>
<td>NH₄₂N₈PO₄ + Mg(NO₃)₂ and NH₄₂N₂PO₄ → Cd</td>
<td>Zeeman</td>
<td>L.S. At 1800–1900°C. LHA.</td>
<td>0.007 μg L⁻¹ in extracts</td>
<td>Tüzence (2003)</td>
<td>44</td>
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<td>Cd</td>
<td>Soil and</td>
<td>Sequential leaching and USEPA 3052</td>
<td>S</td>
<td>NH₄₂N₈PO₄ + Mg(NO₃)₂</td>
<td>Zeeman</td>
<td>L.S. At 1900°C.</td>
<td>0.026 μg g⁻¹ Cd, and 0.13 μg L⁻¹ in acid digest solution</td>
<td>Rucandio and Petit-Domínguez (2002)</td>
<td>46</td>
<td></td>
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<tr>
<td>Cd</td>
<td>Soils</td>
<td>USEPA 3052</td>
<td>S</td>
<td>NH₄₂N₈PO₄ + Mg(NO₃)₂</td>
<td>Zeeman</td>
<td>L.S. At 1900°C.</td>
<td>0.026 μg g⁻¹ Cd, and 0.13 μg L⁻¹ in acid digest solution</td>
<td>Rucandio and Petit-Domínguez (2002)</td>
<td>47</td>
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<tr>
<td>Cd, Pb</td>
<td>Soils</td>
<td>USEPA 3052</td>
<td>S</td>
<td>Mo-Ru coated</td>
<td>Zeeman</td>
<td>L.S.</td>
<td>Na₂CO₃</td>
<td>Kuang et al. (2007)</td>
<td>49</td>
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<tr>
<td>Cd, Cr, Cu, Pb</td>
<td>Soils and sediments</td>
<td>USEPA 3052 and USEPA 3051a</td>
<td>Solid</td>
<td>Zeeman and D₂ lamp</td>
<td>L.S.</td>
<td>L.S. THA.</td>
<td>Nowka et al. (2000)</td>
<td>50</td>
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<tr>
<td>Element</td>
<td>Sample Type</td>
<td>Methodology</td>
<td>Detection Limit</td>
<td>Authors</td>
<td>Year</td>
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<td>Cd</td>
<td>River sediments</td>
<td>USEPA 3052, FIA lab-on-valve to sequential extraction and pre-concentration</td>
<td>LS. At 1400°C</td>
<td>15 ng L-1 in Acid digest solution</td>
<td>Miró et al., 2003</td>
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<tr>
<td>Cd, Cu, Pb</td>
<td>Soils and Sediments</td>
<td>USEPA 3052</td>
<td>Diverse modifiers</td>
<td>Best recoveries were obtained using Sc + Pd + NH₄NO₃ as modifier mixture.</td>
<td>Acar (2005a)</td>
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<tr>
<td>Cd, Cu, Pb</td>
<td>Sediments</td>
<td>Slurry HNO₃ + triton X100 and USEPA 3052</td>
<td>S</td>
<td>(Continued on next page)</td>
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<tr>
<td>Cd</td>
<td>Lake sediments</td>
<td>Slurry HNO₃ + triton X100</td>
<td>S</td>
<td>90-96.3% NH₄N₂PO₄</td>
<td>Baralkiewicz and Gramowska (2004)</td>
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<tr>
<td>Cd</td>
<td>Coal</td>
<td>Slurry HNO₃ + triton X100 + Ethanol</td>
<td>S</td>
<td>40-120%</td>
<td>Bianchin et al. (2006)</td>
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<tr>
<td>Cd</td>
<td>Soils</td>
<td>Leaching with H₂O. with 0.01 M CaCl₂, And CV generation</td>
<td>S</td>
<td></td>
<td>Bujdos et al. (2003)</td>
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<tr>
<td>Cd</td>
<td>Sediments</td>
<td>Slurries with triton X-100 + HNO₃ in ultrasound bath and USEPA 3052</td>
<td>S</td>
<td>100-102%</td>
<td>Borges et al. (2003)</td>
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Table 1

Different analytes, sample matrix types, sample pre-treatments, standards, recovery, modifiers, background correction used, GFAAS spectrometer and detection limits in the determination of As, Cd, Cu, Hg, and Pb by GFAAS in soils and sediments (Continued)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Sample matrix</th>
<th>Sample pretreatment</th>
<th>Standards</th>
<th>Recovery</th>
<th>Modifiers</th>
<th>Back.cor. system</th>
<th>Spectrometer characteristics</th>
<th>Detection limits</th>
<th>Ref.</th>
<th>N°</th>
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<tbody>
<tr>
<td>Cd</td>
<td>Anoxic sediment</td>
<td>Sequential leaching</td>
<td>S</td>
<td>Zeeman</td>
<td>LS.</td>
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<td>Cd, Cr, Cu, Pb</td>
<td>Lake sediments</td>
<td>Sequential leaching</td>
<td>S</td>
<td>LS.</td>
<td>Fytianos and Lourantou (2004)</td>
<td>59</td>
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<td>Cd</td>
<td>Soils</td>
<td>Leaching with HNO₃ 7M</td>
<td>S</td>
<td>Zeeman</td>
<td>LS.</td>
<td>Lindén et al. (2001)</td>
<td>60</td>
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<td>Cd</td>
<td>Soils</td>
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<td>S</td>
<td>LS.</td>
<td>Kashem and Singh (2002)</td>
<td>61</td>
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<td>Cd, Pb</td>
<td>Soils</td>
<td>Leaching with H₂O</td>
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<td>Zeeman</td>
<td>LS.</td>
<td>Zhai et al. (2003)</td>
<td>62</td>
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<td>Cd, Pb</td>
<td>Soils</td>
<td>Sequential leaching</td>
<td>S</td>
<td>LS.</td>
<td>Giacomelli et al. (2002)</td>
<td>64</td>
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<td>Cd, Pb</td>
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<td>Sequential extraction</td>
<td>S</td>
<td>Zeeman</td>
<td>LS.</td>
<td>Schrön et al. (2000)</td>
<td>65</td>
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<td>Cd, Cu, Pb</td>
<td>Soil and Sediments</td>
<td>Solid sampling</td>
<td>3-D cal. Cu (92–118%), Cd (87–105%), Pb (80–106%)</td>
<td>D₂ lamp</td>
<td>LS.</td>
<td>THA.</td>
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<tr>
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<td>Instrument</td>
<td>Drying Temperature</td>
<td>Detection Limits</td>
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<td>Cd, Cr, Cu, Pb</td>
<td>Soils and Sediments</td>
<td>Solid sampling</td>
<td>D₂ lamp</td>
<td>L.S. THA</td>
<td>Nowka et al. (1999) 66</td>
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<td>Cd, Cu, Pb</td>
<td>Lake, river and estuarine sediments</td>
<td>Solid sampling</td>
<td>Zeeman and D₂ lamp</td>
<td>L.S. LHA and THA, At. 1900°C Cd, 2100°C Cu, 2250°C Pb</td>
<td>Nimmerfall and Schrön (2001) 67</td>
<td></td>
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<td>Cd, Cu, Pb</td>
<td>Coal</td>
<td>Solid sampling</td>
<td>D₂ lamp</td>
<td>L.S. At 2000°C Pb 1400°C Cd, 2100°C Cu, THA</td>
<td>Vale et al. (2001) 68</td>
<td></td>
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<td>Cd</td>
<td>Coal</td>
<td>Solid sampling</td>
<td>Ir coated</td>
<td>HR-CS ETAAS. At 1900°C</td>
<td>da Silva et al. (2005) 69</td>
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<tr>
<td>Cd</td>
<td>Soils</td>
<td>Solid sampling</td>
<td>S</td>
<td>W, Ir, Rh, Ru, W + Ir W + Ir coated</td>
<td>Lima et al. (2002b) 70</td>
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<td>Cr and Cr⁶⁺</td>
<td>Soils USEPA 3052 and alkaline leaching</td>
<td>S</td>
<td>D₁ lamp</td>
<td>L.S. At 2500°C</td>
<td>Figuereido et al. (2007) 71</td>
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<td>Cr</td>
<td>Soils and Sediments</td>
<td>Different slurries</td>
<td>D₂ lamp</td>
<td>L.S. At. 2300–2500°C</td>
<td>Felipe-Sotelo et al. (2005) 72</td>
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<td>Cr</td>
<td>Soils and Sediments</td>
<td>Slurry with 4% v/v HNO₃ + triton X-100</td>
<td>Zeeman</td>
<td>L.S. At. 2550°C</td>
<td>Mierzwa et al. (1998) 73</td>
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<td>Cr⁶⁺</td>
<td>Soil</td>
<td>Leaching with basic Solution and separation/Preconcentration with Sephore anion exchange In LOV mode</td>
<td>Zeeman</td>
<td>L.S. At. 2300°C</td>
<td>Long et al. (2006) 74</td>
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(Continued on next page)
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<th>Standards</th>
<th>Recovery</th>
<th>Modifiers</th>
<th>Back.cor. system</th>
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<th>Detection limits</th>
<th>Ref.</th>
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<td>Cu</td>
<td>Sediments</td>
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<td>S</td>
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<td>W + Rh coated Pd + Mg (NO₃)₂</td>
<td>LS.</td>
<td>0.3 µg g⁻¹ (acid digest), 1.6 µg g⁻¹ (slurry)</td>
<td>Lima et al. (2001)</td>
<td>75</td>
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<td>Soils</td>
<td>USEPA 3051a</td>
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<td>LS. USEPA 7060A.</td>
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<td>Chirenje et al. (2004)</td>
<td>76</td>
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<td>Pb</td>
<td>Soils and river sediments</td>
<td>Acid digestion (HNO₃ + HCl + HClO₄) and coprecipitation in FIA</td>
<td>S</td>
<td>95–99%</td>
<td>D₂ lamp</td>
<td>LS.</td>
<td>0.0048 µg L⁻¹ in extracts</td>
<td>Yan and Adams (1997)</td>
<td>77</td>
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<td>Street dust</td>
<td>Slurry with HNO₃ 0.1M.</td>
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<td>D₂ lamp</td>
<td>LS.</td>
<td>Anagnostopoulou and Day (2006)</td>
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<td>Pb</td>
<td>Coal ashes</td>
<td>Slurry HNO₃ + triton X100</td>
<td>S</td>
<td>98%</td>
<td>Zeeman and D₂ lamp</td>
<td>LS.</td>
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<td>Milker-Illi (1997)</td>
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<td>Pb</td>
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<td>Slurry HNO₃ + triton</td>
<td>S</td>
<td>95–104%</td>
<td>Pd + Mg (NO₃)₂</td>
<td>D₂ lamp</td>
<td>LS. At 1700℃</td>
<td>Baralkiewicz (2002)</td>
<td>80</td>
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<td>Pb</td>
<td>Coal</td>
<td>Solid sampling</td>
<td>S</td>
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<td>HR-CS ETAAS.</td>
<td>0.008 µg g⁻¹</td>
<td>Borges et al. (2006)</td>
<td>81</td>
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<td>Hg</td>
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<td>Acid digestion (HNO₃ + HCl) and (HNO₃ + HCl + H₂O₂) FIA sto CV</td>
<td>S</td>
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<td>LS.</td>
<td></td>
<td>Navarro et al. (2006)</td>
<td>82</td>
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<td>Hg</td>
<td>Lake sediment</td>
<td>USEPA 3051a CV generation</td>
<td></td>
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<td>Pd coated</td>
<td>D₂ lamp</td>
<td>LS. In situ trapping, At 1100℃, THA.</td>
<td>Moreno et al. (2002)</td>
<td>83</td>
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<td>Hg</td>
<td>Soil</td>
<td>Acid digestion: (HCl) Rh,</td>
<td>S</td>
<td>97–99%</td>
<td>Pd, Rh, Ir no coated Pd + Ir, Au + Rh coated</td>
<td>Zeeman D2 lamp LS. Using both THA and LHA At 1300°C.</td>
<td>5 μg L⁻¹ in acid digest. Best recoveries using Pd and Au + Rh (coated) Modifiers. Bulska et al. (1996) 85</td>
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<td>Hg</td>
<td>Soils and sediments</td>
<td>Slurry with HNO₃ + HF</td>
<td>S</td>
<td></td>
<td>AgNO₃ + KMnO₄</td>
<td>Zeeman D2 lamp LS. At 1300°C. Fast heating temperature program without pyrolysis</td>
<td>0.1 μg g⁻¹ using 125 mg of solid in 1 mL slurry López-García et al. (1997b) 86</td>
<td></td>
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<td>Hg</td>
<td>Mineral coal</td>
<td>Grinded at &lt;30 μm and slurry with HNO₃ + CV in FIA</td>
<td>S</td>
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<td>Au, Ir, Pd, Rh coated</td>
<td>D2 lamp LS. At 700°C in Au and 1-400°C in Pd and Rh. THA.</td>
<td>0.09 μg g⁻¹ using 10 mg of solid in 1 mL slurry Flores et al. (2001) 87</td>
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<td>Hg</td>
<td>Soils</td>
<td>Slurry glicerol solution (0.02%) and CV generation in FIA</td>
<td>S</td>
<td></td>
<td>Ir coated</td>
<td>No background correction</td>
<td>L.S. In situ trapping. At 1700°C.</td>
<td>0.04–0.6 μg g⁻¹ in 250 mg of solid in 25 mL slurry Moreda-Piñeiro et al. (2002) 88</td>
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<td>Hg</td>
<td>Marine and river sediments</td>
<td>Solid sampling</td>
<td>S</td>
<td></td>
<td>Ir, Pd, Rh, Ru coateds</td>
<td>D2 lamp LS. At 1000°C. THA.</td>
<td>0.2 μg g⁻¹ in samples. da Silva et al. (2002) 89</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 1

Different analytes, sample matrix types, sample pre-treatments, standards, recovery, modifiers, background correction used, GFAAS spectrometer and detection limits in the determination of As, Cd, Cu, Hg, and Pb by GFAAS in soils and sediments (Continued)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Sample matrix</th>
<th>Sample pretreatment</th>
<th>Standards¹</th>
<th>Recovery</th>
<th>Modifiers</th>
<th>Back.cor. system</th>
<th>Spectrometer characteristics²</th>
<th>Detection limits</th>
<th>Ref.</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>Coal</td>
<td>Solid sampling</td>
<td>S</td>
<td></td>
<td>Pd coated</td>
<td>D₂ lamp</td>
<td>LS. In situ trapping. At 1300°C. THA.</td>
<td>0.025 µg g⁻¹ in samples.</td>
<td>Maia et al. (2002)</td>
<td>90</td>
</tr>
<tr>
<td>Hg</td>
<td>Soils</td>
<td>Solid sampling</td>
<td>S</td>
<td>95–110%</td>
<td>KMnO₄</td>
<td>D₂ lamp</td>
<td>LS. At 1200°C. THA.</td>
<td>25 µg g⁻¹ in samples.</td>
<td>Resano et al. (2005)</td>
<td>91</td>
</tr>
<tr>
<td>Hg</td>
<td>Solid and solution standards</td>
<td>Solid sampling</td>
<td>S</td>
<td>98–99%</td>
<td>Au coated</td>
<td>D₂ lamp</td>
<td>LS. In situ trapping. At 950°C.</td>
<td>0.17 µg g⁻¹ in solid samples</td>
<td>Cervený et al. (2007)</td>
<td>92</td>
</tr>
</tbody>
</table>

Spaces with nothing as the cause is because the paper did not explain this trait.

¹Solid = Solid standard, S = standard solution, 3-D cal. = 3-Dimension calibration.

²LS = Line source.
content of the trace element analyzed. The goal of this method is to completely liberate the analyte from sample matrix molecular structures. Chemical analyses by ETAAS of liquid samples from acid digestions have several advantages: a better capacity to manipulate the analyte concentrations in the optimum range of detection, a greater ease in finding an adequate standard and the use of less sophisticated spectrometers. However, if inadequate equipment is used to conduct acid digestion there may be unacceptable losses of analytes such as As and Hg by volatilization.

In recent years, there has been a widespread use of microwaves for acid digestion under pressure with temperature control in order to determine trace elements in soils and sediments (Table 1 and 1–19, 21–52, 71, 76, 77, 82–85). This permits a temperature and/or pressure control that enables the use of large samples (1–2 g) without the danger of vessel rupture and without contamination or analyte losses. The use of modern microwaves is particularly important in solid sample digestions, such as soils and sediments, for As and Hg determination, with the complete mineralization of the sample at low temperature preventing As and Hg losses. The most widely used acid is nitric acid and the methods most commonly employed using it as acid of reference, are the USA Environmental Protection Agency (EPA) methods 3051a and 3052.

The EPA 3051a method involves microwave extraction using conventional heating with HNO₃, or alternatively HNO₃ plus HCl. Several studies have used some variants of this method (Table 1 and 1–14, 31–43, 76, 77, 82, 83). HNO₃ has been also used without the assistance of microwave oven heating (Walker et al., 2003; Anagnostopoulou and Day, 2006). However, other studies have used HNO₃ with alternative acids to HCl, such as H₂SO₄ (Gebel et al., 1998), HClO₄ (Mosbaek et al., 2003) (Table 1). Since this method (or similar ones) does not try to accomplish total decomposition of the sample, the concentration of extracted analyte may not reflect the total content of the sample. However, this method is suitable for environmental studies because the amounts of trace elements obtained are those which are available to trophic chains on a short and medium-large time scale. The EPA 3052 method is applicable to the acid digestion of complex matrices such as soils and sediments with siliceous matrices or other difficult materials, and it achieves practically total sample matrix destruction and trace element recovery in solution. This approach requires the use of HNO₃ + HF and heating within a microwave oven. It includes several optional alternatives such as the addition of HCl, H₂O₂, or HClO₄ (Palumbo et al., 2000; Zhai et al., 2003) to the previous acids. The method is particularly suitable for determining total trace element content and has been widely used during the last decade for As, Cd, Cr, Cu, Hg, and Pb determination in soils and sediments (Table 1 and 1–15–22, 43–53, 71, 84). When different digestion methods have been compared for the determination of As, Cd, Cr, Cu, and Pb in soils and sediments, those conducted using HNO₃ + HF alone or with other acids were the methods that achieved the best recoveries of these analytes (Perämäki et al., 2000; Lima et al., 2000a; Bettinelli et al., 2000; Chen and Ma, 2001). In the case of Hg, good results have been obtained with acid digestion using HCl (Bulska et al., 1996) (Table 1). In Hg determination in soils, acid digestion conducted with HCl has achieved better results than acid digestion with HNO₃ + HF + HCl (Krata and Bulska, 2005) (Table 1).

Alternative to microwave acid digestion, ultrasonic can be coupled to acid digestion to improve sample dissolution during digestion in the determination of Cd and Pb in soils and sediments (Priego-Capote and Luque de Castro, 2007; Kazi et al., 2009). The process is a “cold boiling” process resulting from the creation and collapse of countless micro-bubbles in the liquid. This process accelerates both chemical and physical reactions by increasing the temperature and pressures at the interface of the sonicated solution and the solid matrix, which along with the oxidative power of strong acids results in a high extractive power.
Slurry

Slurry is a suspension of insoluble particles. This is usually achieved in water with acids (Table 1\textsuperscript{n} 18,23,24,35,86,87) or with acid plus other substances such as Triton X-100 and ethanol (Table 1\textsuperscript{n} 17,21,53–55,73,79,80) and less frequently with organic solvents alone (Moreda-Piñeiro et al., 2002). Such treatments allow the homogenization of the sample and a liberation of the trace elements to the solution. Making slurry requires an initial grinding of the sample and does not need high temperatures, hence preventing losses by volatilization. Ultrasounds can increase the release of trace elements to the solution thus increasing their recovery (Table 1\textsuperscript{n} 21,24,57). Several studies have reported good results using slurry, with recoveries comparable to those obtained with other pretreatments such as acid digestions or solid sampling when all these treatments have been applied to the same samples (Sahuquillo et al., 2003). These studies show that slurry is an adequate choice for sample pretreatment for the determination of As, Cd, Cr, Cu, Hg, and Pb by ETAAS in soils and sediments, above all if the aim of the study is to determine the trace element fraction most directly available to plants.

Leaching

When the goal is to determine the amount of trace element that is bio-available or mobile by water lixiviation, other techniques such as liquid-solid leaching are used (Table 1\textsuperscript{n} 11,15,20,25,38,39,51,56,66,71,74). This is the best alternative when we want to determine an element’s bioavailability in soil for plant uptake. Ultrasound assisted extraction is another option to increase the extraction recovery, especially in samples rich in organic matter (Lima et al., 2000a). When the objective is to partition the different chemical forms of the analyte, another possibility is to conduct a sequential extraction with the successive use of more aggressive extractors. This progressively liberates the more occluded analyte fractions, starting from the most directly available fraction for plant uptake until the most residual fraction retained in silicates (Billon et al., 2002; Yaman and Dilgin, 2002; Fytianos and Lourantou, 2004). However, some reported sample pretreatments are in-between a leaching and an acid digestion process (Tijhuis et al., 2002). In the case of As, Cr, and frequently in the case of Hg determination in soils and sediments, it may be important to determine the different chemical species and their partitioning since this provides useful information from an environmental perspective about the different bioavailability and toxicity of the distinct chemical species of the analyte. In many studies several methods of single or sequential extraction to determine Hg in soils and sediments have been used (Issaro et al., 2009). In the case of Cr, the most toxical chemical species is Cr$^{6+}$. It can be easily and selectively extracted from soils or sediments after adequate grinding and with basic water solutions because of its greater solubility in basic conditions than the other more frequent chemical form, Cr$^{3+}$ (Figuereido et al., 2007). In general, when the objective is to determine the total Cr concentration of the analyte, acid digestion or slurry sampling are the most consistent techniques (Figuereido et al., 2007), whereas when the objective is to determine different chemical species of the analyte, it is more adequate to use leaching coupled to some selective extraction method (Fytianos and Lourantou, 2004; Figuereido et al., 2007).

Due to the importance of assessing the bioavailability of trace element fraction (with potential phytotoxic effects) and the possibility of mobilization of trace elements from polluted soils and sediments, diverse single and sequential extraction schemes have been developed. These methods aim to determine different “forms” (speciation) of trace elements,
e.g. mobile/available or carbonate bound (Tessier et al., 1981). Owing to the need for establishing common and comparable methods throughout the literature, some standard methods of single and sequential extraction process have been established in the last decades. Among them, the method developed by the Community Bureau of Reference (BCR) has been the most used (Quevauviller et al., 1993; Ho and Evans, 1997) and the Tessier method (Tessier et al., 1979). These methods release the trace elements with different levels of bioavailability (exchangeable, bound to carbonates, bound to metal oxides, bound to organic matter and residual) and thus provide an environmental valuable information. These methods have been continuously improved and optimized (Sutherland and Tack, 2003; Zimmerman and Weindorf, 2010) and have been successfully used in soil and sediment analyses to determine Cd, Cr, Cu, and Pb (Tessier et al., 1979; Ho and Evans, 1997; Fernández Alborés et al., 2000; Sutherland and Tack, 2003). Similar to these general methods, another specific method has been developed for Hg speciation in sea sediments (Kotnik et al., 2007) and to determine Cr$^{3+}$ and Cr$^{6+}$ concentrations in different levels of bioavailability (Gatehouse et al., 1997; Kalembkiewicz and Soco, 2005). Some of these sequential extraction procedures have been automatized by FIA systems (Shiowatana et al., 2001a) (see below).

Indeed the results suggest that choosing between acid digestion, slurry, or leaching as sample pre-treatment depends on the study objective. If total element recovery is the objective, acid digestion using microwaves, or ultrasonic assisted is the most suitable method. If the soluble or plant available analyte fraction is the objective, slurry or leaching (mainly sequential leaching) is more advisable.

**Solid Sample (Direct Introduction in GF)**

Direct introduction of the solid sample into the graphite furnace is another alternative (Table 18). However, it has been less frequently used, since it has been considered a somewhat bizarre approach by the majority of scientists working in atomic spectroscopy. The method was not really accepted until recently, thanks to the technical improvements at spectrometer and software levels (Vale et al., 2006; Welz et al., 2007a). The main arguments against it have been: (i) the difficulty of handling and introducing the small sample mass; (ii) the considerable imprecision of the results due to the heterogeneity of some natural samples; (iii) the difficulty in calibrating that requires comparable solid standards with a similar matrix composition and structure; (iv) the limiting spectral lines working range of AAS; and (v) the difficult dilution of solid sampling. In spite of these constraints, direct solid sampling is a feasible alternative when the determination of total analytes is required, since this needs almost no sample preparation. Without a preparation step, time and cost are reduced and higher sensitivity is achieved since no dilution is employed. Another advantage of solid sample introduction is the reduction in the risk of sample contamination by avoiding any preparation and any use of chemical reagents. With classical line source (LS) ETAAS, one of the arguments in favor of preparing slurries or acid digests is the possibility of altering the analyte concentration so that it falls within the linear range of the calibration function. This is true if the recovery is 100%; if not, the slurry or acid digests are subject to the same limitations as SS ETAAS due to the natural heterogeneity of the small subsamples used, which is not always improved by reducing particle size (Belarra et al., 1998). However, there are other systems that may be more appropriate than dilution, such as the use of a gas flow during atomization (Belarra et al., 2000, 2003), the use of alternate, less sensitive analytical lines (Belarra et al., 2003; Nomura et al., 2005), or the use of three-field Zeeman-effect (Gleisner et al., 2003; Nomura et al., 2005).
The graphite furnace permits a relatively easy introduction of solid samples, and the residence time of the sample vapor in the absorption volume is greater than in other atomization techniques such as flame. Hence complete vaporization and atomization is possible of even relatively large amounts of sample. Moreover, the spectrometer designs have been improved to achieve reproducible, easy insertion of solid samples into graphite furnaces (Nowka et al., 1999). The other constraint is the relatively high imprecision of the results as a result of the heterogeneity of natural samples. This problem is further aggravated by the small sample mass of around 1 mg that is typically introduced into the graphite furnace. Nevertheless, the relative standard deviation observed rarely exceeds values of 10%, which is quite acceptable in trace analyses (Welz et al., 2007b). Moreover, SS ETAAS permits introducing samples with a size almost two orders of magnitude greater in the atomizer than the other sample techniques, hence improving the sensitivity and detection limits (Vale et al., 2006; Welz et al., 2007a, 2007b). In most studies that have introduced solid samples directly into the graphite furnace, the samples have been ground to fine particles with a diameter size of 0.3–90 μm (Nowka et al., 1999; da Silva et al., 2002; Sahuquillo et al., 2003). This has resulted in an improved sample homogeneity and a better atomization process (Schön et al., 2000; Nimmerfall and Schön, 2001; da Silva et al., 2002; Sahuquillo et al., 2003).

The main constraint that remains only partially solved is achieving adequate calibration using certified reference solid materials with a similar matrix as the samples (Welz et al., 2007b). There are examples in the literature where even calibration with certified reference materials did not produce accurate results (Maia et al., 2002; Welz et al., 2007b). In spite of this, direct sampling determination of Cd, Cu, and Pb in soils and sediments using solid reference materials to calibrate has been successfully conducted (Nowka et al., 1999; Schön et al., 2000; Nimmerfall and Schön, 2001; Vale et al., 2001). In these cases, an accurate homogenization of the ground samples and reference material was found to be critical to obtain accurate results. Moreover, examples from the literature suggest that calibration can also be successfully carried out against aqueous standards, mainly if the analyte is atomized at a lower temperature than the matrix, allowing easy separation from matrix sample (Nowka et al., 2000; Vale et al., 2001). A suitable Hg determination of soils and sediments using aqueous standards to calibrate has been achieved, taking advantage of the high volatility of the Hg analyte when compared with that of most matrix components, and using KMnO₄ as a chemical modifier (da Silva et al., 2002; Resano et al., 2005). KMnO₄ enabled a loss-free determination of Hg (da Silva et al., 2002; Resano et al., 2005). In fact, during the last 15 years several studies have shown that aqueous standards can be used for calibration in the determination of As, Cd, Cu, Hg, and Pb in soils and sediments using conventional line source ETAAS, because interferences can be avoided using careful optimization of temperature programs and choice of modifiers (Table 1). Solid sampling (SS) ETAAS using a deuterium lamp as background correction system (Schrön et al., 2000) has achieved good results in Cd, Cu, and Pb determination in soil and sediment samples (Table 1), in fact better than those achieved with SS-ETV-ICP-OES.

Recently, the introduction of high resolution continuum source ETAAS (HR-CS ETAAS) has provided a variety of new possibilities for developing direct solid sampling methods that were not available previously (Resano et al., 2008). Among these new improvements we should highlight a simpler optimization of furnace programs and the visibility of the spectral environment, which makes it easy to avoid spectral interference and opening up the possibility of simultaneous determination of several elements (Vale et al., 2006; Welz et al., 2007a). This method has improved the detection limits of Cd and Pb determination in coal (Table 1) and merits future studies to extend its application to the determination
of other elements in soils and sediments. For further information the reader is referred to recent review articles we have mentioned, such as Welz et al. (2007b) and Resano et al. (2008).

The Use of FIA and SIA Systems

Flow injection analysis (FIA) systems are frequently used for automatic analyses, especially when processing a large number of samples. In order to alleviate interference effects, a variety of approaches have been proposed ranging from instrument modification to the use of chemical modifiers (see below). However, the most effective way is simply to perform an adequate sample pre-treatment prior to analysis, in order to achieve matrix separation along with analyte pre-concentration (Table 1). Over the last few decades, it has become apparent that the hazardous effects of trace elements should not solely be evaluated on the basis of the total concentrations of these constituents in soils and sediments. Rather it is necessary to determine in which chemical form they are present, because individual species might exhibit widely different characteristics as regards to mobility. In this vein, FIA is a powerful tool for automatic speciation analysis and accommodation of fractionation assays (Miró and Frenzel, 2004; Miró et al., 2005). The processes most commonly implemented on-line in FIA systems are pre-concentration (Colognesi et al., 1997; Wang et al., 2003; Anthemidis and Miró, 2009) by liquid-solid extraction (LSE) (Colognesi et al., 1997; Mosbaek et al., 2003; Wang et al., 2007; Miró et al., 2003, 2008), or co-precipitation (Yan and Adams, 1997; Tyson, 1999; Burguera and Burguera, 2007), chemical speciation of the analyte (Bissen et al., 2000; Vassileva et al., 2000; Zhu and Li, 2001; Zou et al., 2008), separation of different analytes (Tokman and Akman, 2004), sequential extraction (Shiowatana et al., 2001a, 2001b; Wang et al., 2003) and cold vapor (CV) (Tyson, 1999; Flores et al., 2001; Priego-López and Luque de Castro, 2002; Moreda-Piñeiro et al., 2002; Navarro et al., 2006; Burguera and Burguera, 2007) or hydride generation (HG) (Tyson, 1999; Priego-López and Luque de Castro, 2002; Vieira et al., 2002; Matusiewicz and Mroczkowska, 2003) for Hg and As determination (Table 1). For more details see reviews by Burguera & Burguera (2007) and Miró et al. (2008).

LSE is frequently used to pre-concentrate metal species and to remove interfering matrix species. The sample, which is frequently the liquid ensuing from an acid digestion or extraction, passes through a column with an ionic exchange resin. Afterwards, a solution containing a chemical species that displaces the analyte in the resin is introduced into the FIA system. By taking advantage of this process, the eluate to be introduced into the graphite furnace is more concentrated than the original sample (Miezwa et al., 1998; Miró et al., 2003, 2008), thus improving the limits of detection. These methods enable reaching detection limits of 9 ng L$^{-1}$ in Pb and 7–15 ng L$^{-1}$ in Cd determination in aqueous solutions such as those obtained through acid digestions, slurries or leachates of soils and sediments using conventional ETAAS spectrometers (Colognesi et al., 1997; Miró et al., 2003, 2008). However, the on-line solid-phase extraction-pre-concentration performed by permanent packed-columns lacks sufficient reliability due to the progressive contamination of the solid surfaces of the beads and the potential leakage of functional moieties.

Recently, the so-called bead-injection (BI) analysis has overcome the previous shortcomings (Hansen et al., 2006; Miró et al., 2008) by renewing the sorbent material in each analytical cycle by flow programming (Miró et al., 2003, 2008). The sequential injection lab-on-valve (SI LOV) is a novel and powerful method in flow analysis, also called the third FIA generation, which has introduced a new line of advances where all required operations
can be carried out in a miniaturized, automated fashion under strictly controlled conditions (Lenchan et al., 2002). The microconduit unit is a single monolithic structure mounted atop the multi-position valve of a sequential injection assembly. This unit has been designed to incorporate all the necessary laboratory facilities for a great variety of analytical applications including in-valve manipulation of sorbent materials. It is made to contain microchannels working as the bead-retention cell, along with mixing points for chemical derivation of the analyte and as a multipurpose flow-through cell for real-time control of analyte-containing beads (Ruzicka, 2000; Wang and Hessen, 2003). Thus, packed-columns reactors are generated by aspirating beads from a peripheral part of the valve. The use of reverse phase sorbents with great bead size homogeneity such as poly(styrene-divinylbenzene) has allowed high analytical accuracy and precision in LOV-ETAAS systems in determining Cd from the acid digests of sediments (Miró et al., 2008). Large enrichment factors (7.4–17.2) were obtained and low detection limits (5–135 ng L$^{-1}$) for a sample loading volume of 1.25 mL (Miró et al., 2003). In this line, detection limits of 0.001 mg L$^{-1}$ and 0.07 mg L$^{-1}$ for Cd$_{IV}$ and Pb$_{IV}$, respectively, have been obtained by one-line sequential injection LOV-ETAAS analysis of acid digests by injecting 1.8 mL of sample solution into the LOV system (Miró et al., 2005).

In liquid-solid extraction (LSE), apart from the use of ionic exchange resins, a novel approach is being explored as a future tool to improve analytical figures of merit. In this approach very specific and effective sorbents are applied, which pre-concentrate trace elements in solution, increasing the pre-concentration enrichment factor (EF). Recently, some new sorbents have been employed to pre-concentrate different trace elements in water or urine. But the use of these new sorbents remains as a challenge to be applied in FIA systems to determine As, Cd, Cr, Cu, Hg, and Pb in acid digests, leaches, or slurries obtained from soil or sediments. In this field, we highlight the pre-concentration of Cd and Pb in other sampling substrates such as water standards using thioureasulfonamide resin (Senkal et al., 2007) yielded an EF of 90-fold; the determination of Co in human urine (Souza and Tarley, 2009) and V in waters (Gil et al., 2007) by using multiwall carbon nanotubes yielded an EF of 20-fold; the determination of Cu in waters using micro-columns containing 8-hydroxyquinoline azo-immobilized on controlled pore glass (Sawula, 2004); the determination of Cd and Pb (Xingguang et al., 2003) and of As (Jiang et al., 2008) in waters using activated carbon which yielded an EF between 22–50, the sequential simultaneous determination of Bi, Cd, and Pb in urine using a Muromac A-1 resin column (Sung and Huang, 2003); and Pb determination in other sampling substrates such as blood and plant acid digests using macrocycle immobilizing silica gel, which yielded an EF of 23 (Yan et al., 1999).

New equipment that uses more efficient novel sorbents together with LOV FIA systems open new possibilities for advances in the sensitivity and limits of detection by coupling these pre-concentration systems to ETAAS spectrometers. This is a powerful line of research to improve the analytical capacity in the determination of As, Cd, Cr, Cu, Hg, and Pb in solutions resulting from acid digestions or leaching from biological samples. Moreover, ion-imprinted polymethacrylic microbeads have been demonstrated to be a very selective method for Hg pre-concentration from standard acid digest Hg solutions. The improvement has been considerable when coupled to CVAAS, reaching detection limits of $\mu$g L$^{-1}$. This method has shown that interfering matrix components do not influence the extraction efficiency due to the great selectivity for Hg. There is also the possibility of coupling this method to CV ETAAS in the near future (Dakova et al., 2009).

The co-precipitation method is useful to concentrate trace metal ions, and has been combined with ETAAS to determine Pb (Yan and Adams, 1997) in digested soil solutions.
A chelating reagent (diethyldithiophosphate, Ni ammonium pyrrolidine dithiocarbamate or Ce(IV) hydroxide) complexes with the analyte and the resulting complex is subsequently immobilized onto an absorbent agent (silica gel sorbent or polytetrafluoroethylene) with a co-precipitate carrier. After this, a quantitative elution of the retained analyte is performed and the analyte is taken to ETAAS for determination or the co-precipitate obtained is directly measured by ETAAS. Recently, As has been determined in water samples in a process that could be applied to soil extracts or digested soil solutions. This technique allows the selective determination of As(III) and As(V) due to the fact that the co-precipitation of each form depends on the pH of the solution (Zhang et al., 2004). The main requirement for this technique is that the collector has to be separated from the matrix solution. This can be done by filtering or centrifuging, followed by washing of the precipitate.

The possibility of coupling on-line soil extraction or chemical speciation (Long et al., 2006) to a LOV-ETAAS process has been achieved in a sophisticated FIA design to determine Cr$^{6+}$ in soil extracts. It has proved to be a reliable process that can also be applied to the pre-concentration and speciation analyses of other trace elements such as As, Cd, Cu, Hg, or Pb in leachates or acid digests from soils or sediments.

In the case of Cr, the speciation is often needed in environmental studies due to the different biological and physiological properties of Cr$^{6+}$ and Cr$^{3+}$. Cr$^{6+}$ is very toxic, exhibiting genotoxic and carcinogenic actions both in animals and humans, while Cr$^{3+}$ is considered a bioelement with important metabolic function. Some studies have discussed the most adequate methods for speciation analyses of Cr$^{6+}$ and Cr$^{3+}$ (Vassileva et al., 2000), being the most recent tendency the FIA methods with selective preconcentration of Cr$^{6+}$ and Cr$^{3+}$ through microcolumns with specific sorbents prior to elution to detector. In this context, several studies have developed different selective extraction methods that allow both separation and preconcentration of Cr$^{6+}$ and Cr$^{3+}$ at the same time. This has been reached using FIA systems that derived sample solutions to different columns with different selective exchangeable fixed phase (Vassileva et al., 2000; Zhu and Li, 2001; Zou et al., 2008) or by determining first Cr$^{3+}$ in a sample aliquot and by reducing Cr$^{6+}$ to Cr$^{3+}$ in other sample aliquot to determine total Cr$^{6+}$ + Cr$^{3+}$ (Ren et al., 2007). In order to assess the Cr toxicity capacity of a soil or sediment, the selective determination of Cr$^{6+}$ can be sufficient. In this case, HPLC methods selective for Cr$^{6+}$ have proved a great recovery capacity for this chemical Cr specie (Milacic and Scancar, 2000; Scancar et al., 2007). One of the concerns of this method of extraction is the possibility that the retained Cr$^{3+}$ in soil exchangeable complex when is extracted could be oxidized to Cr$^{6+}$ being Cr$^{6+}$ overestimated. Milacic and Scancar (2000) have proved that soluble Cr$^{3+}$ was not oxidized to Cr$^{6+}$ by using KH$_2$PO$_4$/K$_2$HPO$_4$ (at 0.2 M) or with tris-HCl buffers (0.005 M, pH 8.0).

In the case of As determination, hydride generation is a laborious process that can be readily achieved on-line. This process can be coupled to other prior pre-treatments such as matrix decomposition in FIA setups (Lima et al., 2000a).

Another further possibility for using FIA systems for pre-concentration or separation purposes is to apply modern LLE methods. Cd, Cu, and Pb have been determined by FI-LLE-ETAAS in different biological samples using novel LLE techniques such as cloud point extraction (CPE) (Bai and Fan, 2007), supported liquid membrane extraction (SLME) (Malcus et al., 1996), single drop microextraction (SDME) (Anthemidis and Adam, 2009), and single step-LLE (Anthemidis et al., 2003). Unfortunately, the above methods have not been used to determine these elements in soil and sediments, but these processes could be successfully applied to leachates or acid digests of soils and sediments.
Spectrometer Use and Modifier Improvements

Since As and Hg have different volatilities, which are also distinct from Cd, Cr, Cu, and Pb, few studies have used a ETAAS to analyze Cd, Cr, Cu, and Pb together with As or with Hg in the same sample because the sample pre-treatments, the use of program temperatures and the modifiers are so different. For this reason we describe here first GF determination of Cd, Cr, Cu and Pb, then its use for As determination, and finally for Hg determination.

Cd, Cr, Cu and Pb Determination

There are three problems that have limited the use of ETAAS to determine trace metals such as Cd, Cr, Cu, and Pb: (i) low concentration levels often below the detection limits of ETAAS; (ii) interferences from matrix sample components that are one of the main causes of poor detection limits (note such interferences are complex and vary greatly in the case of soils and sediments); and (iii) the necessity of using a specific light source with different analytes, which precludes the simultaneous determination of more than one element at a time.

Recently, several different improvements have progressively appeared in the use of ETAAS spectrometers to determine Cd, Cr, Cu, and Pb in soils and sediments. The most significant advances that we discuss below are those deriving from a greater knowledge regarding the use of adequate modifiers, the continuous improvements in background correction systems that ensure the separation of analytical and non-analytical peaks under exactly repeatable conditions, the development of in situ trapping methods and the improvements in the radiation source, optic system, atomizer designs and detectors. All these together with the appearance of new software advancing data treatment have produced the latest HR-CS ETAAS that reaches low detection limits, improves the use of AAS applied directly to solid samples, and opens the possibility of truly analyzing several elements at once.

Modifier use. One of the first approaches to improve the use of ETAAS to determine Cd, Cr, Cu, and Pb in soils and sediments comes from research on the appropriate use of chemical modifiers that allow thermal analyte stabilization and thermal separation of analyte from the rest of the sample matrix components during the pyrolysis stage. Generally, the analyte is stabilized and the rest of the matrix is removed by volatilization during pyrolysis. The modifiers can be applied together with the sample into the atomizer, but in recent years the use of atomizers coated with modifiers have been successfully applied to the analysis of real samples in ETAAS leading to better results (Baralkiewicz & Gromowska, 2001; Lima et al., 2000b, 2002a). Paladium group metals (PGM) are the most widely used modifiers in the determination of Cd and Pb (Volynsky, 2000, 2004). Paladium used alone or with other metals is the most routinely selected chemical modifier for Cd, Cu, and Pb determination. Its mechanisms of action are considered to be based in the formation of analyte-Pd binary alloys that form solid solutions. Thereafter, under correctly optimized conditions analyte-PGM modifier compounds decompose completely during the atomization stage (Volynsky, 1998, 2000, 2003; Acar, 2005a, 2005b). These modifiers have been mainly relevant in the case of Cd and Pb determination when several studies have used palladium metal modifiers (Pd, Pt, Rh, Ru, and Ir) alone or in combination with other modifiers such as Mg(NO₃)₂, NH₄NO₃, or phosphate group (Taula 1 n 31,32,44,68,80). These last modifiers used without palladium group metals have also provided a good Cd and Pb stabilization in its determination in soils and sediments (Table 1 n 35,44–47,57). Mg(NO₃)₂ and NH₄NO₃ eliminate chloride...
interferences, one of the main causes of background noise in ETAAS, whereas phosphate modifiers form insoluble nonvolatile phosphates with Cd and Pb stabilizing them during pyrolysis stage. Thus the temperature of pyrolysis can be significantly increased (Volynsky, 2003).

A second line of advance was the development of a permanent chemical modifier with a high melting point (W, Mo, Ta, Nb) or with PGM coating in the inner surface of the graphite furnace. The use of high melting point permanent modifiers is especially suitable for Pb because they form stable oxides during pyrolysis whereas PGM is suitable for Cd, Cu, and Pb (Volynsky, 2003). In this way, the use of PGM alone or in mixtures with high melting point permanent modifiers, W + Rh (Lima et al., 2000b; Lima et al., 2001, 2002a, 2002b; Baralkiewicz and Gramowska, 2004), Ir + W (Lima et al., 2002b; Bianchin et al., 2006), Ru + W (Lima et al., 2002a; Bianchin et al., 2006), Mo + Ir (Acar, 2005b), Mo + Ru (Acar, 2005b), Ir (da Silva et al., 2002; Borges et al., 2003; Resano et al., 2005; Bianchin et al., 2006), Rh (Lima et al., 2002a) or Ru (Vale et al., 2001; Lima et al., 2002a; Bianchin et al., 2006) to coat an integrated, transversely heated graphite-furnace atomizer have been successful as permanent modifiers for Cd, Cu, and Pb determination in solutions like acid digests or slurries from soils and sediments. Moreover when different permanent and non-permanent modifiers have been tested via the recovery capacity of soil and sediment standard reference materials, Ru, Ru + Zr, Pd + Rh, Pd + Ru, W + Ir, W + Ru and W + Rh have proven to be the best permanent modifiers for Cd, Pb, and also As determination (Rucandio and Petit, 1999; Vale et al., 2001; Lima et al., 2000a, 2001; Acar, 2004). Cu determination is frequently carried out without the use of modifiers due to its greater stability during pyrolysis. In spite of this, some studies have achieved improvements in Cu determination in sediments using Pd + Mg(NO₃)₂ and W + Rh as a permanent modifier (Bulska et al., 1996; Lima et al., 2000a, 2001), Although both modifier types were effective, better recoveries and lower standard deviations were achieved for the permanent modifier (Bulska et al., 1996; Lima et al., 2001). Moreover, the use of permanent modifiers entails several advantages such as better detection limits, longer furnace lifetime, longer term signal stability, and better repeatability.

In the case of Cr, the use of PGM can be problematic due to the fact that the large amounts of low volatile species of those modifiers may overstabilize the analyte in the graphite furnace (Volynsky, 2004). The use of Mg(NO₃)₂ (Kazi et al., 2009) or the mixture Pd + Mg(NO₃)₂ (Volynsky, 2004) is advisable for the determination of total Cr in acid digests. In fact, Mg(NO₃)₂ is the modifier recomented by Perkin Elmer (Perkin Elmer, 1991) for Cr ETAAS determination.

Another line of research is to find the adequate program of temperatures for each type of sample. Most studies that have reported a GF temperature program to analyze Cd, Cu, and Pb, have used a 4-stage temperature program: typically, one or two drying stages; one pyrolysis stage; one atomization stage; and finally a cleaning stage. In all the programs, the carrier gas flux is stopped during the atomization phase, allowing an increase in atomic vapor time residence in the absorbance cell. The reports that have analyzed Cu used temperatures of atomization between 1900–2300°C (Table 1* 11,37,53,68), which were slightly higher than the atomization temperatures used for Cd and Pb determination. When the spectrometers currently in use were not able to detect more than one element at once, most studies finally used different temperature programs to determine each element. As Cd is more volatile than Cu and Pb, normally its atomization is conducted at lower temperatures than for the latter two elements. The temperatures most widely employed for Cd atomization were 1400–1900°C (Table 1* 32,35,37,44–48,51–54,57,67,68). In contrast, for Pb due to its lower volatility, it is necessary to apply higher temperatures, being in most cases 1800–2250°C
These temperatures ranged according to the sample pretreatment and also to the modifiers used (Table 1). The temperature programs used when the sample was directly introduced as a ground solid are similar to those used with liquid samples (Table 1).

Hydride generation. Another possibility for element determination by ETAAS is to carry out hydride generation (HG) prior to injection in GF. With Pb there are serious problems in carrying out HG and Cu is practically not generated but Cd, the most volatile of the three, can be determined by HG (Tyson, 1999; Bujdos et al., 2003). Nevertheless, as good results can be obtained without using HG, this method is not usually used to determine Cd. There are a few exceptions in studies mainly conducted more than 10 years ago (Matusiewicz et al., 1997; Bujdos et al., 2003) from acid digest solutions of soils and sediments. Due to Cd’s volatility, hydride generation coupled to ETAAS with a heated coated furnace permits in situ trapping of the vapors generated, which improves the detection limits (Matusiewicz et al., 1997). Indeed, HG is a technique that can provide a useful simultaneous separation-concentration step prior to ETAAS determination. The in situ trapping method enables pre-concentration in the graphite furnace in a reproducible and adequate way. Using this possibility, the operator of the ETAAS can choose the pre-concentration factor. This generally depends on the flow rate of the sample solution and the time of trapping stage in the atomizer temperature program. The hydrides generated are transferred to a pyrolytic coated graphite furnace by an Ar flow rate at 200°C. The graphite furnace pre-concentrates the analyte by trapping it (Matusiewicz et al., 1997).

Spectrometer improvements. The progressive change in the form and design of the electrothermal atomizers has been another source of improvement in the sensitivity and detection limits of ETAAS. During the 1990s, the use of platforms inserted into the graphite furnace is the first called L’vov platform (L’vov et al., 1986) and generated a more reproducible and constant atomization process than the cylindrical atomizers (Berglund and Baxter, 1992). When the temperature of the atomizer walls increases quickly, the sample atomization in the platform is retarded because the sample is not directly in contact with the wall. Therefore atomization occurs in a less changing environment, and thus the reproducibility is improved. The classic electrothermal atomizer was heated longitudinally (LHA) and the temperature profile along the tube reached a maximum in the tube center and a minimum in the sides. To improve this shortcoming, the transversally heated atomizers (THA) were designed in order to provide a uniform temperature profile throughout the tube. This configuration decreases the atom losses and the atom condensation in the sides that occurred in LHA, thereby decreasing the detection limits. Although several studies that determined Cd, Cu, and Pb in soils and sediments in the last 10 years were still conducted with ETAAS spectrometers with LHA (Table 1), the most recent studies that have determined Cd, Cu, and Pb in soil and sediment samples have used better general equipment (Zeeman background correction systems, the sequential multielement determination system) and have been conducted with THA (Table 1). When the two atomizer configurations have been used to determine the same analytes in the same matrix, the THA have demonstrated better analytical procedures and figures of merit (Sperling et al., 1996).

As discussed above, the interferences from matrix sample components are frequently the main causes of poor detection limits. To solve this problem some background correction systems have been used in ETAAS (Sanz-Medel and Pereiro, 2008). The continuous
source method has been the first one used, having some limitations; i.e., if the sample contains another element having an absorption line located too close to the analyte resonance line (within the bandpass). Spectral interferences may be undercompensated because only the average non-atomic absorption which occurs over the spectral bandpass is effectively “measured.” Despite these constraints, this methodology has been widely used for the determination of Cd, Cu, and Pb in soils and sediments samples since the mid-1990s to the present (Table 1\textsuperscript{n} 6,12,13,16,17,19,20,23,24,30,35,40,42,50,54,55,57,65,-67,61,72,77–80,83,84,86,87,89–92).

Currently, best results have been obtained using Zeeman-effect background correction (until the advent of HR-CS ETAAS) because the background is always measured at the same wavelength as the atomic absorption of the analyte (Table 1\textsuperscript{n} 6–8,10–12,14,18,21–23,29,31,33,38,41,42,45–48,50–53,58,60,62,67,73,74,79,85,86). The Zeeman 3-field mode-measurement at zero, maximum, and medium magnetic field strength has become an improvement allowing a great sensitivity to be adapted for higher analyte concentrations determination (Gleisner et al., 2003). This method is especially useful when combined with solid sampling, since diluting is not possible. As far as we know, this feature at this moment only has been used for Pb determination in coal (da Silva et al., 2005; Gallindo Borges et al., 2006) and remains to be used for Cd, Cr, Cu, and Pb determination in soils, but it could be useful for analyses conducted in very polluted soils where high concentrations of these analytes are expected.

Before the possibility of using HR-CS ETAAS (see below), a system was used which couples modern spectrometers to a transversally heated atomizer furnished with a Zeeman effect background corrector, as well as using adequate chemical modifiers. This system has recently permitted simultaneous Al, As, Cu, Fe, Mn, and Ni determination in fuel (de Oliveira et al., 2002), and is a possible future tool to be applied to sequential multi-element determination of As, Cd, Cu, and Pb in soil and sediment analyses, both for direct solid sampling and for analyses of solutions from acid digestions and leaches or slurries.

The most significant advances of ETAAS spectrometers provide two alternatives to the conventional hollow cathode lamp: the continuum source, which is the approach that currently seems to show more potential and the diode laser, providing a narrow source emission line. In the past decade several technical advances have permitted concomitantly the implementation of high resolution continuum source ETAAS (HR-CS ETAAS). This approach maintains the conventional use of atomizers (modifiers, temperature program, gas flow) but involving the following novelties: a continuum radiation source (CS) such as a Xenon short-arc lamp, modern furnaces with a transversely heated graphite furnace module, a double échelle monochromator, and high resolution detectors such as a Linear Photodiode Array detector PDA, linear charge-coupled devices (CCDs), two-dimensional charge injection devices (2D-CIDs), or two-dimensional charge-coupled devices (2D-CCDs) (Harnly, 1999; Welz et al., 2005). These advances provide essential improvements to conventional ETAAS as follows:

(i) Since only a few pixels of the array detector are necessary to measure atomic absorption, the rest of them are available for other purposes. The first duty of these detectors is to correct for all spectral events that occur simultaneously on all pixels. This also allows observation of the temporal and spectral behavior of the analyte signal and the background absorption at the analytical wavelength of the surrounding environment with high resolution. This offers a considerably superior approach for the correction of the complex.
(ii) The possibilities of the array detector for simultaneous monitoring of 200 “wavelength sectors,” 200 pixels covering a region of less than 1 nanometer in total, enabling efficient correction for many unwanted spectroscopical events such as lamp ficker noise.

(iii) The optimization of the AAS measurements with respect to the temperature furnace programs; the use of adequate modifiers and the gas fluxes control the result with maximum sensitivity.

(iv) The data obtained can be computed and the software is capable of shortening matrix spectra by detecting molecular absorption at rotational level and subtracting such spectra from the spectra recorded from the sample using adequate least square algorithms.

(v) The much higher radiation intensity of the CS compared to the conventional low source (LS) results in detection limits in HR-CS ETAAS that are frequently fivefold better than in LS ETAAS.

All these improvements confer to ETAAS the capacity to compete with ICP-MS, while requiring considerably less complexity, extending the calibration ranges limited only by the memory of the atomizer and with easier application to solid samples (Harnly, 1996; Welz et al., 2003; Welz, 2005; Heitmann et al., 2006). The compact design of the double monochromator system with a 300 mm prism as a pre-monochromator and a 400-mm prism as an échelle monochromator requires active wavelength stabilization, which has been attained by an internal neon lamp, providing high precision.

Since the first steps to provide combinations between PDA with échelle spectromers (Jones et al., 1989), the characteristics of CS-AAS have improved primarily due to the advances in the technology of multichannel detectors (Harnly et al., 1997; Daminelli et al., 1998; Gilmutdinov and Harnly, 1998; Harnly et al., 2001; da Silva et al., 2004; Heitmann et al., 2006).

But in spite of all these advances, the status of the art is the following:

(i) For the moment, it seems that truly simultaneous multi-element determination by HR-CS AAS with adequate analytical performance would require the use of custom-designed detectors, which would be prohibitively expensive at present. In fact, the HR-CS ETAAS instrument available at this moment (e.g. Analytik Jena ContrAA 700) only allows the simultaneous monitoring of less than 1 mm of spectrum (0.2–0.5 nm in UV region for effective multielement analysis (Resano et al., 2008).

(ii) Heitmann et al. (2006) have introduced a new advance in the HR-CS in AAS that comes from the modification of the conventional GF to a graphite filter atomizer (GFA). The GFA was produced by adapting a commercial transversely heated graphite furnace by Perkin Elmer (Bodenseewerk, Perkin Elmer, Überlingen, Germany) by furnishing the tube with filters and a collector instead of a platform. It provides reduction of interferences without the use of a chemical modifier. This type of atomizer has already been used in the determination of Al, Co, Cr, Ni, Pt, Cd, Fe and Ni in acid digests from soils or sediments (Heitmann et al., 2006). This experimental spectrometer has permitted the sequential determination of Al, Co, Cr, Ni, and Pt and the truly simultaneous determination of Fe, Cd, and Ni by using nearby analytical lines 228,72 nm for Fe, 228,80 nm for Cd, and 228,99 nm for Ni.

(iii) These novel spectrometers will provide new advantages for the determination of trace elements in complex matrices such as environmental solid samples, as for
example observed in Pb determination in coal (Gallindo Borges et al., 2006). In this case an optimum pyrolysis was observed at 700°C without the use of modifiers. The optimum atomization temperature was found to be 1700°C. Under these conditions, interference-free determination could be performed with calibration against aqueous standards in 0.5 HNO₃ solution. A total of six certified reference coal samples were analyzed, and the results obtained were all in good agreement with certified and reported values. A detection limit of 0.008 µg g⁻¹ for Pb was obtained at the 217.0 nm resonance line, a value comparable to those obtained by other sensitive, but much more sophisticated, techniques such as ICP-MS.

(iv) These novel spectrometers will provide new advantages regarding the possibility of a better background absorption correction and a better use of modifiers. The use of Ru, or Ir and a mixture of W + Ir as a permanent modifier in a slurry sampling HR-CS ETAAS of sediments to determine Cd has permitted stabilizing Cd at least to a pyrolysis temperature of 900°C (Bianchin et al., 2006), thus allowing a detection limit of 0.0006 µg g⁻¹ in the solid sample that was injected as slurry in the GF. This shows the great suitability of HR-CS ETAAS to achieve an interference-free determination, highlighting this technique as a way to improve trace element determination in difficult matrices such as soils and sediments, and even with solid sampling (da Silva et al., 2005).

(v) Because of the much higher radiation intensity of the light source in HR-CS ETAAS compared to the traditional line source (at least 1–2 orders of magnitude), detection limits obtained with HR-CS ETAAS are typically fivefold better than those of LS ETAAS (Welz, 2005). These scarce data provide a good prognosis for obtaining a relative cheap and easy instrument to detect Cd, Cu and Pb in soils and sediments at very low detection limits such as below ng g⁻¹ levels with great precision in the near future.

Another future challenge is the use of diode laser as light source (Resano et al., 2008). Diode lasers are robust, low cost, and very stable in terms of wavelength. Adjustable diode lasers in UV region remain as a major limitation for the further use of these sources by the lack at this moment of free Ir diodes and with high Al content the element that shifts the laser wavelength towards shorter UV region tends to crack easily (Krivan et al., 1998; Resano et al., 2008). But in the future the use of new materials could resolve this constraint (Krivan et al., 1998; Resano et al., 2008).

For environmental studies such as soil and sediment analyses it is also important to take into account the possibility to use the portable ETAAS, which has proved to present an accurate capacity for the determination of Cd and Pb in soil samples (3 µg L⁻¹ for Cd and 20 µg L⁻¹ for Pb) (Sanford and Thomas, 1996; Batchelor et al., 1998).

**As Determination**

ETAAS is a widely used method to determine low concentrations of As in soils and sediments (Tijhuis et al., 2002; Matusiewicz and Mroczkowska, 2003). However, its high volatility together with interference problems such as those produced by certain phosphorus compounds, sulphates, Co, Na, K, and Fe (Harnly et al., 2001) make it frequently difficult to determine. However, several technical advances in ETAAS have recently succeeded in improving these constraints, and have enabled reaching significantly lower detection limits. Some advances have been made at the sample pretreatment level as previously mentioned, but the greatest progress has been made as regards the spectrometer. Namely, the use of adequate modifiers with or without *in situ* trapping methods (Table 1n 6,14,17,24,28), the use
of hydride generation coupled to in situ trapping methods (Vieira et al., 2002; Ringmann et al., 2002; Matusiewicz and Mroczkowska, 2003), the advances in the background noise such as Zeeman background correction, and more recently the analytical application of all the modern HR-CS ETAAS spectrometers that has created new progress in As determination in soils and sediments by decreasing the background absorption noise.

Modifiers. Several studies have successfully determined As in soils and sediments without using hydride generation. The use of modifiers is especially pertinent to prevent As volatilization during the pyrolysis stage. The most adequate modifiers are Pd(NO₃)₂ and Mg(NO₃)₂ either in combination (Bissen et al., 2000; Barbosa et al., 2000; Perämäki et al., 2000; Arain et al., 2009) or alone (Vassileva et al., 2001a; Coskun et al., 2006). In these cases, Mg(NO₃)₂ facilitates the partial removal of chloride from the atomizer and helps to stabilize the As that hardly interact with Pd achieving great stabilization (Welz et al., 1992). Such studies reached As detection limits between 1.2 and 20 µg L⁻¹ in the solutions from acid digestion, liquid-solid leaching, or slurries. Several studies taking advantage of the improvements in the use of modifiers and in the systems of background absorption corrections such as the Zeeman system (see below) have determined As in solid samples of soils and sediments (Lima et al., 2003; Sahuquillo et al., 2003; Akdeniz and Yaman, 2005). In these cases, also the use of Pd or Pd + Mg(NO₃)₂ applied as classical modifiers has proven to be useful to prevent As losses during the pyrolysis stage (Sahuquillo et al., 2003; Akdeniz and Yaman, 2005). This effect is produced because it eliminates phosphate interferences efficiently and it allows good stabilization during pyrolysis (Ni et al., 1996). Only Rh must be avoided as modifier for As determination when the sample contains significant amounts of NaSO₄ because the formation of As-Rh-Na₂SO₄ leads to suppression of peak area of As (Volynsky, 2004). The use of high melting point carbides modifiers group is not advisable for As determination because of the greater As losses in pyrolysis stage (Volynsky, 2003), but its combination with PMG improves the stabilization efficiency, e.g. the combinations of W + Ir, W + Rh, or W + Ru used as permanent modifiers coated into the graphite surface have also shown good analytical results (Lima et al., 2003). However, under optimum conditions, the use of Rh and Ir have proved to be the most sensitive and advisable chemical permanent modifiers to As determination (Barbosa et al., 2000; Vassileva et al., 2001b; Volynsky, 2004). HCl for acid digestion, slurry, or extraction must be avoided when As determination is the objective of the study because chloride, even in low concentrations, strongly interferes with the absorbance signal of As (Väisänen and Suontamo, 2002).

Hydride generation. Another approach to improve As determination by ETAAS is to perform hydride generation prior to ETAAS. This method is currently used for total arsenic determination in soils and sediments after acid digestion or slurry (Vieira et al., 2002; Ringmann et al., 2002; Matusiewicz and Mroczkowska, 2003). Hydride generation is frequently conducted on-line in a FIA system (Vieira et al., 2002; Matusiewicz and Mroczkowska, 2003). In such cases, the use of the in situ trapping method is especially beneficial due to the possibility of increasing the capture of the arsenic contained in arsine molecules during the trapping stage (Vieira et al., 2002; Matusiewicz and Mroczkowska, 2003). The trapping can be increased by adjusting the carrier gas flow, thus obtaining an efficient pre-concentration mechanism. The possibility of pre-concentrating the hydride generated from the sample in a graphite furnace, followed by a single release of trapped analyte by heating the furnace, is a very interesting feature that reduces the interferences and permits reaching low detection limits. Thus, GF serves for both steps: collection of the analytical vapor for spectrometric
detection and for the vaporization-atomization stage. The solution from acid digestion or leaching is submitted to hydride generation, then a flow injection of hydride to the atomizer coated with Ir (Vieira et al., 2002; Matusiewicz and Mroczkowska, 2003) is performed for later in situ hydride collection, followed by As AAS determination.

Recently, hydride generation has been conducted directly from a solid sample (filters with atmospheric particles of less than 10 µm) (Moreda-Piñeiro et al., 2007). Due to the small size of the solid particles the hydrides were generated with great recovery. A FIA system injected the hydrides into the GF coated with Ir. The best trapping and atomizer temperatures were 800°C and 2500°C, respectively. Under these conditions, recovery was 98%. The detection limits from the sample matrix (filter) was 0.037 µg L⁻¹. Establishing the optimum trapping temperature was the key factor in increasing the efficiency of the recovery and reaching lower detection limits. These results were comparable to those obtained after a conventional method based on an acid digestion followed by ICPMS (Moreda-Piñeiro et al., 2007).

Recently, Jiang et al. (2009) have developed new methods to extract different species of As, namely As(III) and As(V), in slurry solutions of biological samples by using a hollow fiber liquid phase micro-extraction, followed by in situ trapping in a ETAAS spectrometer with a GF coated with Pd. The detection limit was 0.12 µg L⁻¹. This was an excellent result that suggested the suitability of this method to be applied in the near future to solutions of soil and sediment digests, leaches, or slurries. Another recent study (Tüzenc et al., 2009) established a new pre-concentration and speciation pre-treatment to determine total As, As(III) and As(V) in environmental samples based on As(V) co-precipitation on Al(OH)₃. After oxidation of As(III) using dilute KMnO₄, the novel co-precipitation method was used to determine total As. The study determined As by CV AAS reaching detection limits of 0.012 µg L⁻¹ based on 3σ of the blank. This process could be improved in the future by using an adequate ETAAS spectrometer with pre-concentration of the hydrides formed by in situ trapping.

**Temperature programs.** Another way of improving As detection limits is the use of adequate temperature programs. When measuring As in solutions of soil and sediment digests, leaches, or slurries, typically some arsenic remains in the organic matrix without being completely mineralized. ETAAS permits pyrolysis of the sample and thereafter the removal of the most possible interfering chemical species, thus liberating more As from the matrix components. The use of STPF (Stabilized Temperature Platform Furnace), the incorporation of chemical modifiers with the sample, and the more recent use of in situ trapping methods have enabled the optimization of furnace temperature programs to remove matrix compounds more efficiently before atomization, thus allowing the use of lower temperatures. Such temperature programs, when the samples are analyzed without chemical vapor generation, normally include four stages: drying, pyrolysis, atomization, and cleaning (Table 1). The optimal temperature of atomization for As is between 2100 and 2500°C.

**Spectrometer improvements.** The application of Zeeman background correction has been widely used in the last decade in As determination in soils and biomasses (Table 1). This has allowed a decrease in interference from several matrix chemical compounds, such as sulphates and phosphates (Deaker and Maher, 1999; Beccaloni et al., 2002). When all the methods explained above are employed together with Zeeman background correction, the analytical results are comparable to those obtained from ICP-MS (Beccaloni et al., 2002; Kazi et al., 2009). When a Zeeman system is not
available, a D₂ lamp and a 188.98 line are used, which is less sensitive but entails no interferences from sulphates and phosphates (Beccaloni et al., 2002).

The application of the novel HR-CS ETAAS method to As determination in soil and sediment samples could help overcome several constraints in the AAS determination of this trace element such as a further step to diminish background noise allowing good sensitivity with a short analysis time and low sample volume. To date, few studies have been conducted to determine As in environmental samples using HR-CS ETAAS and as far as we know there is no published study on determining As in soils and sediments using HR-CS ETAAS. More studies are necessary to adapt HR-CS ETAAS for As determination in environmental samples. Chemical vapor generation coupled to HR-CS ETAAS spectrometers acting as an in situ pre-concentration system should achieve better analytical figures of merit in the near future for the determination of As and also Hg in liquid samples such as those coming from soil acid digests or leaching.

**Hg Determination**

Until a few years ago, ETAAS was not very suitable for Hg determination due to its relatively low sensitivity for this element. Moreover, in the complex matrices of soils and sediments, the high volatility of Hg species hinders the use of elevated pyrolysis temperatures, even if a modifier is used. Therefore the method of choice for Hg determination is CV generation prior to AAS determination. This method is particularly appropriate in a matrix where Hg is not strongly retained. However, soils and sediments are complex matrices in which Hg is strongly bound by chelation with organic molecules, with clay and loam, or by the formation of species such as methyl-Hg. For this reason, for total Hg determination, the CV method requires a prior treatment of the samples to mineralize the matrix or an extraction method, if only the available or more mobile Hg is to be determined. In both cases part of the Hg can escape determination if it is not completely mineralized during the acid digestion process or if some organic molecules with Hg have been leached. Moreover, in the digestion procedure Hg losses by volatilization can be significant. For this reason, and taking into account the possibility of solid sample analysis using the pyrolysis stage in GF as the matrix destruction process, several attempts have been conducted recently to overcome these constraints in Hg determination by GFAAS.

Some authors have progressively solved these problems, benefiting from the new improvements of ETAAS analyses. The use of ETAAS takes advantage of the high volatility of Hg when compared to that of most matrix components. Some analytical processes have been developed to determine Hg from slurries or from acid digestion solutions directly, without CV generation (Bulska et al., 1996; López-García et al., 1997b; Krata and Bulska, 2005). Good results were obtained when samples with a very low particle size were submitted to a slurry treatment (López-García et al., 1997b). In this case spectrometers with a Zeeman background corrector, an adequate thermal program with no pyrolysis step, and a low temperature of atomization (900°C) (López-García et al., 1997b) were used in conjunction. When acid digestion solutions have been analyzed, the best modifiers have been Pd (Bulska et al., 1996; Krata and Bulska, 2005), Rh + Pd (Bulska et al., 1996; Krata and Bulska, 2005), or Au + Rh (Bulska et al., 1996) as permanent modifiers via metal reduction on the inner graphite surface by thermal or electrochemical processes. As commented in an extensive review of modifiers use, in Hg determination by ETAAS, PGM are the most successful (Volynsky, 2004) because they allow the Hg stabilization at highest pyrolysis temperature. Using this approach, good recoveries have been obtained in Hg determination from standard reference material analyses, but poor recoveries have been
observed with this method when compared to conventional CVAAS or ICP-MS (Krata and Bulska, 2005) due to the difficulty in stabilizing Hg during the pyrolysis and atomization stages (Krata and Bulska, 2005).

Another, more frequent group of studies has taken advantage of the fact that ETAAS can be applied after CV generation by in situ trapping using different permanent modifiers coated in the inner graphite furnace. In the case of acid digestion from solid soil samples or from solutions of soil and sediment digests, leachates or slurries, the use of CV ETAAS using in situ trapping has achieved good results. These methods have been used to concentrate mercury vapor from CV generated by conventional SnCl₂ + HCl reduction from slurries (Flores et al., 2001; Moreda.Piñeiro et al., 2002) as well as used when Hg has directly proceeded from digest (Moreno et al., 2002; Navarro et al., 2006), enabling Hg stabilization during the pyrolysis stage by employing noble metals as permanent modifiers in the GF. The adequate use of modifiers frequently permits the use of temperature programs without the pyrolysis stage and at low atomization temperatures (Flores et al., 2001; Moreda.Piñeiro et al., 2002; Moreno et al., 2002; Navarro et al., 2006). This allows a total Hg atomization before the corresponding permanent modifier reaches its atomization temperature. When acid digestion was applied to enable detecting all the Hg contents, this is the most critical analytical process and must be conducted at low temperature in closed vessels (Moreno et al., 2002; Navarro et al., 2006) to prevent Hg losses by volatilization. The use of various matrix modifiers (Table 1) mainly of the PGM modifiers allow the Hg proceeding from cold vapor to be concentrated, employing Ir (Moreda Piñeiro et al., 2002), Pd (Moreno et al., 2002), Rh (Flores et al., 2001), or Au (Flores et al., 2001).

The aforementioned analyses using the in situ trapping technique together with the optimum use of fixed modifiers, pre-concentration processes, and temperature programs accomplish detection limits of 0.009–0.6 µg g⁻¹ in solid samples (Flores et al., 2001; Moreda Piñeiro et al., 2002), i.e. in the range of the detection limits of CVAAS and ICPMS. Further improvements can be further achieved by the use of recently developed methods for CV generation based on the electrochemical generation of CV (Cervený et al., 2007; Zhu et al., 2008), or photochemical vapor generation (Vieira et al., 2007). These methods, in turn, could be coupled to modern HR-CS ETAAS. At the moment, these methods of CV generation have been used in the determination of Hg in aqueous standard solutions and in acid digests from biomasses coupled to ICPOES (Zhu et al., 2008; dos Santos et al., 2008), or CVAAS (Vieira et al., 2007). But some preliminary results (Cervený et al., 2007) suggest that these methods can also be successfully coupled to ETAAS. Cervený et al. (2007) have used electrochemical generation of Hg CV and its in situ trapping in a graphite furnace coated with Au for Hg determination in natural waters. The absolute limits of detection reached with this novel method of CV were 80 pg, which is 35% lower than those achieved with traditional CVAAS (124 pg) using the chemical reductant NaBH₄ for CV generation. Due to the good recoveries and low detection limits accomplished with these CV generation methods, there is a future possibility of coupling them to modern HR-CS ETAAS for Hg determination in soils and sediments.

Solid sampling ETAAS for Hg monitoring in soils and sediments is an interesting tool as a screening method in monitoring studies when there are a great number of samples to be analyzed and the main objective of the study is the determination of total Hg (Resano et al., 2005). The advantage lies in its capability of providing fast results. Other crucial aspects, such as the potential of the technique for straightforward calibration with aqueous standards and its robustness, have also been demonstrated (Maia et al., 2002; da Silva et al., 2002; Resano et al., 2005). The samples must be ground to low particle size
The use of a deuterium background corrector (da Silva et al., 2002; Maia et al., 2002; Resano et al., 2005) together with the use of adequate modifiers have resulted in detection limits between 0.025 and 0.2 µg g⁻¹ in soil samples (da Silva et al., 2002; Maia et al., 2002; Resano et al., 2005). This has been possible by using Pd or other elements of the PGM as a coating in the internal surface of GF (da Silva et al., 2002; Maia et al., 2002). The solid sample is introduced in the graphite furnace using a special sampling platform. The Hg is quantitatively released from the sample during the pyrolysis stage and is trapped in the furnace wall. The platform is removed from the tube prior to the atomization stage. A loss-free determination of Hg in aqueous standards could only be achieved with the use of KMnO₄, which permits carrying out direct solid analyses using aqueous standards for calibration (da Silva et al., 2002; Maia et al., 2002).

The application of HR-CS ETAAS shows promise to be a significant step forward in reaching figures of merit in Hg determination with low sample manipulation efforts and saving of time. The possibility of using HR-CS ETAAS for Hg determination has been tested only recently (da Silva et al., 2006). Hg has been determined directly from solid biomass samples with calibration against aqueous standards. The detection limits, 0.1 µg g⁻¹, and the great precision and sensitivity make this method suitable for routine monitoring purposes due to its simplicity. The possibility of coupling CV generation with HR-CS AAS is an approach with considerable potential that requires further study. To date, this possibility remains to be explored and several new experiments are necessary to develop the use of these novel spectrometers for Hg determination in soils and sediments.

**Conclusions and Future Perspectives**

Many studies have used ETAAS for the trace determination of As, Cd, Cr, Cu, Hg, and Pb in soils and sediments in the last fifty years. During this period there have been continuous improvements in the method by enhancing the precision, reproducibility, and sensitivity of the graphite furnace and reducing the detection limits in the determination of these trace elements. These improvements have implied changes at different stages of the analytical process from sample pretreatments to advances in the optical components and detectors of the spectrophotometer.

Regarding pretreatments, acid digestion using HNO₃ alone or in combination with other acids or slurry formation is the most useful method to totally liberate the analyte from the sample matrix. This method is pertinent if the aim is to determine the total amount of analyte in soils and sediments or those that potentially can be available to plant uptake at short, medium and long term. However, if we want to determine the more mobile or the bio-available analyte fraction at short term, extraction by liquid-solid leaching is an alternative possibility.

ETAAS allows automating all the sample pretreatments including chemical vapor generation by an on-line FIA system. These FIA systems are especially relevant in studies of environmental monitoring, when a great number of samples have to be analyzed over long periods. On the other hand, the recent improvements in FIA systems such as LOV systems with bead injection can also be coupled to the most advanced ETAAS spectrometers achieving great progress, permitting the use of modern sorbent substances for separation and preconcentration of the analyte in order to decrease the detection limits and the analytical accuracy, sensitivity, and reproducibility.

The advances of in situ trapping methods in the furnace coupled with improvements in the methods to supply the sample into the furnace with adequate temperature programs have led to a significant reduction in the detection limits in As and Hg determination. The
Electrothermal Atomic Absorption Spectrometry

separation of analyte from the sample matrix using a solid sample coupled to ETAAS is a possibility developed by several authors who have determined As, Cd, Cu, Hg, and Pb in soils and sediments with very good recoveries and analytical figures of merit. In addition, the improvements in the use of modifiers, the improvements in the graphite furnace design and in the background absorption correction systems, such as Zeeman background correctors, have together enabled attaining detection limits near or below 1 µg L\(^{-1}\) in sample solutions from acid digests or leaches, and have led to the commercial development of sequential multi-element ETAAS spectrometers.

The use of modern HR-CS ETAAS spectrometers improves the capacity to reduce background noise and to determine As, Cd, Cu, Hg, and Pb from solid samples, but this technique needs to be improved to achieve faster concurrent multi-element determination without prohibitively expensive custom designed detectors. Meanwhile, a truly simultaneous multi-element AAS determination of certain groups of elements has been possible when an appropriate two dimensional CCD array is used and when absorption lines of the elements to determine are close. The use of new filter vaporizers based on the introduction of on-line sources may be particularly suitable for high and medium volatile elements such as As and Hg. This approach avoids the use of chemical modifiers and copes with large sample sources. Following this approach, a transversely heated graphite filter atomizer (GFA) has been used with good results in As, Cd, Cu, and Pb determination in acid digests, slurries, or leaches from biological samples (Ngobeni et al., 2003; Katskov, 2007) and soils and sediments (Srogi, 2008), thus opening a new path where further advances are possible. For example, the use of GFA in HR CS ETAAS spectrometers offers new prospects for overcoming the slowness of element determination, one of the most serious limitations of ETAAS. Moreover, the possibility of coupling HG or CV generation to HR CS ETAAS spectrometers to pre-concentrate the analyte prior to atomization is not far off. This possibility would broaden the capacity to analyze volatile elements such as As and Hg and should accomplish new advances in decreasing the limit of detection of these elements in soils and sediments.

Further possible improvements in the software, in detectors, and in the atomizer can prevent vapor condensation on the atomizer surface, improving the long-term repeatability of analytical signals, and reducing even more the interferences and the time between sequential measurements by more efficient cooling of the atomizer. At present and in the near future, the possibility of combining the improvements at the level of efficient sample concentration using the new FIA systems, together with the advances in the spectrometer’s optical system that are coupled to background correction systems based on HR-CS ETAAS, should permit connecting chemical vapor generation and solid sampling to HR-CS ETAAS. With these improvements, ETAAS can compete in figures of merit and cost with the other available analytical spectrometry methods, particularly when dealing with samples in complex matrices such as soils and sediments.

References


