8. Sample preparation for spectroanalytical determinations based on microwave-assisted procedures: An alternative towards greener strategies

Mário H. Gonzalez¹, Eveline A. Menezes², Wladiana O. Matos³
Silmara R. Bianchi², Ana Rita A. Nogueira² and Joaquim A. Nóbrega¹

¹Grupo de Análise Instrumental Aplicada, Departamento de Química, Universidade Federal de São Carlos, P.O. Box 676, 13560-970, São Carlos-SP, Brazil; ²Grupo de Análise Instrumental Aplicada, Embrapa Pecuária Sudeste, P.O. Box 339, 13560-970 São Carlos - SP, Brazil; ³Departamento de Química Analítica e Físico-Química Universidade Federal do Ceará, Campus do Pici, 60455-760, Fortaleza - CE, Brazil

Abstract. The amount and the toxicity of the produced wastes are as important as any other analytical feature during the development of new analytical procedures and researches have been focused on the development of methods more friendly to the environment and to humans. The number of publications with this focus has increased significantly demonstrating that microwave radiation can be used in different fields of chemistry, such as digestion and extraction procedures.

Lately, new procedures for sample preparation were developed including microwave induced combustion, vapor-phase digestion, sample addition to pre-heated reagents, combination of ultraviolet...
radiation and on line microwave digestion. This chapter presents an overview about microwave-assisted sample preparation procedures for spectroanalysis and a discussion about how these strategies led to greener procedures.

Introduction

Many chemical processes may cause a negative impact to the environment. Aspects such as environmental responsibility, use of clean methods, and sustainable development have been increasingly considered. It is well known that the development of chemical analysis procedures aims the minimization of these impacts by reduction of the reagents volume, decrease of waste production associated to reduced energy consumption.

The green chemical term was introduced in the USA about 15 years ago by the Environmental Protection Agency (EPA) together with American Chemical Society (ACS) and the Green Chemistry Institute. The definition of green chemistry is “the design, development and implementation of chemical processes and products to reduce or eliminate substances hazardous to human health and the environmental” [1, 2].

Green chemistry also aims the ambient responsible care and the sustainable development [3-5]. Different areas have evolved, such as homogeneous catalysis [6, 7], micro flow system [8], flow analysis [9, 10], medicinal chemistry [11], and industrial specialties applications [12] for implementing green chemistry approaches.

In the early 1970’s the use of microwave energy in sample preparation was firstly proposed by Abu Samra et al. [13]. Microwave energy is a non ionizing radiation that causes molecular motion by migration of ions and rotation of dipoles, but does not cause changes in molecular structure. The frequency of 2450 MHz is the most commonly used. The typical energy output in a microwave system is 600-700 W. Two mechanisms are responsible for microwave heating: ionic conduction and dipole rotation. Ionic conduction occurs when species migrate either in one direction or in the other according to the polarity of the electromagnetic field. This depends on the size, charge, and conductivity of the ions, and the interaction with solvent species [14]. Dipole rotation refers to the molecular dipoles aligned with the applied electric field. The electric field oscillates forcing the dipole molecules to move and the resulting friction heats the solution. At 2450 MHz the dipoles align and then randomize 5 billions times a second [15], and the effect is an extremely rapid heating. The efficiency of heating by dipole rotation depends on dielectric relaxation time that is related to temperature and viscosity of the sample [14].
Microwave heating offers advantages over conventional heating, such as:
a) non-contact heating, b) rapid heating, c) material selective heating, d) volumetric heating, e) quick start-up and stopping, f) heating starts from inside the material body and g) higher level of safety and automation [16].

Instrumental techniques based on atomic spectrometry, such as flame atomic absorption spectrometry (FAAS), hydride generation atomic absorption spectrometry (HGAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma optical emission spectrometry (ICP OES), and inductively coupled plasma mass spectrometry (ICP-MS), are normally used for inorganic analysis. This chapter presents an overview about microwave-assisted sample preparation before spectroanalytical measurements based on strategies that led to greener procedures.

1. Sample preparation

A chemical analysis involves, generally, the following steps: collection of the sample, drying, storage, digestion, volumetric dilution, removal of particles, determination of analytes of interest and action to be taken [17]. The procedure to be followed depends on the matrix of which the analyte(s) will be isolated. The quantification of inorganic elements frequently requires a sample preparation step. However, this step still presents a relatively limited development and may be generally considered the slowest step in an analysis, not following the instrumentation speed and efficiency of chemical analysis [18].

Microwave energy is applied in various fields of analytical chemistry including digestion for elemental analysis, extraction, drying, and combustion. Different types of samples can be digested or extracted using microwave energy: biological, botanical, zoological, geological, environmental, alloys, synthetics materials, foods, sludge, coal and ash samples.

1.1. Digestion procedures

The use of microwave radiation ovens gained popularity when it was associated with acid digestion, reducing the time of sample preparation and minimizing the amount of reagents and waste generated [19, 20].

In wet decomposition, the combination of one or more acid is frequently used. The physical and chemical characteristics of each acid are combined to improve the efficiency of decomposition. Another way to improve the decomposition efficiency is the use of closed vessels at high pressure and high temperature. The consequent increase in the boiling point of acids makes feasible reaching high temperatures and decomposition is more efficient, additionally losses of volatile analytes and contamination are avoided [21].
Closed vessels have been employed for sample preparation and a large number of publications describing the experimental procedures and the commercial equipments employing such vessels with various safety devices are described. Among the acids that can be used for sample digestion, nitric acid is often employed owing to its simplicity of manipulation, easy purification and efficiency in the oxidation of organic compounds [18, 22, 23]. A concentrated nitric acid solution suffers thermal decomposition and may generate different compounds, such as NO, NO₂, NO₃⁻, N₂O, N₂O₃, N₂O₄, N₂O₅, N₂O₆, HNO and HNO₂, all them soluble in water and with recognized oxidant action [24]. Concentrated solutions of nitric acid when heated in closed systems have NO₂ as main decomposition product. When diluted nitric acid solutions are used, the main product of the reaction is NO. The NO formed reacts in an oxidizing atmosphere, leading to the formation of NO₂, which is reabsorbed in water and regenerates HNO₃ and HNO₂. These acids decompose, leading to the formation of NO again, providing a chain reaction, as demonstrated by the equations [25, 26]:

\[
\begin{align*}
2 \text{NO}(g) + \text{O}_2 & \rightarrow 2 \text{NO}_2(g) \\
2 \text{NO}_2(g) + \text{H}_2\text{O}(l) & \rightarrow \text{HNO}_3(l) + \text{HNO}_2(l) \\
2 \text{HNO}_2(l) & \rightarrow \text{H}_2\text{O}(l) + \text{NO}_2(l) + \text{NO}(l)
\end{align*}
\]

These processes may explain the feasibility of using diluted solutions of nitric acid for decomposition of biological materials. Additionally, the interaction of microwave radiation with solvent is one of the main factors responsible for fast increasing of the pressure inside reaction vessels [21].

Zhou et al. [19] carried out a study using diluted acids associated with microwave radiation for extraction of trace elements in biological samples. A standard reference material, apple leaves, was digested with 5.0 mL volume of solutions containing 10, 14 % v v⁻¹, and concentrated HNO₃. The proposed procedure presented recoveries bigger than 95% for Cu, Fe, Mg, and Mn in all media.

Chow et al. [27] employed diluted acids for determination of Cu, Hg, and Pb in traditional Chinese medicines and certified reference materials (CRM's). Both, Pd and Cd, were determined by FAAS, and Hg by CVAAS. The method proved to be efficient, simple and with few interferences, additionally led to reduced generation of acid fumes and final solutions with a low acid concentration, i.e. lower than 4% v v⁻¹.

Dugenevest et al. compared conventional procedures for acid digestion of waste incineration and procedures based on diluted acids heated by microwave radiation [28]. The procedure using microwave radiation was fast,
simple, less expensive and efficient for the determination of As, Ca, K, Na, Pb, and Zn in samples.

Garcia-Rey et al. used a solution containing 50 % v v⁻¹ nitric acid for determination of Ca, Cd, Cu, Mg, Fe, Pb, and Zn in raw meat by FAAS [29]. This method was compared with a reference method and applied to a bovine muscle certified reference material.

The use of diluted acids has many advantages compared to conventional methods, namely, reduction of the extraction time, simplification of the process, avoidance of chemical emissions to the atmosphere and losses of metals by volatilization.

The use of hydrogen peroxide (H₂O₂) may be required as an auxiliary oxidizing agent when small volumes of acids or diluted acids are employed. Wu et al. reported a decrease in residual carbon content and remaining residual species, when the volume of H₂O₂ was increased [30]. An increase of internal pressure in closed systems was studied by Veschetti et al. showing a great efficiency of oxidation of organic matter even at low temperatures [31]. Gouveia et al. pointed out that proper efficiency of digestion using diluted acids and reduction of the volumes of H₂O₂ are feasible due to the high pressure and high temperature reached in closed systems, which provide a more complete destruction of the sample matrix improving the reliability of the results [32].

Araújo et al. [33] evaluated the efficiency of microwave-assisted acid digestion of plants using different concentrations of nitric acid with hydrogen peroxide (30 % m m⁻¹) by measuring the residual carbon content using ICP OES with axial viewing. It was demonstrated that plant materials can be efficiently acid-digested in a closed-vessel microwave system using 2 mol L⁻¹ HNO₃ solution. The accuracy of the method was proved using certified reference materials.

Soybeans grains, bovine blood, bovine muscle and bovine viscera were digested in a cavity-microwave oven using oxidant mixtures in different acid concentrations. The ¹H NMR spectra obtained for digests in diluted nitric acid medium were simpler than those obtained when using 14 mol L⁻¹ HNO₃. Concentrated solutions presented a wider variety of organic compounds, such as nitro-derivative aromatic compounds, and a higher amount of aromatic aliphatic compounds when compared with diluted solutions. The separation of isomers o-, m- and p- nitrobenzoic acid was possible employing ion-pair reversed-phase HPLC-UV. The m-nitrobenzoic acid was formed in most digestion conditions [34].

There are many authors that recommended small volumes of concentrated acids along with the addition of water in the digestion vessel [35-39]. Others recommended the use of the small volumes of reagents, as concentrated acid and H₂O₂ (Table 1) for obtaining more efficient
Table 1. Microwave-assisted digestion using small volumes of reagents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reagents and volumes</th>
<th>Analytes</th>
<th>Digestor apparatus</th>
<th>Instrumental Technique</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biological samples</td>
<td>2 mL HNO₃ and 1 mL H₂O₂ 30% (m⁻¹)</td>
<td>Al, B, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, P, S, Zn</td>
<td>ETHOS 1600</td>
<td>ICP OES</td>
<td>40</td>
</tr>
<tr>
<td>Baby food</td>
<td>3 mL HNO₃ and 0.5 mL H₂O₂ 30% (m⁻¹)</td>
<td>Co, Cu, Mn, Ni</td>
<td>MLS 1200 (Milestone)</td>
<td>ETAAS</td>
<td>41</td>
</tr>
<tr>
<td>Animal diet</td>
<td>0.4 mL HNO₃ and 0.1 mL H₂O₂ 30% (m⁻¹)</td>
<td>Pb</td>
<td>MDS 2000 (CEM)</td>
<td>GFAAS</td>
<td>42</td>
</tr>
<tr>
<td>Marine animal and plant</td>
<td>1 mL HNO₃</td>
<td>Ag, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, P, Pb, Se, V, Zn</td>
<td>MDS 81 (CEM)</td>
<td>ICP-MS</td>
<td>43</td>
</tr>
<tr>
<td>tissues</td>
<td>Beer</td>
<td>Al, Cd, Cu</td>
<td>MLS 1200 (Milestone)</td>
<td>ETAAS</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>3.0 mL HNO₃, and 0.5 mL H₂O₂ 30% (m⁻¹)</td>
<td>Al, Ba, Ca, Cd, Cu, Fe, Mg, Mo, Pb, Zn</td>
<td>MLS 1200 (Milestone)</td>
<td>ICP OES, ETAAS</td>
<td>45</td>
</tr>
<tr>
<td>Heroin</td>
<td>3.0 mL HNO₃</td>
<td>Al, Bi, Cd, Co, Cr, Hg, Mn, Mo, Ni, Pb, Sb, Tl</td>
<td>ETHOS 900 (Milestone)</td>
<td>ICP-SF-MS</td>
<td>46</td>
</tr>
<tr>
<td>Biological fluids</td>
<td>Urine: 0.5 mL HNO₃, Serum: 1 mL HNO₃ Whole blood: 2 mL HNO₃</td>
<td>Al, Bi, Cd, Co, Cr, Hg, Mn, Mo, Ni, Pb, Sb, Tl</td>
<td>MLS 1200 (Milestone)</td>
<td>GFAAS, ICP-MS, ICP OES</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>Human brains</td>
<td>Mn, Mo</td>
<td>MLS 1200 (Milestone)</td>
<td>ICP-SF-MS</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>2 mL HNO₃ and 0.5 mL H₂O₂ 30% (m⁻¹)</td>
<td>Pt, Pd, Rh</td>
<td>MARS 5 (CEM)</td>
<td>ICP-SF-MS</td>
<td>49</td>
</tr>
<tr>
<td>Urban aerosol</td>
<td>2 mL. aqua regia and 0.5 mL HF</td>
<td></td>
<td>WL 5001 (Fei Yue</td>
<td>RP-HPLC</td>
<td>50</td>
</tr>
<tr>
<td>Herbal medicines</td>
<td>2.5 mL HNO₃ and 2.5 mL H₂O₂ 30% (m⁻¹)</td>
<td>Pb, Cd, Hg, Ni, Cu, Zn, Sn</td>
<td>Analytical Instrument</td>
<td>HG-AAS, ICP-SF-MS</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Peat and plant</td>
<td>As</td>
<td>Factory</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample</td>
<td>Reagents and volumes</td>
<td>Analytes</td>
<td>Digestor apparatus</td>
<td>Instrumental Technique</td>
<td>Ref.</td>
</tr>
<tr>
<td>---------------------------------------</td>
<td>----------------------------------------------------------</td>
<td>----------</td>
<td>----------------------------------------</td>
<td>------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Species of woodlice and their skins</td>
<td>4 mL aqua regia, 1, 2, or 3 mL HF and 12, 24 or 36 mL H$_2$BO$_3$ 3 mL HNO$_3$</td>
<td>Al, Ca, K, Ti, Fe, Mg, Na, Si</td>
<td>MLS 1200 (Milestone)</td>
<td>ICP OES</td>
<td>51</td>
</tr>
<tr>
<td>Lichens</td>
<td>3.5 mL HNO$_3$ and 1.5 mL H$_2$O$_2$ 30% (m m$^{-1}$) 2 mL aqua regia, 1 mL H$_2$O$_2$ 30% (m m$^{-1}$) and 1 mL HF</td>
<td>d, Cr, Cu, Ni</td>
<td>Multiwave (Anton Paar)</td>
<td>ICF OES</td>
<td>52</td>
</tr>
<tr>
<td>Soils</td>
<td>0.1 mL HNO$_3$</td>
<td>Al, Ba, Ca, Cr, Cu, Fe, Mg, Mn, V, Zn</td>
<td>PROLABO 7195 (OI Analytical)</td>
<td>FAAS</td>
<td></td>
</tr>
<tr>
<td>Human liver</td>
<td>1 mL HNO$_3$ and 0.5 mL H$_2$O$_2$ 30% (m m$^{-1}$) 3.5 mL aqua regia and 1 mL H$_2$O</td>
<td>Sr, Mn, Fe, Ni, Cu, Zn, Rb, Pb U, Th</td>
<td>MDS 2100 (CEM) MLS 1200 (Milestone)</td>
<td>ICP-MS, TXRF SF-ICP-MS</td>
<td>55</td>
</tr>
<tr>
<td>Urine</td>
<td>2 mL HNO$_3$ and 1 mL H$_2$O$_2$ 30% (m m$^{-1}$)</td>
<td>Sr, Mn, Fe, Ni, Cu, Zn, Rb, Pb U, Th</td>
<td></td>
<td>ICP-MS, TXRF SF-ICP-MS</td>
<td>56</td>
</tr>
<tr>
<td>Wine</td>
<td>1 mL HNO$_3$ and 0.5 mL H$_2$O$_2$ 30% (m m$^{-1}$)</td>
<td>Sr, Mn, Fe, Ni, Cu, Zn, Rb, Pb U, Th</td>
<td></td>
<td>ICP-MS, TXRF SF-ICP-MS</td>
<td>56</td>
</tr>
<tr>
<td>Human hair, pig kidney, dogfish liver, dogfish muscle and lobster</td>
<td>3 mL HNO$_3$ and 1 mL H$_2$O$_2$ 30% (m m$^{-1}$)</td>
<td>Pb, Cd, Ni, Cr</td>
<td>Not informed</td>
<td>GFAAS</td>
<td></td>
</tr>
<tr>
<td>Scalp hair, blood and urine</td>
<td>3 mL HNO$_3$ and 2 mL HF</td>
<td>Cu, Mn, Cr, V, Li, Pb, Sn, Mg, U, Ba, Sr, Zn, Sb, Rb, Ce</td>
<td>Not informed</td>
<td>JSS-ETV-ICP-MS</td>
<td></td>
</tr>
<tr>
<td>Silicon based minerals</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample</td>
<td>Reagents and volumes</td>
<td>Analytes</td>
<td>Digester apparatus</td>
<td>Instrumental Technique</td>
<td>Ref.</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>---------------------------------------</td>
<td>-------------------------------</td>
<td>---------------------------------</td>
<td>----------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Mushrooms</td>
<td>1.5 mL HNO₃ and 1.5 mL H₂O₂ 30% (m²)</td>
<td>Se</td>
<td>MLS 1200 (Milestone)</td>
<td>ICP-MS</td>
<td>61</td>
</tr>
<tr>
<td>Nutritional supplements</td>
<td>3 mL HNO₃ and 0.5 mL H₂O₂ 30% (m²)</td>
<td>Se species</td>
<td>MLS 1200 (Milestone)</td>
<td>HPLC-ICP-MS</td>
<td>62</td>
</tr>
<tr>
<td>Plant materials</td>
<td>0.5 mL HNO₃ and 5.5 mL H₂O₂ 30% (m²)</td>
<td>P</td>
<td>Multiwave 3000 (Anton Paar)</td>
<td>ICP OES</td>
<td>63</td>
</tr>
<tr>
<td>Plants and water</td>
<td>1.75 mL HNO₃ and 6 mL H₂O₂ 30% (m²)</td>
<td>Pb</td>
<td>ETHOS 1600 (Milestone)</td>
<td>ICP-MS</td>
<td>64</td>
</tr>
<tr>
<td>Algae</td>
<td>3 mL HNO₃ and 0.5 mL H₂O₂ 30% (m²)</td>
<td>Pb, Cd</td>
<td>MLS 1200 (Milestone)</td>
<td>ETAAS</td>
<td>65</td>
</tr>
<tr>
<td>Plants</td>
<td>1.5 mL HNO₃ and 1.5 mL HF 48%</td>
<td>Se, organic Se species</td>
<td>MLS 1200 (Milestone)</td>
<td>HPLC-ICP-MS</td>
<td>66</td>
</tr>
<tr>
<td>Soil</td>
<td>4 mL HNO₃ and 1 mL H₂O₂ 30% (m²)</td>
<td>Pd</td>
<td>MLS 1200 (Milestone)</td>
<td>ICP-MS</td>
<td>67</td>
</tr>
<tr>
<td>Water and biological samples</td>
<td>1.5 mL H₂SO₄ (conc.), 2 mL HNO₃, and</td>
<td>Pb</td>
<td>Not informed</td>
<td>ETAAS</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>1 mL H₂O₂ 30% (m²)</td>
<td>Rare earth elements</td>
<td>Multiwave Paar (Paar)</td>
<td>SF-ICP-MS</td>
<td>69</td>
</tr>
<tr>
<td>Wine</td>
<td>2 mL HNO₃</td>
<td>Li, Be, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Cd, Cs, Ba, Hg, Pb</td>
<td>Multiwave 3000 (Anton Paar)</td>
<td>ICP OES, ICP-MS, FI-ICP-MS</td>
<td>70</td>
</tr>
<tr>
<td>Coal</td>
<td>3 mL HNO₃</td>
<td>Mn</td>
<td>DGT 100 (Proyecto Analítica)</td>
<td>GFAAS</td>
<td>71</td>
</tr>
<tr>
<td>Feces and fish feed</td>
<td>2.5 mL HNO₃ and 0.5 mL H₂O₂ 30% (m²)</td>
<td>Be, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sn, Sb, Ba, TI, Pb, Hg</td>
<td>MARS 5 (CEM)</td>
<td>CVAAAS, ICP-MS</td>
<td>72</td>
</tr>
<tr>
<td>Marine species</td>
<td>2 mL HNO₃, 1 mL H₂O₂ 30% (m²) and 0.3 mL HF</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample</td>
<td>Reagents and volumes</td>
<td>Analytes</td>
<td>Digester apparatus</td>
<td>Instrumental Technique</td>
<td>Ref.</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>--------------------------------------------</td>
<td>------------------</td>
<td>--------------------</td>
<td>------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Welding fume</td>
<td>2 mL HNO₃ and 0.5 mL H₂O₂ 30% (m m⁻¹)</td>
<td>Cr, Mn, Ni, Co, Fe</td>
<td>MARS 5 (CEM)</td>
<td>ICP OES, ICP-MS</td>
<td>73</td>
</tr>
<tr>
<td>Soil and soil amended with sewage sludge</td>
<td>4 mL HNO₃ and 2 mL H₂O₂ 30% (m m⁻¹)</td>
<td>Cu, Zn, As, Cd, Cr, Ni, Pb</td>
<td>Not informed</td>
<td>FAAS, ETAAS</td>
<td>74</td>
</tr>
<tr>
<td>Water</td>
<td>4 mL HNO₃ and 2 mL H₂O₂ 30% (m m⁻¹)</td>
<td>Se, As</td>
<td>ETHOS 1600 (Milestone)</td>
<td>WCAAS</td>
<td>75</td>
</tr>
</tbody>
</table>

decomposition. The advantage of these procedures are the lower amount of residue generated during sample preparation.

Compared to concentrated nitric acid, diluted nitric acid solutions reduce the volume of the reagents and the variety of digestion residues, led to lower standard deviations, and do not require high dilution factors before analyte measurements. The use of diluted acids was proven to be a feasible and recommendable alternative. These mechanisms allow the application of microwave energy in green chemistry, considering that water and ionic solutions could be used as alternative solvents in substitution of toxic solvents, and decrease in concentrated acid volume.

1.2. MAE – Microwave assisted extraction

Extraction is a type of sample treatment that consists in the migration of the analytes by desorption, diffusion and/or solubilisation processes in a suitable solvent. The interaction between the solvent and the analytes must be stronger than the interaction between the analytes and the matrix in order to achieve a quantitative extraction [76].

A traditional extraction method is the Soxhlet developed in 1879 [77]. In this method, the solid sample is placed in a thimble holder and during the operation is gradually filled with condensed fresh solvent from a distillation flask. When the liquid reaches an overflow level, a siphon aspirates the whole content of the thimble holder and unloads it back into the distillation flask, carrying the extracted analytes in the bulk liquid. This operation is repeated until complete extraction is reached. The advantages of this method are: the sample takes into contact with portions of solvent vapor many times, the temperature of the system is higher than the room temperature and any filtration step is required. On the other hand, this operation demands long time (about 8 – 48 h) and elevated reagent volumes (about 500 mL) producing high amounts of toxic residues [78].

Many factors should be taken into account to choose an extraction technique to be applied in analysis: the efficiency and reproducibility of extraction, the facility of operation, cost, time, degree of automation, possibility of hyphenation, safety and the compromise with the environment [76]. This last item has become the most critical factor to researchers and industries due to the development of restrictive legislation regarding to the waste of chemical residues. Therefore, extraction methods that require less operation time, minimum amount of solvents, fewer risks to the operator and reduced generation of toxic residues are gradually substituting conventional extraction methods.
Microwave radiation has been employed in extraction processes (MAE – microwave-assisted extraction) aiming to accelerate the sample preparation step through the application of appropriate radiation power and time. Additionally, it makes possible the treatment of many samples simultaneously, provides the rupture of the analyte-matrix interaction easier than others extraction methods, has possibility of automation, avoids the loss of volatiles analytes and demands less volume of extracting solvents, producing less quantity of residues [76-79].

Microwave AE has been applied to organic, organometallics, and inorganic analytes leached from environmental, food, biological, and industrial samples. Basic parameters, such as extraction medium, applied power, exposition time, extracting volume and sample size have been optimized. Due to the possibility to control the radiation power and exposition time, MAE has been important for sample preparation in chemical speciation analysis [80]. According to the IUPAC – International Union of Pure and Applied Chemistry - chemical speciation is the analysis that makes possible to determine the distribution of the chemical species of an element in a sample. Chemical species are the specific forms of a chemical element, such as molecular structure and oxidation state [81]. In speciation analysis, the extraction of the species should be evasive, but, simultaneously gentle, since the degradation of the original forms of the analyte is not desired.

In MAE applications for organic compounds extraction, toxic solvents are generally employed. However, recently, micellar medium and ionic liquids have been used as extractant to procedures of organic compounds extractions under microwave radiation from different samples replacing organic solvents (Table 2).

The combination of MAE and micellar medium is called MAME (microwave-assisted micellar extraction) and the association of MAE with ionic liquids is denominated as ILMAE (ionic liquid-based microwave-assisted extraction). Some applications are described in Table 3.

Microwave AME employs the cloud point extraction principles and the microwave energy as source of heating [110]. Cloud point extraction (CPE) consists in an extraction and preconcentration procedure that has been applied for analysis of inorganic elements, organic compounds, elemental speciation and anions in different types of matrix. The principle of cloud point phenomenon is based on the aggregation of non-ionic surfactants monomers when the surfactant solution conditions, such as temperature and pressure, are appropriately altered. When this aggregation of monomers occurs, micelles are formed and during this process the analyte may be trapped into the micelles. The surfactant solution becomes turbid and separate
Table 2. Applications of MAME.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surfactants</th>
<th>Analytes</th>
<th>Digestor apparatus</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marine sediment</td>
<td>POLE*</td>
<td>PAHs</td>
<td>MDS 2000 (CEM)</td>
<td>82</td>
</tr>
<tr>
<td>Marine sediment</td>
<td>POLE*</td>
<td>PAHs</td>
<td>MDS 2000 (CEM)</td>
<td>83</td>
</tr>
<tr>
<td>Marine sediment</td>
<td>POLE and Genapol X-80””</td>
<td>PCBs</td>
<td>MDS 81 D (CEM)</td>
<td>84</td>
</tr>
<tr>
<td>Marine sediment</td>
<td>POLE*</td>
<td>PAHs</td>
<td>Not informed</td>
<td>85</td>
</tr>
<tr>
<td>River sediment</td>
<td>Polyoxyethylene(23) dodecyl ether, Polyoxyethylene(10) dodecyl ether, CTAB””</td>
<td>PAHs</td>
<td>Not informed</td>
<td>86</td>
</tr>
<tr>
<td>Marine sediment</td>
<td>POLE*</td>
<td>PAHs</td>
<td>MDS 2000 (CEM)</td>
<td>87</td>
</tr>
<tr>
<td>Marine sediment</td>
<td>POLE*</td>
<td>Chlorophenols</td>
<td>Multiwave (Anton Paar)</td>
<td>88</td>
</tr>
<tr>
<td>Marine sediment</td>
<td>POLE* and Genapol X-80””</td>
<td>PCDDs</td>
<td>Multiwave (Anton Paar)</td>
<td>89</td>
</tr>
<tr>
<td>Soil</td>
<td>POLE* and Genapol X-80””</td>
<td>Organophosphorus pesticides</td>
<td>Multiwave (Anton Paar)</td>
<td>90</td>
</tr>
<tr>
<td>Soil</td>
<td>POLE*</td>
<td>l’phenols</td>
<td>Multiwave (Anton Paar)</td>
<td>91</td>
</tr>
<tr>
<td>Tomato</td>
<td>POLE* and Genapol X-80””</td>
<td>Organophosphorus pesticides</td>
<td>Not informed</td>
<td>92</td>
</tr>
<tr>
<td>Soil</td>
<td>Polyoxyethylene(10) dodecyl ether</td>
<td>Organochlorine pesticides</td>
<td>Multiwave (Anton Paar)</td>
<td>93</td>
</tr>
<tr>
<td>Soil</td>
<td>POLE*</td>
<td>Organochlorine pesticides</td>
<td>Multiwave (Anton Paar)</td>
<td>94</td>
</tr>
<tr>
<td>Soil</td>
<td>POLE* and Genapol X-80””</td>
<td>Benimidazole fungicides</td>
<td>Not informed</td>
<td>95</td>
</tr>
</tbody>
</table>
Table 2. Continued

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surfactants</th>
<th>Analytes</th>
<th>Digester apparatus</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seaweed</td>
<td>POLE*</td>
<td>Organochlorines</td>
<td>Multiwave (Anton Paar)</td>
<td>96</td>
</tr>
<tr>
<td>Wood extractives</td>
<td>CTAB***, Triton X-100****</td>
<td>Alkyl-methoxy-phenolic</td>
<td>Focused MW® Synthesis System (CEM)</td>
<td>97</td>
</tr>
<tr>
<td>Wood</td>
<td>POLE*</td>
<td>Chlorophenols</td>
<td>Focused MW® Synthesis System (CEM)</td>
<td>98</td>
</tr>
<tr>
<td>Sediment</td>
<td>POLE*</td>
<td>Pharmaceuticals residues</td>
<td>Multiwave (Anton Paar)</td>
<td>99</td>
</tr>
<tr>
<td>Molluscs</td>
<td>POLE*</td>
<td>Pharmaceuticals</td>
<td>Multiwave (Anton Paar)</td>
<td>100</td>
</tr>
<tr>
<td>Medicinal herb</td>
<td>Genapol X-80°°°</td>
<td>Alkaloids</td>
<td>Focused Microwave-assisted extraction Unit Star System 2 (CEM)</td>
<td>101</td>
</tr>
<tr>
<td>(Rhizoma Captidis) Mud</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquorice root</td>
<td>Triton X-100°°</td>
<td>Organochlorine pesticides</td>
<td>Not informed</td>
<td>102</td>
</tr>
<tr>
<td>Molluscs</td>
<td>POLE*</td>
<td>Glycyrrhizic acid</td>
<td>Not informed</td>
<td>103</td>
</tr>
<tr>
<td>Salvia miltiorrhiza</td>
<td>Genapol X-80°°</td>
<td>Tanshinones</td>
<td>Not informed</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* POLE - polyoxyethylene(10)lauryl; ** Genapol X-80 trimethylammonium bromide; *** Triton X-100 - t-octylphenoxypolyethoxyethanol
Table 3. Applications of ILMAE.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surfactants</th>
<th>Analytes</th>
<th>Digestor apparatus</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medicinal herb (Rhizma polygoni Cuspidati) Water</td>
<td>1-butyl-3-methylimidazdium bromide</td>
<td>Trans-resveratrol</td>
<td>MAS-I Microwave oven (Sineo)</td>
<td>106</td>
</tr>
<tr>
<td>Sediment</td>
<td>1-hexyl-3-methylimidazdium</td>
<td>Chlorobenzenes</td>
<td>Domestic microwave oven (Samsung)</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>1-hexadecyl-3-methylimidazdium bromide</td>
<td>PAHs</td>
<td>Focused MW™ Synthesis System (CEM)</td>
<td>108</td>
</tr>
<tr>
<td>Medicinal herb (Nelumbo n. Gaertn)</td>
<td>1-alkyl-3-methylimidazdium</td>
<td>Phenolic alkaloids</td>
<td>Domestic microwave oven (Glanz)</td>
<td>109</td>
</tr>
</tbody>
</table>
in two phases: one rich in the surfactant and contained the analyte trapped and an aqueous phase. The surfactants used in CPE procedures are environmentally friendly and the amount of extractant necessary is minimum compared with the volume of organic solvents required to conventional extraction methods [111]. In this way, MAME provides, specially, the reduction of operator exposition to toxic vapors and production of residues.

In general, MAME has been exploited to organic compounds extraction that are determined using gas chromatography-mass spectrometry (GC-MS) and high-pressure liquid chromatography (HPLC) with ultraviolet or fluorescence detector, therefore, the use of this method for extracting inorganic elements and compounds associated to spectroanalytical techniques may be a new application field. Furthermore, multielemental speciation employing MAME to extract simultaneously different elemental species from the same matrix and determination by ICP-MS is a possible strategy. However, in this case, limitations for introduction of surfactants into the plasma have to be solved.

The ILMAE method uses room temperature ionic liquids (RTILs) as extractants and microwave radiation heating. Ionic liquids are molecules that present low vapor pressure, good thermal stability, tunable viscosity, wide liquid range and low toxicity. Moreover, these extractants are miscible with water and organic solvents and are suitable for energy dissipation with microwaves [106]. However, there are few works with this type of extractant (Table 3), so investigations to examine the extraction of others analytes from different solid matrices are certainly necessary.

2. New trends in sample preparation

Procedures based on microwave-assisted digestion have been implemented in laboratories as a rapid and safe alternative to conventional procedures [20]. The current technology can be divided into systems with microwave cavity, which are generally operated under high pressure and temperatures, and in systems with focused microwave radiation, which often involve operation at atmospheric pressure [20]. Recently new strategies were proposed based on less conventional approaches, such as microwave-induced combustion [112-113], vapor phase digestion [114-118], combination of ultraviolet and microwave radiation [29], and sample addition to pre-heated acid with important effects on transport interferences [119 and Section 2.3.]. These procedures were implemented using furnaces with cavity or focused radiation.
2.1. Microwave-induced combustion

Microwave-induced combustion (MIC) involves the combustion of organic samples in a quartz closed-vessel pressurized with oxygen and the ignition is made by microwave radiation. After the combustion, gases are absorbed in an appropriate solution, and a reflux step may be necessary to ensure complete recoveries of analytes. Diluted acids may be used in MIC as absorbing solution for many analytes [113, 120]. The determination of residual carbon content allows evaluating the efficiency of the process [120]. Combustion technique is recommended for digestion of coals when determining Cl [121-123], F [124] and Hg [125]. Other applications include the determination of Br [126, 127], Cl [127], and S [128-130] after burning rubber and plastics and in the digestion of carbonaceous materials for subsequent determination of S [131].

The main characteristics of MIC are: a) combustion of up to 500 mg of sample is possible in a relatively low volume vessel, b) ignition is carried out using microwave radiation, avoiding additional devices such as metallic electrodes or infrared lamps, c) conventional wet digestion vessels are the same for the MIC technique and no changes in the vessel, rotor parts or pressure control device are necessary, d) up to eight samples can be simultaneously processed, e) blanks are low, and f) contrary to other combustion techniques, MIC allows a reflux step that minimizes potential losses due to analyte adsorption [120].

Flores et al. applied MIC for certified [112] materials of bovine liver, pig kidney, and skim milk. Cadmium and copper were determined in these samples by electrothermal atomic absorption spectrometry. The agreement between determined and certified values was between 96 and 105% for both analytes. They observed that only with the combustion step, the residual carbon content (RCC) was below 1.3%, and decreased to less than 0.4% when an additional reflux step with concentrated nitric was applied [112].

Mesko et al. evaluated a procedure for sample digestion based on MIC. The system was adapted in a microwave oven with quartz closed vessels. A quartz piece is used simultaneously as a sample holder and as protection to the cap of quartz vessel from the flame generated in the combustion process. The influence of the absorption solution (diluted and concentrated nitric acid or water) on the recoveries of copper and zinc was evaluated. The authors evaluated the combustion process in relation to the influence of sample mass on the ignition time, combustion time and maximum operation pressure. Bovine liver, milk powder and oyster tissue certified reference materials were used to evaluate the accuracy of the procedure for determination of copper and zinc [113].
In another interesting application Moraes et al. studied a rapid digestion procedure for determination of Al, Fe, Mn, Sr and Zn in carbon black-containing elastomers (30%) by using MIC. Samples of nitrile-butadiene rubber and ethylene-propylene-diene monomer were decomposed. They evaluated the influence of the absorption solution (nitric acid or water) and the necessity of an additional reflux step. Results were also compared to those obtained by using wet acid digestion in closed systems [132].

Duarte et al. applied the microwave-induced combustion (MIC) for seafood digestion and further total arsenic determination using hydride generation coupled to atomic spectrometry techniques. The agreement between determined and certified values was from 96 to 103% using 0.1 mol L\(^{-1}\) HNO\(_3\) as absorbing solution and 5 min of reflux. The agreement of results for As determination by FI-HG AAS and FI-HG-ICP-MS was better than 98% when compared with results obtained by ICP-MS after digestion. The proposed method by MIC allowed shorter digestions than other procedures and with low residual carbon content (< 0.5%). Using this procedure up to eight samples could be processed simultaneously in 25 min. Taking into account that concentrated acids were not necessary, the proposed procedure is in agreement with green chemistry recommendations [133].

The limitations for this technique are similar to those observed for the Trace-O-Mat technique, and include possible analyte adsorption in the quartz holder, the necessity to press the solid samples, and unsuitability to use HF [120].

2.2. Vapor-phase digestion

Vapor-phase digestion using different acids has been used for preparation of samples using either conductive heating system or microwave radiation and it is based on the contact between the vapor acid, its condensates and sample [114, 115, 134-136]. This procedure is characterized by low consumption of reagents and simultaneous purification of them, reduction of the risk of contamination, and improvement of the limits of detection due to low analytical blanks [118], which are important requirements for green chemistry.

Matusiewicz et al. initially studied vapor-phase acid digestion of inorganic and organic matrices for trace element analysis using a microwave heated bomb. The authors concluded that the use of vapor-phase microwave digestion method for marine sediment and marine biological tissue has the advantage of producing a dry digestion product that is soluble in water or slightly acidified water. Therefore, tedious evaporation of excess of acids is avoided [114].
Araújo et al. studied the effect of experimental parameters on Co and Fe determination in biological samples using microwave single vessel acid-vapor extraction with nitric acid under atmospheric pressure [116]. These authors evaluated particle sizes effects on digestion efficiency. It was demonstrated that temperature was the main parameter for efficient recovery of both Fe and Co in biological samples, and higher temperatures led to lower RCC's.

Trevizan et al. studied an acid vapor partial digestion procedure for bovine liver using a focused microwave oven and a laboratory-made PTFE support. The support was equipped with three cups of approximately 4 mL volume each one and the cups were adapted to the glass reaction vessel of the microwave oven. A mixture containing nitric plus sulfuric acids was heated to 120 °C to generate acid vapors [117].

In vapor-phase digestion procedures the use of small amounts of sample is common because digestion cups are usually of reduced volume and this improves the acid–vapor interaction with sample particles. This feature is attractive when the sample size is limited, such as in toxicological analysis of biological tissues [137]. The use of certified reference materials to evaluate accuracy may be difficult, because most of them are certified for a minimum sample mass around 250 mg to ensure sample homogeneity [138].

Barnes et al. developed a new and fast procedure for cleaning autosampler cups using acid-vapor steam-cleaning with a miniaturized assembly in a microwave–heated closed PTFE vessel. A glass cactus-shaped holder was made to support six polyethylene autosampler cups inside a 100 mL microwave vessel. They obtained lower blank values for chromium with cleaned cups compared to untreated cups [139].

Eilola and Perämäki developed a modified medium pressure microwave vapor-phase digestion method for difficult to digest organic samples [140]. The accuracy of the method was tested with certified reference materials. The modified method digested efficiently almost all tested materials, including reference materials composed by corn brain, dogfish liver, Cd in polyethylene, 2-nitrobenzoic acid (2-NBA), 4-nitrobenzoic acid (4-NBA) and 4''4''4''-tetrasulfonic acid tetrasodium salt (CPS), but could not digest 3-nitrobenzoic acid (3-NBA).

The position of the sample in the cups is intrinsically related to the temperature and interaction with the microwave radiation and it has pronounced effect on the process of digestion. Parameters such as temperature and particle sizes affect the efficiency of digestion [118].

Brancalion and Arruda evaluated the efficiency of decomposition of medicinal plants using microwave ovens and mini-vials for Cd determination by thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS). They observed that the RCC obtained varied from 0.30 to 0.45% and cadmium concentration was lower than 0.80 μg L⁻¹ in three plants [141].
2.3. Sample addition to pre-heated reagents

Recently a procedure was proposed for digestion based on the gradual addition of liquid samples to microwave-assisted heated concentrated acids [142, 143]. This procedure allows the digestion of large volumes of samples with small volumes of concentrated acids, reducing the acidity of the digestate and allowing lower dilution for its introduction using pneumatic nebulizers. When adding sample aliquots to heated concentrated acids, there is always an excess of reagent under proper conditions to react, increasing the formation of reactive radicals which improve the oxidation of organic matter and led to lower blank values [144]. This procedure was proposed as an alternative in focused microwave ovens where typically large amounts of concentrated acids are employed for reaching efficient digestion.

Santos et al. carried out a study for acid digestion of bovine milk samples in a microwave focused oven [143]. The effects of the sequential addition of sample aliquots to microwave-heated concentrated acids, such as nitric and sulfuric acids, and temperature-time programs were examined taking into account RCC, elemental recoveries, and final acid concentration of the digestates.

Bressani et al. developed a procedure for digestion of samples of encapsulated lubricating oil manually added to the microwave-assisted pre-heated concentrated digestion mixture. The encapsulation of the samples was a simple strategy that allowed the addition of viscous samples to the acid mixture heated in a focused microwave oven. The digestates obtained were characterized by lower levels of acidity and RCC. Lower volumes of concentrated reagents and lower temperatures of digestion than conventional digestion were used conferring to the procedure cleaner characteristics [145].

2.4. Combination of ultraviolet and microwave radiations

The combination of two types of radiation, ultraviolet and microwave, provides many benefits, such as the ability of UV radiation to form radicals and break structures associated to the fast heating by microwave action, thus achieving efficient decomposition of complex organic matrices [146]. This combination is possible employing special UV lamps activated by microwave radiation (MWL), which allow accomplishing photo-degradations simultaneously with microwave-assisted heating. The combination of these two radiations (UV-MW) has potential to make feasible the decomposition of organic compounds using photo-oxidative reactions such as Fenton or titanium dioxide.

Würfels and Jackwerth discussed the difficulty of complete oxidation of compounds such as benzoic acid in decomposition systems at high pressure heated by microwave radiation [23]. On the other hand, Mokrini et al.
showed that benzoic acid can be degraded by UV [147]. Combination of both energies would probably speed up the process and increase the efficiency of decomposition.

Klán et al. studied applications, limitations and prospects of using discharge lamps without electrodes, when irradiated by microwave radiation (MWL). As advantages they cited the possibility to promote photochemical reactions at higher temperatures, good photochemical efficiency, easy operation, low cost, and intense incident radiation in the solution because the lamp source is immersed in it. Disadvantages such as the inability to activate the MWL at low temperatures, care in the use of flammable or toxic solvents, the use of polar solvents, which are efficient microwave radiation absorber causing overheating, and not allowing the proper activation of the MWL [148, 149].

Florian and Knapp presented the combination of ultraviolet and microwave radiation using MWL and they obtained excellent results when compared to conventional systems of decomposition with UV radiation [150].

Gromboni et al. evaluated the coupling of microwave radiation with photo-Fenton reaction for wastewater treatment. Efficiency was based on determination of RCC. It was verified that the combination of MWL and Fenton reaction degraded pesticide residues efficiently (>98%) in about 4 min [146].

Alternative systems that do not use a separate lamp are currently available in the market in the form of vials. They emit UV radiation directly into the solution contained in them when activated by microwave radiation. These flasks use the same principle of operation of MWL without electrodes, where the inside of the flasks contains mercury vapor that emit UV when excited by microwave radiation. They are mainly used for chemical synthesis. Otherwise, Sottoriva et al. used these 15 mL vials for the degradation of various colored reagents using hydrogen peroxide as an oxidant. All colors disappeared after reaction times of approximately 120 min [151].

Horikoshi et al. also exploited the phenomenon of activation of the lamp by microwave radiation and designed an on-line photo degradation system with microwave heating, where two UV lamps activated by microwave radiation were positioned around a quartz tube through which continuously flows and recycles the solution. Titanium dioxide was used as a catalyst for decomposition of rhodamine-B dye. A complete decomposition was obtained after 30 min of recycling. The system proved to be very robust and promising for effluent treatment [152].

2.5. On-line microwave digestion

The use of microwave radiation associated to flow injection manifold offers many advantages compared to off-line methods: it enables complete
automation, reduces expensive time delay between sample delivery and analyte measurement, protects the sample from contaminations caused by the laboratory environment, increases personal safety and reduces reagents consumption [153-154]. These systems usually involve the introduction of the sample in the slurry form. The slurry is digested as it passes through coil made out of a microwave-transparent material located inside the oven’s cavity. Finally, the digestate may be injected into a carrier stream, and then carried to the appropriate instrument for analysis [155]. Table 4 shows some representative procedures based on on-line microwave digestion.

This technique has some limitations associated with the formation of gas bubbles that lead to erratic flows and dispersion effects, which could impair measurement and with the presence of organic materials, which may compete with the reagent by the analyte. These problems may cause losses in sensitivities and as a consequence apparent low recoveries observed for high acid concentrations. Other drawbacks are the need for rigorous control for solid particles size in order to obtain reproducible sample suspensions and limitations in the amount of solid material that can be homogeneously suspended, making micro-constituents determination a difficult task [170]. Finally, the generation of gases during the digestion process increases the pressure inside the manifold and requires a hardware that can deal with relatively high pressures.

3. Conclusion

The microwave radiation energy allows expansion of laboratory capabilities in different applications. This technology is simple, safety, and easily applied to a wide range of chemicals such as acids, solvents, and different types of samples.

The use of microwave radiation was proven to be a feasible and recommendable alternative, reducing the volume and amounts of the reagents according to green chemistry principles.

Acknowledgements

The authors acknowledge the financial support provided by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, Grant 2006/59083-9). Grants from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Coordenação de Aperfeiçoamento de Nível Superior (CAPES) are also acknowledged.
### Table 4. On-line Microwave Digestion.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reagents and volumes</th>
<th>Analytes</th>
<th>Digestor apparatus</th>
<th>Instrumental Technique</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole blood</td>
<td>Triton X-100, HCl, HNO₃</td>
<td>Cu, Fe, Zn</td>
<td>Domestic microwave oven</td>
<td>FAAS</td>
<td>156</td>
</tr>
<tr>
<td>Solid Sample</td>
<td>HNO₃</td>
<td>Pb</td>
<td>Domestic microwave oven</td>
<td>FAAS</td>
<td>157</td>
</tr>
<tr>
<td>Water and urine</td>
<td>HCl, KBrO₃, NaBH₄, KBr, K₂S₂O₇, KMnO₄, H₂SO₄, HNO₃, K₃Cr₂O₇, NaOH</td>
<td>Hg</td>
<td>MX 350 (Prolabo Maxidigest)</td>
<td>FAAS, HG-AAS, FI-CV-AAS</td>
<td>158</td>
</tr>
<tr>
<td>Biological and environmental</td>
<td>HCl, KBrO₃, NaBH₄, KBr, HNO₃, (NH₄)₂SO₄, CH₃COOH, H₂SO₄, NaOH</td>
<td>As, Bi, Hg, Pb, Sb, Se, Sn, Te</td>
<td>MX 350 (Prolabo Maxidigest)</td>
<td>HG-AAS, CV-AAS</td>
<td>159</td>
</tr>
<tr>
<td>Urine and environmental</td>
<td>K₂S₂O₇, HCl, KBrO₃, NaBH₄, KBr, HNO₃, (NH₄)₂SO₄, CH₃COOH, H₂SO₄, NaOH, Tartaric acid</td>
<td>As, Bi, Hg, Pb, Sn, Te</td>
<td>Model 8507 (Panasonic) and Model 4782 Parr Microwave Acid Digestion Bomb</td>
<td>HG-AAS, CV-AAS</td>
<td>160</td>
</tr>
<tr>
<td>Bovine whole blood</td>
<td>K₂S₂O₇, HCl, KBrO₃, NaBH₄, KBr, HNO₃, NaOH, KMnO₄, Dow Corning DB 110 A : Si anti foaming agent, Triton X - 100</td>
<td>Hg</td>
<td>MX 350 (Prolabo Maxidigest)</td>
<td>FI-CV-AAS</td>
<td>161</td>
</tr>
<tr>
<td>Artichoke, dietary products, sewage sludge, certified tomato leaves</td>
<td>HNO₃, H₂O₂</td>
<td>Cu, Mn</td>
<td>Domestic microwave oven</td>
<td>FAAS</td>
<td>162</td>
</tr>
<tr>
<td>Bovine liver, orchard leaves, botanic standards</td>
<td>HNO₃, aqua regia</td>
<td>Al, Ba, Cd, Cu, Fe, Mg, Mn, Zn</td>
<td>Domestic microwave oven</td>
<td>ICP OES</td>
<td>163</td>
</tr>
</tbody>
</table>
Table 4. Continued

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reagents</th>
<th>Analytes</th>
<th>Digestor apparatus</th>
<th>Instrumental Technique</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mussel, chlorella, sargasso, pepperbrush, bovine liver</td>
<td>HNO₃</td>
<td>Fe, Ca, Mg, Zn</td>
<td>MDS81 (CEM)</td>
<td>FAAS</td>
<td>164</td>
</tr>
<tr>
<td>Horse kidney reference material, bituminous, powder pine needles, oyster tissue needles, oyster tissue</td>
<td>Triton X-100, HNO₃</td>
<td>Fe, Ca, Cd, Mg, Zn</td>
<td>MDS81 (CEM)</td>
<td>FAAS, ICP OES</td>
<td>165</td>
</tr>
<tr>
<td>Mussels, bovine liver, fish samples</td>
<td>HNO₃, H₂O₂</td>
<td>Co</td>
<td>Domestic microwave oven MW-1350 (CCE)</td>
<td>ETAAS</td>
<td>166</td>
</tr>
<tr>
<td>Oyster tissue, fish homogenate and mussel</td>
<td>HNO₃, aqua regia, ascorbic acid, phenanthroline</td>
<td>Fe</td>
<td>Domestic microwave oven MW-1350 (CCE)</td>
<td>UV-VIS</td>
<td>167</td>
</tr>
<tr>
<td>Biological fluid</td>
<td>HNO₃</td>
<td>Ca, Mg</td>
<td>Domestic microwave oven MW-34 (CCE)</td>
<td>FAAS</td>
<td>168</td>
</tr>
<tr>
<td>Geothermal fluid</td>
<td>H₂O₂, CCl₄</td>
<td>Fe</td>
<td>Domestic microwave oven</td>
<td>ETAAS</td>
<td>169</td>
</tr>
</tbody>
</table>

FI-CV-AAS: Flow injection - cold vapor atomic absorption spectrometry; UV-VIS: Ultraviolet visible spectrophotometry.
References

25. Nekrásov, B.V. 1940, Química General, Mir, Moscou, 560.
Microwave for greener strategies


157. Carbonell, V., De la Guardia, M., Salvador, A., Burguera, J.L., and Burguera, M.
*Talanta*, 40, 1609.