MICROWAVE RADIATION STRATEGIES TO GREENER ANALYTICAL CHEMISTRY: AN ALTERNATIVE FOR MINIMIZATION OF CHEMICAL WASTES AND ANALYTICAL THROUGHPUT*

Eveline A. Menezes[1,2*] (PG), Fernanda S. Chaves[1,2] (PG), Mario H. Gonzalez[1,3] (PG), Wladiana O. Matos[1,2] (PG), Gilberto B. Souza[1,3] (PG), Joaquim A. Nóbrega[2] (PQ), Ana Rita A. Nogueira[1] (PQ)

[1]Grupo de Análise Instrumental Aplicada, Embrapa Pecuária Sudeste, São Carlos SP, Brazil
[2]Departamento de Química, Universidade Federal de São Carlos, São Carlos SP, Brazil
[3]Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos SP, Brazil
evelineabreu@yahoo.com.br

Abstract

A key element of planning an experiment involves assessing the hazards and potential risks associated with the chemicals and laboratory operations to be performed (NRC, 1995). Thus, efforts have been carried out in order to reduce or eliminate the undesirable component of chemical activities: the production of toxic wastes. This has resulted in the development of greener, yet efficient, procedures on the bench or industrial scale. During the development of a new analytical procedure, the amount and toxicity of the produced wastes are as important as any other analytical feature and some work has been focused on the development of methods less harmful to humans and to the environment (Rocha *et al.*, 2001). Nowadays, analytical methods are well established for environmental monitoring. However, a paradoxical situation has emerged because most of the analytical methodologies employed to investigate environmental problems generate chemical wastes, resulting in an environmental impact. In some circumstances, the chemicals employed are even more toxic than the species being monitored (Anastas, 1999). However, new technologies combining minimization of residues and efficiency of analytical process are being developed.

The applicability of most methods of analysis depends on quantitative conversion of solids to homogeneous solutions. Conventional wet-sample preparation methods for the decomposition of solid samples are usually carried out in vessels containing the sample and a large volume of concentrated reagent(s), typically 15 to 100 ml. This mixture is heated for several hours using hot plates, heating mantles, or ovens. This type of open-vessels digestion has many drawbacks, such as the use of large volumes (and multiple additions) of reagents, potential for contamination of the sample by material and laboratory environment, and the exposure of the analyst and work area to corrosive fumes (Richter, 2003). To avoid these problems, new dedicated and more safety microwave ovens especially devoted to laboratory applications were developed, and sample preparations procedures using microwave radiation have been proposed. The number of publications increased significantly proving that microwave radiation can be used in different fields of chemistry, such as organic synthesis, organometallic compounds synthesis, inorganic compounds, and catalysis. The progresses in sample preparation field can be observed in a recent compilation (Gaia, 2006). Closed-vessel microwave decomposition has several unique characteristics that have led analysts to reduce the source of errors and contributions to the analytical blank that were previously obscured by

lengthy sample preparation procedures, and a drastic reduction in the analysis time and reagents consumption is verified (Richter, 2003). Microwave technology was also applied for developing focused microwave ovens. Although less frequently used comparatively to cavity-microwave ovens, there are many analytical procedures that can be better and safer implemented using focused systems, such as the digestion of large masses of samples (Nobrega *et al.*, 2002).

In this work, it will be presented some sample preparation procedures developed using microwave radiation, focusing the reduction of generation of residues, and also looking for improvements in the quality of results. The following procedures will be discussed: a) use of diluted acids as oxidant reagent. As an example, it was demonstrated that plant samples can be efficiently acid-digested in a closed-vessel microwave system with the use of diluted acid, producing less residues than when using concentrated nitric acid (Araujo *et al.*, 2002); b) use of vapor phase digestion in focused microwave – the single vessel approach was exploited (Nobrega *et al.*, 2002; Araujo *et al.*, 2000; Trevizan *et al.*, 2003); c) evaluation of the microwave radiation associated with photo (MW-UV) and photo-Fenton process for organic compound degradation (Gromboni *et al., in press*); d) alternative methods in nutritional laboratories, such as fiber determination in neutral and acid detergent (NDF and ADF), by using nylon bag technology (Nunes *et al.*, 2005); e) soil and plants dry matter determination by microwave radiation – the soil drying in greenhouse (method normally used) requires at least 12 h for complete dehydration, while only about 10 min is necessary by action of microwave radiation. For forage crops and silage samples, the drying time in greenhouse at 105ºC is about 12 h and at 65ºC, around 72 h; however, this process can be performed using microwave radiation in 14 min (Souza *et al.*, 2002); f) gradually adding sample aliquots to hot concentrated acid – this strategy decreases the amount of acid, and simultaneously increases the sample volume that can be digested (Nobrega *et al.*, 2002). Owing to the particular characteristic of microwave energy, it presents a great capacity for applications in different areas of chemistry. The control and repeatability of microwave digestions and separations reduce the operator dependency and improve analytical precision. The control of conditions reduces the number of artifacts generated by traditional methods, reducing analytical interferences and improving some traditional operations in chemistry (Kingston, 1997). Chemists are becoming increasingly aware of the versatility of this energy source. The use of microwave radiation in analytical methods has contributed to greener analytical chemistry, but there is a long road ahead and the potentialities have not been fully exploited, since only some 10% of the laboratories in the world are equipped with laboratory-designed microwave ovens (Collins, 2001). In a general point of view, it can be affirmed that microwave-assisted heating provides faster and safer decompositions compared to conventional heating. Otherwise, it is not a panacea for all energy needs in laboratories. Understanding how microwave energy can enhance chemical reactions or separations is important in deciding when and where it is the choice as the energy source.

References

Anastas, P.T. *Crit. Rev. Anal. Chem.*, 1999, 29, 167.

Araújo, G.C.L., Gonzalez, M.H., Ferreira, A.G., Nogueira, A.R.A., Nóbrega, J.A. *Spectrochim. Acta B*, 2002, 57 (12), 2121.

Araújo, G.C.L.; Nogueira, A.R.A.; Nóbrega, J.A. *Analyst*, 2000, 125(10)1861.

Collins, M. *X Annual Workshop on Practical Methods of Microwave Digestion for Trace Analysis*, Keynote Lecture, University of Massachusetts and University Research Institute for Analytical Chemistry, Amherst, USA, 2001.

GAIA – Grupo de Análise Instrumental Aplicada. *Procedimentos - Preparo de Amostras por Radiação Microondas*. CD-ROM; www.dq.ufscar.br/labs/gaia. 2006.

Gromboni, C.F.; Kamogawa, M.Y.; Ferreira, A.G.; Nóbrega, J.A.; Nogueira, A.R.A. J. Photochem. Photobiol. A: Chem., *in press*.

Kingston, H.M., Haswell, S.J., Eds., *Microwave-Enhanced Chemistry. Fundamentals, Sample Preparation and Applications.* American Chemical Society, Washington, 1997.

Nóbrega, J.A., Trevizan. L.C., Araújo, G.C.L., Nogueira, A.R.A., Spectrochim. Acta B, , 2002, 57, 1855.

NRC – *Prudents practices in the laboratory: handling and disposal of chemicals*. National Academy of Sciences, Washington, 1995.

Nunes, C. S.; Velasquez, P. A. T., Carrilho, E. N. M.; Souza, G. B.; Nogueira, A. R. A.; Oliveira, S. G.; Berhielli, T. T. *Anais 42ª Reunião Anual da SBZ*, 2005.

Richter, R., *Clean Chemistry. Techniques for the Modern Laboratory*. Milestone Press, Monroe, 2003.

Rocha, F.R.P., Nóbrega, J.A., Fatibello-Filho, O., *Green Chem.*, 2001, 3, 216.

Souza, G. B.; Nogueira, A. R. A.; Rassini J. B. *Determinação de matéria seca e umidade em solos e plantas com forno de microondas doméstico*. Embrapa, São Carlos 2002.

Trevizan, L.C.; Nogueira, A.R.A.; Nobrega, J.A. *Talanta*, 2003, 61, 81.

*FAPESP, CNPq.