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CONSIDERATIONS ON MICROWAVE-ASSISTED DIGESTION: TOWARDS A CONCEPTUAL MODEL

TRAIAN GAVRILOAIEI[1]

[1]University ”Al. I. Cuza” Iaşi, Faculty of Geography Geology, Department of Geology,
Bd. Carol I, no 20A, 700505 Iaşi, Romania

Abstract

A wide range of information is now available on the microwave digestion of different samples, from food products or human hair to rock or plant samples. The external environmental conditions and the sample characteristics determine the work conditions for chemical digestion. A preliminary conceptual model can be drawn, which relates the sample nature to the working conditions, in order to be applicable at a range of materials. The further research needs carrying out an extension of this method for high values of temperature or pressure.

Sample digestion plays an essential role in almost all analytical processes, but is not recognized as an important step in analytical chemistry. In the last period, it is recognize the importance of the sample digestion (wet/dry digestion or decomposition) for the obtaining of high-quality analytical and valid results. The operation is the source of any potential errors: contaminants from the vessels, impurities from the chemical reagents etc. The aim of this paper it is not to discuss or to avoid the systematic errors which appears during the sample digestion in the laboratory. The paper wish to be a pertinent review for a topic analytical technique, namely microwave digestion, like a rapid and productive wet-digestion analysis.

Keywords: wet digestion, sample preparation, microwave digestion, analytical technique

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[1] e-mail: tgavrilo@uaic.ro

Introduction

The classical samples digestion is the critical step of any chemical analysis, and involves procedures for partial or total digestion. The wet digestion method is used for solid and liquid sample pre-treatment and include wet descomposion and dissolution of the organic and inorganic samples, in open and closed systems, using thermal and microwave energy.

The goal of any digestion procedure is to realise a complet decomposition of a solid matrix, without any losses or contamination of the sample. After Majors, 2003 the time necessary for a sample chemical analysis is more than 60% from the total time of working, meaning from the sampling moment, until to the results interpretation are done, for any sample (fig. 1). In this context, wet chemical digestions are carried out using various minerals acids, hydrogen peroxide or other reagents, either in open system (under atmospheric pressure), or in closed vessels (under high temperature or pressure).

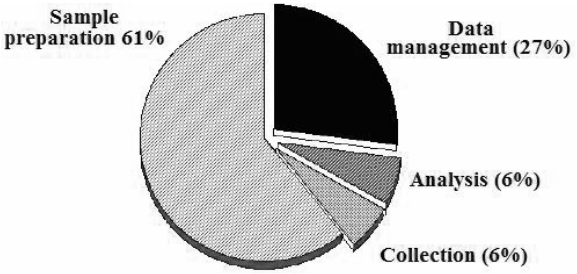

Fig. 1 Distribution of time for analytical chemist spend on sample analysis (Majors, 2003)

Wet digestion

Wet digestion with acids (oxidising or not) is the simply way in chemical analysis of geological samples. Many of the sample preparation methods are used before 1900. In 1831, Berzelius used the conversion of silica into volatile compound, SiF_4 by reaction with fluorhidric acid, in platinum crucibles. In the same period, the basic principles of gravimetry analysis for many elements were established, even for organic materials. The appearance of *aqua regia* (the mixture of concentrated nitric acid and concentrated hydrocloric acid, usually in a volumetric ratio of 1:3) represented a large progress in wet chemical analysis of rocks (Chen and Ma, 2001). Numerous mix solutions of mineral acids were used in wet chemical analysis and some of these are listed in the literature (Harris, 1998, Gavriloaiei, 2007). Concentrated nitric acid in closed system under high temperature was used since 1894 by Carius; after that, Kjeldahl, 1883 used sulphuric acid to digest organic matter (after Matusiewicz, 2003). Later, hydrogen peroxide was introduced by Classen and Bauer in 1884 for organic matter, and $HClO_4$ was used by Stcherbak in 1893 at elevated temparature, with very good results for digestion of silicate minerals. The utilization of mixture oxidizing agents is a relatively new procedure of desintegration. The first mixture was used by Van Slyke (H_2SO_4+H_3PO_4+KIO_3+$K_2Cr_2O_7$) in 1954, for wet carbon combustion and, after that, Polley and Miller, in 1955 show that a mixture of H_2O_2 and H_2SO_4 (conc.) is the most powerful oxidizing agent for the determination of mercury in biological and mineral materials. The appeareance of HO radical resulted from hydrogen peroxide in wet analysis led to a new tehchnique for biological samples, at temperature below 110^0C (after Matusiewicz, 2003).

In the last forty years, the interest for digestion procedures is evident for wet digestion methods and numerous papers are dedicated to this subject. Also, the other procedures are involve, such as chemical extraction, chemical leaching, acid-base solubilization, enzymatic or thermal decomposition.

In the literature there are some terms used for this procedure: the term of *decomposition* involve organic materials, while the term of *dissolution* involve inorganic materials. Other similar terms are *mineralization*, *digestion* (with derivatives *acid-digestion*, *alkaly-digestion*, *wet-digestion*, *dry-digestion*), *ashing* or *destruction* which are used specially, for rocks or plants chemical analysis. The chemists used the term of *dissolution* and rarely, in French literature is used the term of *désagrégation*. In this paper, the general term will be *digestion*, which is specified for wet chemical analysis of rocks and it is recommended by the International Union of Pure and Applied Chemistry (IUPAC). *Dissolution* is defined as a chemical attack for a sample dissolving in a suitable reagents (especially water), at relatively low temperature. The term of *decomposition* denotes a complex process that can involve a lot of factors and activities for the analyst and represents the oldest procedure and frequently used procedure for various sample matrices (Jeffery, 1983).

The classical procedures for rock samples digestion are time-consuming operations and involve the convertion of the solid-state into the liquid-state sample, for futher analysis. All the laboratory digestions involve numerous procedures, which several times are imprecise and introduce impurities of the analyzed solutions. To convert the solid state to liquide state, these kinds of procedures need energy (heat) and numerous chemical reagents. The amount of reagents used is dictated by the sample size and nature, which in turn, depends on the sensitivity of the analytic method. The digestion of the sample is often the most important step in chemical analysis, which can influence the further results. However, the solubilising process of any solid sample is considered to introduce the allmost all contaminants in the solution. The majority of procedures involve the use of a single or some combinations of oxidizing acids, hot or at room temperature, diluted or concentrated acids (HCl, H_2SO_4, HNO_3, $HClO_4$, HF, H_2O_2 etc.) (Jeffery, 1983, Gavriloaiei, 2007). Commonly digestion agents used in classical technique include nitric acid, hydrocloric acid, sulphuric acid, perchloric acid or mixture of these. The main properties of the common mineral acids used in the digestion operations are given in table 1.

All of these compunds are corrosive (even at room temperature) and should be handled with caution. Wet digestion has the advantage to be used for both inorganic and organic samples (rocks, plants, sediments, steel, ceramics etc.) and follow either to destroy/to remove the sample matrix or to reduce/to eliminate interferences.

Tab. 1 Some mineral acids used in digestion of mineral samples (Harris, 1998, Jeffery, 1983, Gavriloaiei, 2007)

Mineral acid	Physical properties	Some applications in chemical analysis
HCl	37% (12 M), 1.19 g·mL^{-1}	Non-oxidant acid, used for most metals solubilzation, metal oxides, carbonates and phosphates.
HNO_3	68% (16 M), 1.42 g·mL^{-1}	Oxidant acid, universal digestion reagent used for organic matter descomposition, metal sulphides, arsenides, selenites, telurites, silicates.
H_2SO_4	95-98% (18 M), 1.84 g·mL^{-1}	Oxidant acid, used for metal solubilization and organic matter digestion, good dehidratated agent.
H_3PO_4	85% (15 M), 1.70 g·mL^{-1}	Hot acid solves ceramics and refractory materials, unsoluble in other acids. It is used beside oxidant acids (HNO_3, H_2SO_4, $HClO_4$).
HF	50% (29 M), 1.16 g·mL^{-1}	Specially used for silica volatilization, like SiF_4, beside H_2SO_4 or in mixture with oxidants acid, (HNO_3, $HClO_4$); in exces, HF is evaporated with hot H_2SO_4, $HClO_4$.
$HClO_4$	60-72%, 1.54-1,67 g·mL^{-1}	In concentrated solution, $HClO_4$ is an extremly oxidant acid used (where the other acid give not precious results) to ceramics and refractory materials, numerous silicates, sulphates, sands, soils. $HClO_4$ is efficiently for insolubilized silica.
HBr	48-65%	Similar properties with HCl concerning the solubilizing abilities.
H_2O_2	30% (10 M) 1.12 g·mL^{-1}	Good oxidative properties, usual in conjunction with other mineral acids

Consequence, nitric acid and hydrocloric acid are the most widely used digestion reagents (with oxidant or non-oxidant properties, single or in mixture), for mineral or organic samples, since it does not interfere with the components determinations. Perchloric acid is efficiently for mineral samples and is forbiden to use it to organic matter. Sulphuric acid may interfere with the determination of stable compounds. Mixtures of two or more acids are generally used for samples containing inorganic matrices and mixtures with hydrofluoric acid are used to evaporate insoluble silicates. The wet digestion methods involve a strong chemical attack on the samples structure and special conditions of working in the laboratories. Additionally, most of them are conducted under strictly conditions, concerning temperature, crucibles, types of flasks, reagents etc. The suitability of materials may be estimated according to some criteria: heat resistance and conductance, hardness and resistance to chemical attack of acids or basis, surface properties, whereby the specific characteristics of working samples. All the instruments that are used for wet digestion procedures must be efficiently cleaned and tested for possible contamination. Detailed discussion of the main materials used in wet digestion is presented elsewhere (Harris, 1998, Matusiewicz, 2003). Most applications of wet digestion involve samples of rocks or sediments, also waters or waste waters, biological samples, plants or food samples, steels or ceramics samples, sands or coal samples etc. (Kucak and Blanusa, 1998, Doyle et al., 2004, Capar et al., 2007).

Discussions

The wet digestion in open systems is one of the oldest and common techniques for dissolution of inorganic/organic materials used in chemical analysis. This technique is a routine analysis because it can be automated; the working parameters (time, temperature, chemical reagents) can be modified function on the samples nature and on the analytical goal. The wet digestion comparable with the dry digestion has the speed advantage and it use low maximum digestion temparature (the temperature must not exceed the ambient-pressure boiling point of the digestion acid). On the other hand, the wet digestion methods present the risk of sample contamination through unknown compounds or losses of small parts of the samples. Usually, to keep a low level of losses the analyst must work in excess of reagents (specially acids for digestion) or with a low temperature beside an extension time for solubilization.

Microwave digestion system

One of the modern and innovative source of energy is microwaves, because the heating takes place inside the digestion mixture. The technique is more efficient than the classical digestion with conventional heating and it increase the speed of the operation. For microwave digestion there are some terms which describe the process, namely ***pressure digestion***, ***microwaves (acid)digestion***, ***microwaves descomposition***. Using the microwaves implied a special terminology for the process, usual for acid attack on the sample, ***microwaves digestion*** being the ordinar name. Abu-Samra et al., 1975 (after Matusiewicz, 2003) were the first scientifics who mentioned the application of microwaves to wet digestion for biological samples. The method was developed for numerous kinds of samples, such as geological, biological, clinical, food, environmental, sludge, coal and ash, metallic and synthetic materials (Doyle et al., 2004, Capar et al., 2007). Microwave digestion in open system at normal pressure is applicable for strictly objectives, and the results are reproductible for similar working parameters. Organic materials are generally descomposed into carbon dioxide with oxidizing acids, specially nitric acid or hydrogen peroxide. Before the oxidation attack, the materials are dehydrates with sulphuric acid, but the process needs caution because either the products can be explozive or the reactions can be exothermic. The procedures for this kind of samples must be slowly heated, in contrast with the inorganic materials which need higher temperatures.

A compact instrument in which the sample is irradiated with microwaves has been developed and consequently, the interest for this method has been increased. Close system for wet sample preparation presents the advantage that the analyst is not involve in sample preparation during the digestion; the operation is performed under the synergistic effects of temperature and pressure. The microwave digestion in close system is more efficient than the open system digestion, because the loss of volatile elements are strictly controlled and the digestion of difficult minerals are possible. To decrease the losses problems at high temparature, it was introduce the HPA-Knapp (high-pressure ashing) technique, which reduce the digestion time and also, increase the efficiency of solubilization for resistant materials (Knapp, 1985). In the last decades, numerous practical informations and papers have been obtained and the geochemists consider that for trace elements, the microwave digestion is the most suitable procedure. Because of automatization, the new microwave digestion instruments are able to process 10 to 12 samples in the same time, which permit a rapid manipulation of the solution formed after the heating. Dissolution can be accelerated by mixing the reagents with the samples., through the special stirring bar.

Microwave Digestion System, md 7295 (O-I Analytical) (fig. 2) is a versatile, timesaving instrument in order to prepare the samples for chemical analysis by instrumental methods (AAS, ICP, ICP-MS etc.). It can reduce sample preparation time by more than 90% comparable with the classical chemical analysis throught digestion.

Fig. 2 Front view of microwave digestor system

The system´s design increases the operator safety, instrument reliability and ease-of-mentenance. Safety components incorporated into the system include an acid-resistant oven, exhaust module, pressure control system (with programmable pressure setting and a fail-safe default system), the finest in precise fiber-optic temperature measurement and analytical microwave vessels. Patent-pending high pressure vessels have all the benefits for standard vessels and even more. They have been designed for maximum safety by incorporating a dual pressure relief mechanism that employs a safety rupture membrane for over pressure venting at 600 psi and a breakaway safety disk for rapid pressure relief at aprox. 1000 psi.

In principle, microwave energy heats the sample and the microwave-absorbing reagents contained inside the crucibles. These crucibles are microwave-transparent, closed and pressurized to achieve a higher temperature necessary for digestion. All the systems which are used for applications can be monitored for pressure and temperature from inside the vessels and the informations are used to determine the amount of microwave energy applied for the sample. With additional vessel modules, multiple sample can be prepared for digestion. The instrument was designed to work with batch runs, with the most reactive sample placed in the control vessel. Soil sample-type should be analysed together and not mixed with water or biological solutions. If necessary, these samples should be digested in their own run. The pressure and temperature control system include 10 steps of operations points, with system programming capabilities from 0 psig (0 Bar) to 600 psig (40.8 Bar) or more. Low pressure digestion (< 20 bar) is limited to *ca.* 180^0C, whereas the high presure digestion (> 20 bar) may exceed 300^0C. Microwave digestion vessels present dual wall construction for maximum thermal stability and minimal heat lost. In order to build-up a safety device, the outer vessel tube is transparent and moulded from polythermal chemically-resistant resin. The inner tube from PFA Teflon is acid resistant and microwave transparent, with a special construction to avoid the rinsing back of acid solutions. The safety membrane covers completely the inner tube and maintains the samples in a contamination-free environment, isolated from all other components of the system. The cleaning operation is simply and eliminates the risk of unknown contamination. The vessels design provides an easy setup and safety working conditions.

For total chemical analysis, there are some methods microwave assisted acid digestion, which utilizes volumes of sample and concentrated acids, in different rates depending on the nature of samples (Pruseth et al., 2005). Utilization of beakers, watch glasses and proper cleaning steps are completely eliminated thereby saving labour costs. The Teflon digestion vessels used in this procedure are reusable and the clean-up step is relatively easy and less time consuming.

The main methods used for microwave digestion for organic or inorganic samples have beed studied in many papers. A brief summary of these techniques for different matrices, (in open or closed systems, ordinary or microwaves digestion) is presented in table 2. In table 3 some advantages/disadvantages of the method are presented.

Tab. 2 Applications of wet digestion procedures for chemical analysis (Matusiewicz, 2003, Pruseth et al., 2005)

Material sample	Reagents for digestion	Digestion technique
Water(s)	HNO_3, H_2O_2, HCl	Open system, UV radiation
Coal	HNO_3, HF, HCl	Open and close system
Coal fly ash	*Aqua regia* + HF	Open and close system
Dust	*Aqua regia* + HF	Open and closed system
Catalysts	*Aqua regia*	Open system
Sewage sludge	HNO_3, HCl	Open and closed system
Waste waters	HNO_3	Flow system
Plants	HNO_3+ H_2O_2+ HF	Open and closed system
Clinical	HNO_3	Open and closed system
Marine	HNO_3	Open and closed system
Forensic	HNO_3	Open and closed system
Food(s)	HNO_3	Open and closed system
Drink(s)	HNO_3, H_2O_2	Open and closed system
Soils	*Aqua regia* + HF	Open and/or closed systems
Sediments	*Aqua regia* + HF	Open and/or closed systems
Rocks	*Aqua regia* + HF, H_2SO_4, $HClO_4$	Open and closed systems
Ores	*Aqua regia* + HF, H_2SO_4, $HClO_4$	Open and closed systems
Minerals	HF+H_2SO_4, HCl	Open and closed systems
Glasses	HF	Open system
Fuels	HNO_3+ HCl	Open and closed system
Oils	HNO_3+ HCl	Open system
Drugs and pharmaceuticals	HCl, HNO_3	Open system
Ferrous metals	HNO_3+(HF/HNO_3/H_2SO_4)	Open systems
Non-ferrous metals	HCl/HNO_3/HF	Open system
Alloys	*Aqua regia* + HF	Open system
Steels	HCl+HNO_3, $HClO_4$	Open system
Polymers	HCl, HNO_3, HF, H_2SO_4	Open or closed systems
Ceramics	HCl, HNO_3, HF, H_2SO_4, H_2O_2	Open or closed systems
Composites	HCl, HNO_3, HF, H_2SO_4, H_2O_2	Open or closed systems
Nuclear materials	HNO_3 or HCl, H_3PO_4, $HClO_4$	Open or closed systems

Materials for microwave digestion

Most vessels (crucibles) used in microwave digestion are constructed from PTFE-, PFA- or FEP-polymers, although quartz, ”*glassy carbon*” or hard-plastic vessels are available for some purposes. The quartz vessel or *glassy carbon* vessel is stabilized during the digestion process under strictly control of pressure. Some physical properties of synthetic materials used in chemical applications are given in table 4. Only materials which are totally chemically inert (with respect to mineral acid or reagents) may be used in vessels contruction of microwave digestion.

Tab. 3 Comparative table for open and closed system digestion (Majors, 2003)

Open system digestion	Closed system digestion
Max. temperature is limited by the solution´ boiling point	Max. temperature is 200-260^{0}C or more
Large amount of samples in use	Small amount of samples in use
High acid consumption	Reduced acid consumption
The digestion quality frequently unsatisfactory	High digestion quality
Contamination and errors risks	Low risk of contamination
Digestion time: 2-15 hours	Digestion time: 20 to 60 min.
Loss of volatile compounds (e.g., Hg, S, Pb salts)	No loss of volatile compounds

Tab. 4 Some materials used for the construction of microwave digestion instruments (Gavriloaiei, 2007)

Polymer reference	Chemical name	Properties			
		mechanical	thermal	electrical	chemical
PTFE	Polytetrafluoro-ethylene	Good stability, high rate of creep	Excellent (-180 to 260^{0}C)	Excellent	Excellent
FEP	Fluoroethylene-propylene	Good stability, high rate of creep	Excellent (-190 to 205^{0}C)	Better	Excellent
PFA	Perfluoroalkoxy	Better, high rate of creep, low resistance to abrasion	Excellent (-150 to 260^{0}C)	Better	Excellent
ETFE	Ethylene-tetrafluoroethylene coplymer	Excellent, high tensile strenght	Better (-100 to 150^{0}C)	Excellent	Good
ECTFE	Ethylene-chloro-trifluoroethylene	Exccellent abrasion resistance	Better (max use at 150^{0}C)	Excellent	Excellent
PCTFE	Polychloro-trifluoroethlylene	Excellent low creep	Better (-250 to 150^{0}C)	Good	Excellent

Chemically speaking, PTFE is *polytetrafluoroethene* or *polytetrafluoroethylene* polymer and represents a synthetic fluoro-compound, with numerous apllications. Liquid solutions did not wet the wall of PTFE and do to this property it is used as a non-stick coating of numerous cookware. It presents a remarcable non-reactivity to corrosive chemicals. PTFE was accidentally found in 1938 by Roy Plunkett and was registred under Teflon name. After 1950, Teflon was commerciallized for domestic activities, but further it was used like scientific ustensiles in chemist laboratories.

Nonadays, there are numerous digestion instruments companies, which produce these ”*digestion bombs*”. The most popular company is *Parr Instruments Co., USA*, followed by *Uniseal Decomposition Vessels LTD., Israel* or *Berghof Laborprodukte GmbH, Germany* (for stainless-steel pressure vessles with Teflon inserts) or *CAL Laborgeräte GmbH, Germany* (for pressure digestion systems). A safelty system of wet digestion under high temperature and pressure was developed by Knapp is available now, by HPA-S High Pressure Asher System (Anton PAAR AmbH, Austria) (Knapp, 1985).

The advantage of closed-system digestion comparable with the open-system digestion, lies in the significantly higher working temperatures which can be achieved. If temperatures in open system are limited by boilling pointing of the acid solution, in closed digestion system usually, the temperature can reached the range of 200-260^{0}C. For the main material (food, plastics, minerals, tissue and water), the time digestion it lasted from 2 to 10-12 hours (fig. 3), while the time for microwave digestion it extended less 1 hour, so it is clear that temperature and pressure represent the most significant working parameters. The analytic results for open system digestion are less than real values, for volatile compounds, while for closed system digestion the results are closed to real values.

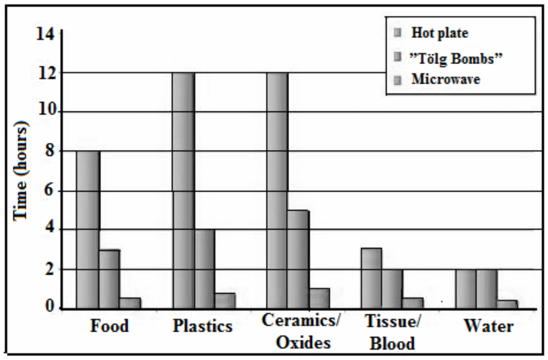

Fig. 3 Times typically required for digestion operations (*www.berghof-instruments.de*)

The microwave digestion of rock samples has some advantages comparable with classical digestion technique. Among these, the most obvious is that the microwave system did not allow loss of the samples through evaporation when the samples are digested in closed Teflon vessels. The second advantage is the more efficient dissolution achieved due to increased vapour pressure in a relative small time and volume. In the last period, the interest for wet method digestion is increased and this paper tray to give an overview of the development and applications for chemical analysis.

Conclusions

Sample preparation is a critical step in trace chemical analysis. A classical digestion method required hours to days of working to ensure complet destruction of ores samples. Microwave heating is a relatively new technique and a widely used laboratory method. The microwave digestion method represents one of the best solutions for rocks or minerals solubilization in chemical analysis. As a result of direct absorption of microwave energy, the technique involve a rapid and safety heating comparable with other techniques. Differences in working conditions between ordinary conditions and microwaves conditions should be examinated before energy is applied to any sample or reagent.

The closed vessel digestion have numerous advantages comparable with the open vessel system, but there is one disavantage, namely the expensive vessel for working. The vessels used for laboratory applications are either low-pressure or high-pressure bombs. The working conditions are enlarge until 260^0C (softening point of Teflon) for temperature and until 100 bar for pressure. Closed vessel techniques use the same reagents for digestion like the open vessel technique (specially, mineral acids). The procedure prevent the losses of volatile components during digestion and reduce semnificantly the working time.

From this discussion, it is clear that microwave acid digestion is more efficient than the open system digestion and have a large applicability (from non-metallic to minerals materials). Consequently, the analytic results for open system digestion are less than real values (specialy for volatile compounds), while for closed system digestion the results are closed to real values. The actual systems of microwaves digestion are equipped with different sensors to monitor the pressure and temperature digestion (like reaction parameters), as well as to allow the microwave power to be controlled on the basis of readings returned by these systems.

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