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Short communication

Influence of microwave heating on fluoride, chloride, nitrate and sulfate concentrations in water

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ABSTRACT

This paper describes a study about the influence of microwave radiation using closed vessels on fluoride, chloride, nitrate and sulfate concentrations in aqueous media. The experiments were processed by heating water using PFA vessels and a microwave cavity oven, determining the anions by ion chromatography. The influence of the exposure time, the atmospheric composition, the kind of heating (water bath or microwave radiation) and the possible formation of hydrogen peroxide were investigated. The limits of quantification for fluoride, chloride, nitrate and sulfate were respectively of 0.17, 0.15, 0.55 and 0.57 $\mu g\,L^{-1}$, and precision, expressed as RSD, was <4% for all considered anions. The hydrogen peroxide was quantified by spectrophotometry, and the limit of quantification and precision were 24 $\mu g\,L^{-1}$ and <5% ($n = 10$), respectively. The results demonstrate a significant increase in the anion concentration levels (between 63 and 89%) when microwave heating was used in comparison with heating by water bath. In addition, these changes observed can be mainly attributed to the species transfers, either between gaseous (atmospheric gases) and liquid (water) phases for nitrate, or between vessels walls and water for fluoride, chloride and sulfate. Additionally, hydrogen peroxide concentration higher than 45 $\mu g\,L^{-1}$ was determined when water was exposed to microwave radiation.

1. Introduction

The application of microwave energy as a heating source started in the 1950s, when microwave ovens were widely adopted in the kitchen. Since then, they have been taken seriously in chemistry laboratories [1], with different applications being proposed, such as sample decomposition [2–6], extraction [7–10], and synthesis [11–13], among others. The increase in popularity of microwave ovens for laboratory purposes is due to the reduced time consumed for carrying out chemical reactions, accurate control of time, power and/or temperature, the evolution of new materials, the development of new designs of vessels, and the implementation of different feedback systems, improving the safety of these devises [1].

The theory of microwave heating is well established, and both dipole rotation (intermolecular friction) and ionic conduction [14] explains some advantages of microwave heating in contrast to conductive heating. It is well known that microwaves heat all of the sample fluid simultaneously without heating the vessel, and the solution reaches its boiling point quickly. Since the rate of heating is high, substantial localized superheating can occur [14]. When closed-vessels are used the heating helps increase the pressure inside the vessel, and vice versa. This process allows an increase of the boiling point of the reagents, which has important kinetic and thermodynamic implications [15].

Although microwave radiation is non-absorbed by the gaseous phase present inside the vessels, this phase can play an important role in oxidation processes, such as the regeneration of nitric acid by recombination of NO_x and water vapor inside the vessels [16–18]. Recently, Bizzi et al. [19] demonstrated the importance of the gaseous phase for sample decomposition, with the vessels being pressurized with oxygen (from 0.5 to 2 MPa). At higher oxygen pressures, higher amounts of sample mass as well as lower acid

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volumes were attained when compared to not adding oxygen to the vessels.

In this way, as different mechanisms are involved in microwave heating as commonly achieved when considering convection heating, the gaseous phase as well as some impurities present in the vessels can indirectly influence environment of the solutions contained inside the vessels. It is to suppose that some modifications can occur in the solution after submitting the liquid phase to microwave heating. Then, this work evaluated the influence of microwave radiation on the heating of ultra-pure water (used as proof-of-concept) in terms of the variations in the fluoride, chloride, nitrate and sulfate concentrations as well as it compares the heating being produced by microwave or water-bath.

2. Experimental

2.1. Instrumentation

A Milestone Start E microwave oven (Sorisole, Italy) equipped with an ATC-400-CE automatic temperature control device was employed for sample heating.

The determination of the inorganic anions was performed using the "MIC-2 Advanced" modular Ion Chromatography system (Metrohm AG, Herisau, Switzerland), which comprises a serial double-piston high-pressure pumping unit, a two-channel peristaltic pump for use with the Metrohm Suppressor Module (MSM), a separation center, a conductivity detector and an interface to connect with a computer. Ion chromatograms were recorded using the Metrohm IC Net 2.3 software.

The spectrophotometric system for hydrogen peroxide determination was comprised of a three-piece injector commutator, an Ismatec peristaltic pump (Ismatec IPC-12, Glattzbrugg, Switzerland), and a Femto spectrophotometer, model 482 (São Paulo, Brazil) equipped with a 1-cm optical pass flow cell. Teflon® tubes (0.8 mm i.d.) were used as transmission lines, with Tygon® and Viton® tubes being used for propelling sample and reagent solutions.

For water pH measurements a Digimed DM20 pH-meter (São Paulo, Brazil) was used and the samples were maintained at 25 °C.

2.2. Reagents and solutions

All the glassware and flasks were kept in ultra-pure water during 2 h with posterior cleaning (3-times) with ultra-pure water. The solutions used for building the analytical calibration curves were prepared with analytical grade chemicals (NaF, NaCl, $NaNO_3$ and Na_2SO_4) from Merck (Darmstadt, Germany), and ultra-pure water (>18.2 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, Bedford, USA). It is important to mention that all microwave vessels used (built in perfluoroalkoxy) were new ones in order to avoid contamination problems. The procedure for their initial utilization was that recommended by the manufacturer.

2.3. Influence of microwave heating time on the anion concentrations and pH of water

The experiment was carried out by weighing 20 g of Milli-Q water to the PFA (perfluoroalkoxy) vessel, with the water mass being submitted to different microwave heating intervals (2, 8 and 16 min). The power and temperature were fixed at 1000 W and 120 °C, respectively. Afterward, the vessels were cooled at room temperature and the concentrations of fluoride, chloride, nitrate, and sulfate were determined by ion chromatography. For each new experiment, the flask was washed and a new aliquot of water was weighted.

The chromatographic system for fluoride, chloride, nitrate and sulfate determinations was run in the isocratic mode with the column operated at room temperature. The assays were carried out with a Metrohm Metrosep A Supp 5 analytical column (150 mm × 4.0 mm i.d., particle size of 5 μm, polyvinyl alcohol packing material functionalized with quaternary ammonium groups), using a mixed solution of sodium carbonate and bicarbonate at 3.2 and 1.0 mmol L^{-1}, respectively, as mobile phase, according to the manufacturer. The water temperature was at 25 °C for sample introduction.

2.4. Determination of anions and hydrogen peroxide in water

The determination of hydrogen peroxide produced in the radiated water was indirectly carried out in a spectrophotometric flow injection system adapted from Pereira-Filho et al. [20], based on the kinetic reaction between Tiron (4,5-dihydroxy-1,3-benzene disulfonic acid) and hydrogen peroxide, catalyzed by cobalt. Briefly, the reagent solution was formed by a mixture of 10 μg L^{-1} Co(II), 1 mol L^{-1} NaOH and 0.5 μmol L^{-1} Tiron aqueous solutions, each one pumped at 0.5 mL min^{-1} toward to a confluence point, where the reagent zone was mixed with the carrier solution (0.014 mol L^{-1} HNO_3), which was pumped at 1 mL min^{-1}. A sample loop of 100 μL was used to insert the standard/sample aliquots into the analytical path and a reaction coil of 100 cm was used before of the detector (426 nm) to improve sensitivity.

2.5. Digestion of PFA vessel using microwave-induced combustion

Focused microwave-induced combustion was used to decompose a whole cap of a Teflon vessel. The experimental conditions were similar to that proposed by Flores et al. [21].

3. Results and discussions

3.1. Figures of merit

The method for fluoride, chloride, nitrate and sulfate determinations in water by ion chromatography presented a linear range from 30 to 300 μg L^{-1} ($r > 0.999$; $n = 5$). Limits of quantification for fluoride, chloride, nitrate and sulfate were, respectively, 0.17, 0.15, 0.55 and 0.57 μg L^{-1}, and obtained in accordance to IUPAC recommendations [22]. The precision, expressed as RSD, was <4% for all considered anions. The adapted method for indirect spectrophotometric determination of hydrogen peroxide presented a linear concentration range from 24 to 1000 μg L^{-1} ($r > 0.998$; $n = 5$). A limit of quantification (in accordance to IUPAC recommendations [22]) and the precision (as RSD) were 24 μg L^{-1} and <5% ($n = 10$), respectively.

3.2. Influence of microwave heating time on the anion concentration and the pH of water

The results are presented in Fig. 1, which shows an increase in the ion concentrations by increasing the microwave heating time interval. This behavior is observed for all the evaluated species when the microwave radiation was increased from 2 to 8 min. For intervals larger than 8 min, there was a similar behavior for chloride, nitrate and sulfate, with decreases in their concentrations. Probably, the long time of microwave heating increases the temperature of vessel wall by convection, decreasing the condensation processes and consequently the concentration of these species in the solution. It is important to comment that fluoride, nitrate and sulfate were not detected when the water aliquot was not heating.

According to the pH of water, an initial value of 7.2 (without microwave heating) was measured. However, after 2, 8 and 16 min

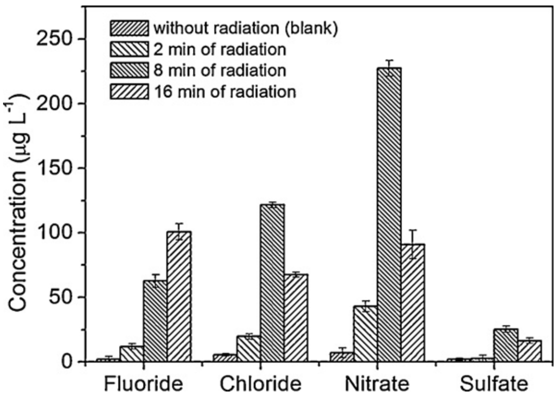

Fig. 1. Influence of microwave irradiation time on the increase of anion concentrations in water.

of microwave radiation, new values were respectively attained as 7.1, 6.6, and 5.9, showing progressive decreases from the initial one. It is important to emphasize that, as far as possible, the water used in these studies was not exposure to the atmosphere avoiding modification in the pH. Thus, the flasks were kept capped during cooling until room temperature and the pH was measured immediately after water collection (for unheated samples), and immediately after cooling and opening the flasks (for heated samples). The decrease of pH can probably be explained due to carbon dioxide incorporation (from the gas phase present in the upper region of the vessels) by the combination with the water vapor produced inside the vessel when the liquid is heated by microwave energy. All these results are interesting, since they show a different behavior of the ions in the water under the influence of the microwave radiation. This fact becomes important when microwave heating is used for sample preparation procedures, mainly that addressed for fluoride, chloride, nitrate and sulfate determination. Frequently, these species are determined in river water or in food samples, after sample preparation by digestion using microwave heating.

3.3. *Influence of air or argon atmosphere on anion concentrations present in water after microwave heating*

To understand the results previously obtained under different microwave heating conditions, two hypotheses were formulated:

(1) Anionic species are produced from the equilibrium between gas and liquid phases;
(2) The ions in the final solution are proceeding from a solid (PFA flask material).

The first hypothesis was investigated by appraising the anion concentrations after heating of water, with air or argon being the gaseous phase inside the vessels. For this purpose, the same procedure as presented in the previous section was carried out, with argon being bubbled (*ca.* 0.5 L min^{-1}) into the water during 5 min, and the vessel under argon atmosphere quickly closed. The results are presented in Fig. 2, and a decrease in anion concentrations in water can be verified when Figs. 1 and 2 are compared. The results shown in Fig. 1 were obtained with air atmospheres, indicating that the atmosphere inside the vessels plays an important role on the final concentration of fluoride, chloride, nitrate and sulfate in water.

With 8 min of microwave heating, an interesting behavior can be pointed out. Decreases on *ca.* 42, 83 and 50% were detected related to the chloride, nitrate and sulfate species, respectively, while fluoride concentrations remains almost the same when considering the heating carried out under air or argon atmospheres. These results can indicate different origins of the anions. The major differences in the concentrations are for nitrate (83%), which can be correlated to the oxygen and nitrogen contributions from the air atmosphere over the water. However, the concentrations of fluoride, sulfate and chloride are not so influenced by the atmosphere, indicating that these ions are probably lixiviated from the vessels walls.

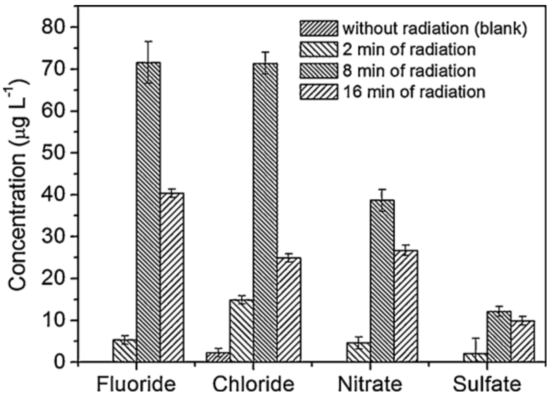

Fig. 2. Influence of microwave radiation interval on the increase of anion concentrations in water bubbled with argon during 5 min.

Gases such as N_2 (78%), O_2 (20%) and CO_2 (0.04%) are present at higher concentrations in the air atmosphere, while SO_2, SO_3 and Cl_2, among others [23], are present at trace levels. When taking chlorine as an example, this is present in air at *ca.* 0.001 mg L^{-1} [24] and, considering the gaseous volume of the vessel as 130 mL, the chlorine present in the air contained into the vessel is enough to increase its concentration in the water only by 6.5 µg L^{-1}.

As the contribution of the gas phase does not explain the changes related to sulfur and chloride, the cap of a Teflon vessel used in all experiments was decomposed using microwave-induced combustion (MIC) [21], for checking the second hypothesis mentioned in this section. After the MIC procedure, sulfur and chloride concentrations were *ca.* 5 µg g^{-1} and *ca.* 3 µg g^{-1}, respectively, strongly indicating that the increase in anion concentrations is related to their lixiviation from the Teflon vessel.

Thus, the atmosphere and some impurities in the vessels walls can play an important role in microwave-assisted processes, influencing the final concentration of some anions, and explaining the effects observed in terms of changes in the anion concentrations.

3.4. *Influence of microwave heating on the hydrogen peroxide formation in water*

As microwave heating plays an important role in the equilibrium of the species present in both the gaseous and liquid phases, as previously demonstrated, the possibility of the formation of some reactive species such as hydrogen peroxide was also investigated.

Recently, Bizzi et al. [19] demonstrated the effect of pressurization of the microwave vessels with oxygen, indicating that the gaseous phase plays an important role in sample digestion. As super-heating points (at microscopic dimensions) are created during microwave heating [14], there is a substantial increase in both pressure and temperature, with probable formation of radicals, as also observed during ultrasonic radiation [25]. The possible formation of H and OH radicals may produce H_2O_2 after recombination of OH radicals [25].

The H_2O_2 formation was investigated submitting 20 g of water to different microwave heating interval (0.2–40 min), and determining the hydrogen peroxide concentrations at each condition. The results showed an increase in the concentration of hydrogen peroxide by increasing the microwave radiation time up to 10 min. For 0.2, 10 and 20 min of microwave heating, the H_2O_2 results were, respectively, <LOQ (24 µg L^{-1}), 48 ± 4 and 38 ± 3. These results

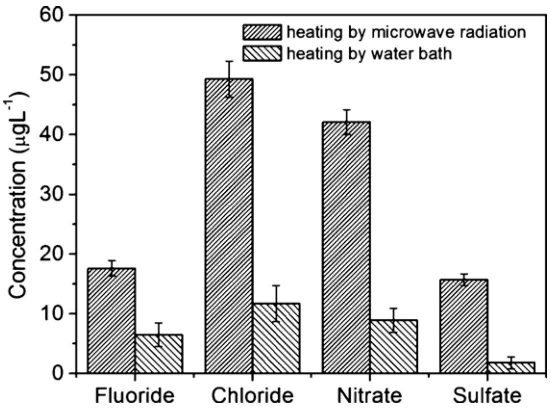

Fig. 3. Comparison between increases of anion concentrations in water after heating with microwave radiation or water-bath.

confirm that this specie is being formed, increasing the oxidant power of the system during microwave heating. For microwave radiation times larger than 20 min, a linear decrease in hydrogen peroxide formation was noted, must probably due to its decomposition during the heating process.

3.5. *Influence of heating source (microwave over or water-bath) on anion concentrations in water*

Since an increase in anion concentrations was verified after microwave heating, this possibility was also investigated when the heating is promoted by a water bath. Thus, 20 g of water were transferred to a PFA flask (the same flask used in the microwave experiments) and they were accommodated in a water-bath (adjusted at 120 °C). The temperature of the water in the PFA flasks was periodically monitored during 1 h, resulting in a heating ramp from 25 to 65 °C during 40 min, remaining constant at 65 °C during 20 min. After this process, fluoride, chloride, nitrate and sulfate concentrations were determined. In the same way, 20 g of water were heated using microwave radiation under the same temperature conditions as previously obtained for water-bath heating (25–65 °C—40 min ramp, plus 20 min at 65 °C), the anion concentrations also being determined. As shown in Fig. 3, the anion concentrations using a water-bath were between 63 and 89% lower than those obtained with microwave radiation. As heating through microwave is produced from the inner to outside of a solution and the temperature gradient is formed along the vessel, contributing to condensation, microwave heating produces convection waves more efficiently, also contributing to an effective interaction between gaseous and liquid phases. In contrast, using a water-bath the temperature is the same throughout the vessel, reducing the condensation and the incorporation of these species into the solution.

4. Conclusions

The use of microwave heating for sample preparation resulted in changes in anion concentrations in water samples. In most cases, an increase and then a decrease of concentration levels were observed for shorter and longer exposure time, respectively. Besides, the nature of changes can be mainly attributed to species transfer between atmospheric gases and water (for nitrate), and between vessel walls and water (for fluoride, sulfate and chloride).

Another important conclusion is that heating using a water bath results in no significant changes in concentrations levels in the water, in comparison with heating by microwave radiation. This fact is probably attributed to the formation of hydrogen peroxide during microwave radiation, as experimentally observed. This reactive species can contribute to anions incorporation into water, either from atmosphere gases or from the vessel walls.

Finally, these results are important to the sample preparation area since they can alert researchers, when the determination of fluoride, chloride, nitrate and sulfate are the main objective of the analysis, especially when the concentrations of these analytes are obtained by techniques that allow speciation analysis, such as the electroanalytical ones.

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