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Article

Alternative Igniters Based on Oxidant Salts for Microwave-Induced Combustion Method

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In this work, solutions of oxidant salts were evaluated as alternative to nitrate solution for the ignition step in microwave-induced combustion (MIC) method. Aqueous solutions of $KClO_4$, $K_2Cr_2O_7$, $KMnO_4$ and $K_2S_2O_8$ in several concentrations were evaluated and it was observed that the ignition was dependent on the concentration and type of igniter solution. Moreover, it was possible to observe that ignition and combustion times are not related with sample mass, which was confirmed by evaluating sample masses ranging from 100 to 500 mg of whole milk powder. Certified reference materials were digested using $K_2Cr_2O_7$ as igniter solution and digests analyzed by inductively coupled plasma optical emission spectrometry (ICP OES), with good agreement to certified values. The obtained results suggest that MIC can be performed using solutions of oxidants salts. In addition, the proposed study contributed to a better undestanding and explaining the ignition with microwaves.

Keywords: microwave-induced combustion, microwave ignition, oxidants salts, sample preparation, sample digestion

Introduction

Combustion methods have been used for digestion of organic substances since the organic matrix could be completely eliminated, leading to clean digests that are compatible with most of analytical techniques. The efficiency of combustion methods can be related to the high temperature achieved during sample combustion (in general higher than 1200 °C).[1] An important advantage of combustion methods is the low risk of contamination, because oxygen, a relatively clean reagent, is used as the main reagent in comparison to wet digestion methods, where concentrated inorganic acids are commonly required.[2-4]

Many combustion systems have been evaluated for sample digestion, but microwave-induced combustion (MIC) has presented a recent and widespread use for the digestion of several kinds of organic matrices, such as coal,[5] polymers,[6,7] crude oil and related products,[8-13] elastomers,[14,15] carbon nanotubes,[16,17] botanical[18] and biological materials[19] for further determination of a variety of elements as metals, halogens, rare earth, among others.[8-10,12,19-22] In MIC method, samples are digested using closed vessels, allowing minimum risk of analyte losses, low reagent consumption, the possibility of using a subsequent reflux step after sample combustion, the use of diluted solutions for analytes absorption and high efficiency of digestion, even for samples considered hard to bring into solution.[11,14-16]

In MIC method, organic samples are combusted under oxygen pressurized atmosphere (generally 20 bar) and ignition step is performed using filter paper (low ash content) and an igniter solution as combustion aid under microwave irradiation. Pelletized samples (in the range of 100 to 500 mg) are positioned on a filter paper previously wetted with ammonium nitrate solution (50 µL, 6 mol L^{-1}), which is the most used igniter. Then, a quartz holder containing the sample is placed inside the digestion vessels, previously charged with a selected volume of absorbing solution. After, vessels are pressurized with oxygen and the microwave heating program is started.

Although several works using MIC method have been published, the mechanism of ignition has not been completely elucidated. Recently, a study related to the role of NH_4NO_3 and other solutions of nitrates, such as $Ca(NO_3)_2$, KNO_3, $Mg(NO_3)_2$ and $NaNO_3$, was performed for the ignition step in MIC system.[23] According to the

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authors, it was observed that the ignition was dependent on nitrate concentration and seems to be related to the previous oxidation of organic matter by NO_3^-, which releases enough energy for starting a chain reaction, leading to combustion.[23]

Despite the evidence of oxidative action of igniter solution, other salts with similar properties were still not evaluated. In this regard, the present work investigates the feasibility of using several solutions of salts with oxidant properties as igniters for MIC method. Solutions of oxidant salts ($KClO_4$, $K_2Cr_2O_7$, $KMnO_4$ and $K_2S_2O_8$) were used and the ignition and combustion times were evaluated. The more reproducible condition for combustion of filter paper was applied for pelletized organic sample in order to evaluate the proposed igniter as alternative for MIC method. After optimization of parameters, an igniter solution of $K_2Cr_2O_7$ was used for MIC digestion of two certified reference materials (CRMs) of milk powder and further analysis by inductively coupled plasma optical emission spectrometry (ICP OES) was performed.

Experimental

Instrumentation

Microwave-induced combustion was carried out using a Multiwave 3000 Microwave Sample Preparation System (software version v1.27-Synt, Anton Paar, Graz, Austria) running with a maximum pressure rate of 3 bar s^{-1}. This system was equipped with up to eight high-pressure quartz vessels with 80 mL of internal volume and maximum operational temperature and pressure of 280 °C and 80 bar, respectively. A commercial quartz holder (Cat. No. 16427, Anton Paar, Graz, Austria) was used for inserting filter paper and sample into digestion vessel.

For the evaluation of ignition and combustion times, a digital chronometer (HS-3V 1BR, 10 ms of precision, Casio, Tokyo, Japan) was used, as well as a digital camera for video recording (DSC-W800, 20.1 MP of resolution, Sony, Tokyo, Japan). These parameters were evaluated taking into account the light emission observed during combustion. In this sense, times were recorded when starting light emission, which was the time considered as ignition time. In the same way, the time related to the period when flame was still observed (light emission) was considered as combustion time.

An analytical balance (model AY 220, max. 220 g, 0.0001 g of resolution, Shimadzu, Kyoto, Japan) and a hydraulic press (Specac, Orpington, UK) were used for weighing and pressing samples as pellets, respectively.

Metals determination was carried out by ICP OES (model Optima 4300DV, Perkin Elmer, Shelton, USA) with an axial view mode and equipped with a GemCone® nebulizer. Operational conditions used for metals determination are shown in Table 1.

Table 1. Operational conditions for determination of metals by ICP OES

Parameter	ICP OES
RF power / W	1400
Plasma gas flow rate / (L min^{-1})	15.0
Auxiliary gas flow rate / (L min^{-1})	0.2
Nebulizer gas flow rate / (L min^{-1})	0.70
Sample flow rate / (mL min^{-1})	2.1
Spray chamber	cyclonic
Nebulizer type	GemCone®
Observation view	axial
Analyte	Wavelength / nm
Ca	393.366
Cu	324.752
Fe	238.204
Mg	285.213
Mn	257.610
Mo	202.031
Zn	213.857
C	193.091[a]
Y	371.029[a]

[a] Used for residual carbon content (RCC) determination.

Reagents, samples and solutions

All the salts evaluated as igniter solutions were of analytical grade (Merck, Darmstadt, Germany). Water was purified using a Milli-Q system, (18.2 MΩ cm, Millipore, Billerica, USA) and it was used to prepare different concentrations of solutions by direct dissolution of salts. Small disks of filter paper (15 mm of diameter, about 15.3 ± 0.3 mg) with low ash content (Black Ribbon Ashless, Schleicher & Schuell, Dassel, Germany) were used to aid the combustion process. The filter paper was previously cleaned with water for 10 min in an ultrasonic bath and further dried in a class 100 laminar bench (CSLH-12, Veco, Campinas, Brazil) before use. Concentrated HNO_3 (65%) was distilled using a sub-boiling system (model DuoPur, Milestone, Sorisole, Italy) and was used as absorbing solution for MIC. Multielement stock standard solution containing 10 mg L^{-1} of all the evaluated elements (SCP33MS, SCP Science, Quebec, Canada) was used to prepare analytical standards by sequential dilution in 5% (v/v) HNO_3 in the range of 1 to 100 µg L^{-1}. For the residual carbon content (RCC) determination, a stock reference solution was prepared by dilution of a citric acid in water and standard solutions, prepared by sequential dilution in 5% (v/v) HNO_3 and yttrium (1000 mg L^{-1}, Spex CertPrep, Metuchen, USA) was used as internal standard. For plasma generation, nebulization and auxiliary gas, argon with a purity of 99.996% (White Martins-Praxair Inc., São Paulo, Brazil) was used. Oxygen (99.6%, White Martins-Praxair Inc., São Paulo, Brazil) was used for pressurization of digestion vessels. Commercial sample of whole milk powder (fat content about 26%) used for adult nutrition was obtained from a local market. Accuracy of MIC using the most proper alternative igniter was evaluated by analysis of CRMs of whole milk powder (NIST 8435) and skim milk powder (BCR 151).

Evaluation of oxidant salts as igniter solution in MIC method

The solubility of each salt was considered to prepare igniter solutions at variable concentration, as follows: $KClO_4$ (0.15 mol L^{-1}), $K_2Cr_2O_7$ (0.1, 0.3 and 0.51 mol L^{-1}), $KMnO_4$ (0.1, 0.3 and 0.48 mol L^{-1}) and $K_2S_2O_8$ (0.1 and 0.17 mol L^{-1}). A volume of 50 µL of each solution was added to the filter paper before microwave irradiation (without the presence of sample). Additionally, experiments using igniter solutions were also performed using filter paper plus a pellet of whole milk powder (13 mm inner diameter, prepared using a hydraulic press set at 3 t). When solutions of $K_2Cr_2O_7$ and $KMnO_4$ were evaluated for the combustion of whole milk powder, 50 µL of the most concentrated igniters and 100 mg of sample were used. When the dependence of ignition and combustion times were evaluated as a function of sample mass, experiments were carried out using 50 µL of $K_2Cr_2O_7$ solution as igniter and sample mass in the range of 100 to 500 mg.

For evaluating the behavior of the proposed igniters, a commercial quartz holder, containing the filter paper alone or filter paper with sample (previously wetted with igniter solution), was placed inside the digestion vessels previously charged with 6 mL of water as absorbing solution. After closing the vessels, they were positioned in the rotor and pressurized with oxygen (20 bar). The rotor was inserted inside the microwave oven with the vessel positioned in front of its front door. A change in the original protective case of vessel was performed to allow the visualization of combustion process (Figure 1).

In order to provide a safe operation during these experiments, an acrylic wall (45 × 60 cm, 10 mm thickness) was positioned in front of the door of microwave oven. The microwave heating program was applied by 1400 W during 60 s. Microwave irradiation was immediately stopped in the beginning of combustion reaction and respective time was recorded. Further, the quartz vessel was carefully opened for releasing the pressure after 5 min of the end of the combustion reaction.

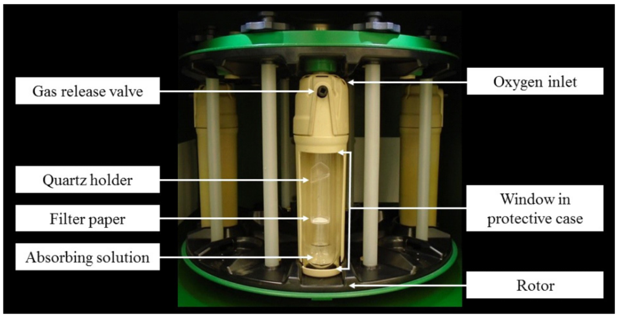

Figure 1. Front view of microwave oven and quartz vessel with a window opened in the protective case.

Sample and CRM digestion by MIC

For the digestion of CRMs (NIST 8435, whole milk powder; and BCR 151, skim milk powder) and commercial sample of whole milk powder by MIC for subsequent metals determination, sample pellets were weighed and positioned with the filter paper on the commercial quartz holder. The holder containing the sample was placed inside the quartz vessels, previously charged with 6 mL of 2 mol L^{-1} HNO_3 (used as absorbing solution) according to previous work.[19] An igniter solution of $K_2Cr_2O_7$ (50 µL of 0.51 mol L^{-1}) was added to the filter paper. After closing the vessels and capping of rotor, vessels were pressurized with oxygen (20 bar) and the microwave program was started as follows: 1400 W for 5 min (reflux step) and 0 W for 20 min, for cooling. The resultant solutions were directly transferred to volumetric flasks and diluted with water to 25 mL.

Results and Discussion

Initially, solutions of $KClO_4$, $K_2Cr_2O_7$, $KMnO_4$ or $K_2S_2O_8$ were evaluated as igniters using only filter paper (without sample) wetted with 50 µL of igniter solution. The obtained results are shown in Table 2.

It was possible to observe that filter paper burned when $K_2Cr_2O_7$ and $KMnO_4$ solutions were used as igniters. In this sense, combustion of filter paper was only observed when more concentrated solutions of $K_2Cr_2O_7$ and $KMnO_4$ were used (0.3 mol L^{-1} or higher concentration for both compounds). Although no combustion was observed using $KClO_4$ and $K_2S_2O_8$ solutions, the final aspect of filter paper indicated a partially oxidation promoted by both salts after microwave irradiation (Figure 2).

These results shown that in spite of the oxidation of filter paper presented using these salts, it was not enough for

Table 2. Evaluation of filter paper combustion (without sample) using igniters solutions

Igniter solution[a]	Concentration / (mol L^{-1})	Observed combustion[b] / replicates		
		Experiment 1	Experiment 2	Experiment 3
$KClO_4$	0.15	No	No	No
$K_2Cr_2O_7$	0.10	No	No	No
	0.30	Yes	Yes	Yes
	0.51	Yes	Yes	Yes
$KMnO_4$	0.10	No	No	No
	0.30	No	Yes	No
	0.48	Yes	Yes	Yes
$K_2S_2O_8$	0.10	No	No	No
	0.17	No	No	No

[a]Volume of 50 µL; [b]combustion performed using 6 mL of H_2O as absorbing solution, microwave power of 1400 W, 60 s and 20 bar of oxygen pressure; n = 3.

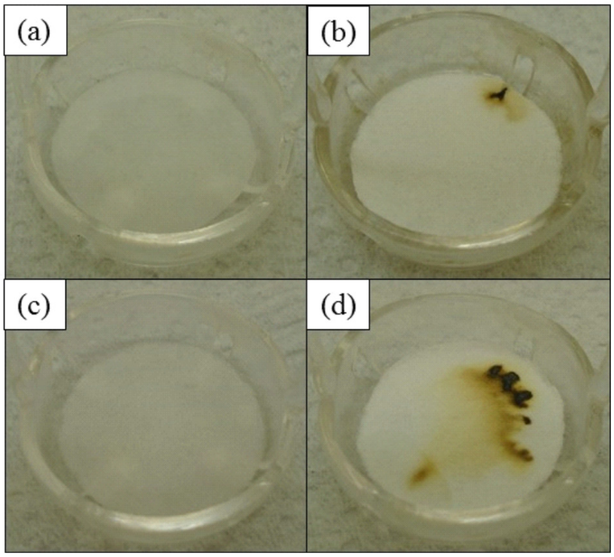

Figure 2. Aspect of filter paper wetted with 50 µL of $KClO_4$ and $K_2S_2O_8$ solutions. Solution of 0.15 mol L^{-1} $KClO_4$: (a) before and (b) after microwave irradiation; solution of 0.17 mol L^{-1} $K_2S_2O_8$: (c) before and (d) after microwave irradiation. Experiments were performed using 6 mL of H_2O as absorbing solution; microwave power of 1400 W, 60 s and 20 bar of oxygen pressure.

causing combustion and only darkening of filter paper was observed. The low concentration of evaluated solutions could not provide energy enough to allow the ignition of paper and only a partial oxidation was observed. Despite the relatively low solubility of these salts (0.15 and 0.17 mol L^{-1} for $KClO_4$ and $K_2S_2O_8$, respectively), it was performed an evaluation with multiple addition and drying steps for obtaining larger masses of these igniters impregnated over filter paper. However, even using such approach, the combustion of paper was not observed and further evaluation was not performed with solutions of $KClO_4$ and $K_2S_2O_8$.

For relatively diluted solutions of $K_2Cr_2O_7$ or $KMnO_4$ (0.1 mol L^{-1}), combustion did not occur, but it was possible to observe a more intense oxidation of filter paper in relation to the use of $KClO_4$ and $K_2S_2O_8$ solutions (Figure 3).

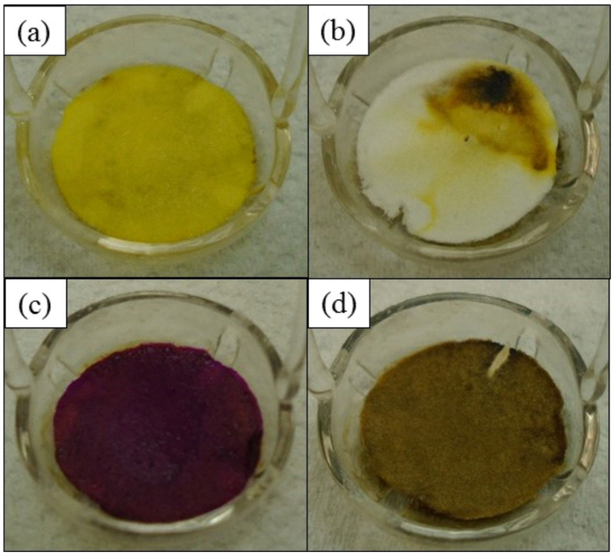

Figure 3. Aspect of filter paper wetted with 50 µL of $K_2Cr_2O_7$ and $KMnO_4$ solutions. Solution of 0.1 mol L^{-1} $K_2Cr_2O_7$: (a) before and (b) after microwave irradiation; solution of 0.1 mol L^{-1} $KMnO_4$: (c) before and (d) after microwave irradiation. Experiments were performed using 6 mL of H_2O as absorbing solution; microwave power of 1400 W, 60 s and 20 bar of oxygen pressure. The dark purple aspect of filter paper before microwave irradiation is due to the color of permanganate solution.

Experiments were also performed using more concentrated solutions of $K_2Cr_2O_7$ and $KMnO_4$. For 0.3 mol L^{-1} $KMnO_4$ solution, the combustion of filter paper was observed in only one experiment (Table 2). On the other hand, the use of 0.3 mol L^{-1} $K_2Cr_2O_7$ provided a filter paper ignition and it was more repeatable ignition when compared to previous tests. In addition, it was observed that filter paper burned when solutions of both compounds (0.51 mol L^{-1} $K_2Cr_2O_7$ and 0.48 mol L^{-1} $KMnO_4$) were used as igniters (Figure 4). In case of $KMnO_4$, this concentration was suitable for starting the combustion process, providing a better repeatability of experiments.

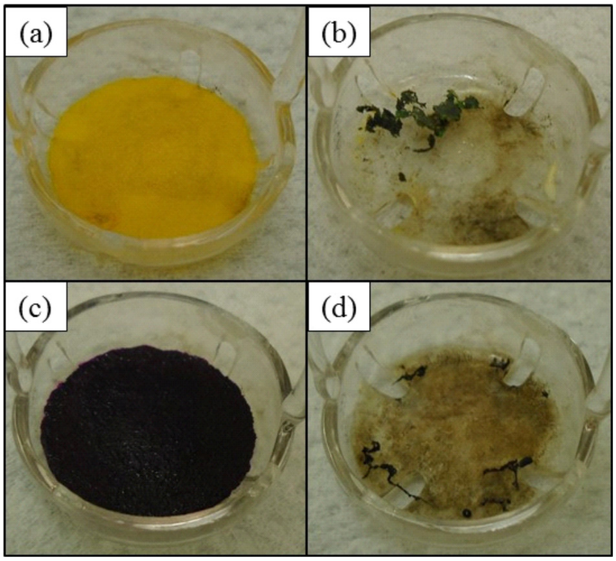

Figure 4. Aspect of filter paper wetted with 50 µL of $K_2Cr_2O_7$ and $KMnO_4$ solutions. Solution of 0.51 mol L^{-1} $K_2Cr_2O_7$: (a) before and (b) after microwave irradiation; solution of 0.48 mol L^{-1} $KMnO_4$: (c) before and (d) after microwave irradiation. Experiments were performed using 6 mL of H_2O as absorbing solution; microwave power of 1400 W, 60 s and 20 bar of oxygen pressure. The dark purple aspect of filter paper before microwave irradiation is due to the color of permanganate solution.

It is important to notice that the final aspect of quartz holder (dark residues) after filter paper combustion (Figures 4b and 4d) was not observed when ignition was performed in the presence of sample or if a reflux step was used. This dark aspect of quartz holder was due to the relative low heat released during combustion of filter paper (burning only 15 mg of organic matter) and the absence of reflux step for washing the internal parts of digestion vessel. Normally, when MIC method is applied in the conventional way for organic matrices digestion, a more clean aspect of quartz holder is observed after combustion and reflux step.

Evaluation of ignition and combustion times

Another important information about MIC is related to the minimum time of microwave irradiation required to start the combustion reaction (ignition), as well as the time for complete combustion process.[23] These parameters were evaluated taking into account the light emission observed during combustion, using the commercial system of MIC especially modified for this purpose.[3]

In this sense, for evaluating the ignition and combustion times, filter paper was wetted with 50 µL of $K_2Cr_2O_7$ and $KMnO_4$ solutions for monitoring the time necessary to start the combustion reaction and the time for filter paper burning. The obtained results are shown in Table 3.

Table 3. Evaluation of ignition and combustion times of filter paper (without sample) with the use of $K_2Cr_2O_7$ and $KMnO_4$ solutions as igniters

Igniter solution[a]	Concentration / (mol L^{-1})	Ignition time / s	Combustion[b] time / s
$K_2Cr_2O_7$	0.30	20.0 ± 1.6	6.0 ± 0.8
	0.51	13.0 ± 2.2	5.3 ± 0.9
$KMnO_4$	0.30	9.2[c]	14.3[c]
	0.48	6.3 ± 1.2	7.3 ± 1.2

[a]Volume of 50 µL; [b]combustion performed using 6 mL of H_2O as absorbing solution, microwave power of 1400 W, 60 s and 20 bar of oxygen pressure; [c]only one experiment occurred filter paper combustion (n = 1); n = 3; results are the mean and standard deviation.

It was observed that the higher the concentration of $K_2Cr_2O_7$ solution the shorter the time required for ignition. When 0.51 mol L^{-1} $K_2Cr_2O_7$ solution was used, the filter paper ignition occurred in about 13 s, whereas the use of a more diluted solution (0.3 mol L^{-1} $K_2Cr_2O_7$) required about 20 s to start the combustion process.

Similarly, with the use of 0.3 mol L^{-1} $KMnO_4$, the observed ignition and combustion times were higher than those using more concentrated solution (0.48 mol L^{-1} $KMnO_4$). The obtained results showed a delay for the ignition time for more diluted solutions of $KMnO_4$ and a non reproducible combustion was observed. Additionally, a higher combustion time may be explained due to the inconstant flame observed during filter paper combustion.

When the comparison of ignition time using $K_2Cr_2O_7$ and $KMnO_4$ solutions was carried out, it was always observed a shorter time for filter paper ignition for $KMnO_4$ solution. Taking into account the more reproducible condition (0.51 mol L^{-1} $K_2Cr_2O_7$ or 0.48 mol L^{-1} $KMnO_4$), when $KMnO_4$ solution was used, the filter paper combustion occurred faster than that by using $K_2Cr_2O_7$ (around 6 and 13 s, respectively). Such difference for ignition time showed that the kind of salt can directly affect the ignition time of filter paper. Due to a higher oxidant potential of $KMnO_4$, the filter paper ignition was faster in comparison to $K_2Cr_2O_7$ solution (standard reduction potential in aqueous solution at 298 K of 1.51 and 1.36 V, respectively).[24] As expected, it was not observed difference (analysis of variance, ANOVA; confidence level of 95%) for the combustion time when $K_2Cr_2O_7$ and $KMnO_4$ solutions were used, because the mass of filter paper (15 mg, corresponding to 9.26×10^{-5} mol, considering it as $C_6H_{10}O_5$) and O_2 amount (20 bar, 1.97 g, 0.616 mol) were kept constant and no changes in combustion process were observed.

As previously reported,[23] it is important to notice that when ignition time was evaluated using NH_4NO_3 solution (igniter normally used for MIC), the ignition time decreased from 7.3 to 4.3 s, while the concentration of solution increased from 1 to 12 mol L^{-1} NH_4NO_3. Thus, it was also observed in this work that the higher the concentration of nitrate solution the shorter the time required for ignition, due to the fast oxidation of filter paper caused by the increase of nitrate concentration.[23]

Evaluation of $K_2Cr_2O_7$ and $KMnO_4$ solutions as igniters in the presence of sample pellet

After the evaluation of $K_2Cr_2O_7$ and $KMnO_4$ solutions, it was investigated their use for digesting whole milk powder. In this regard, sample was prepared as a pellet (100 ± 5 mg) and positioned on the filter paper previously wetted with 50 µL of igniter solutions. As it was performed when evaluating the ignition of filter paper alone, vessel was previously filled with water as absorbing solution. For this experiment, sample combustion of whole milk powder always occurred when $K_2Cr_2O_7$ or $KMnO_4$ solutions (0.51 and 0.48 mol L^{-1}, respectively) was used. For both solutions, ignition and combustion times were lower than 13 s and 9 s, respectively, and no sample residues remained in quartz holder after combustion process (Figure 5). Thus, $K_2Cr_2O_7$ and $KMnO_4$ solutions were considered as suitable for ignition using microwave irradiation.

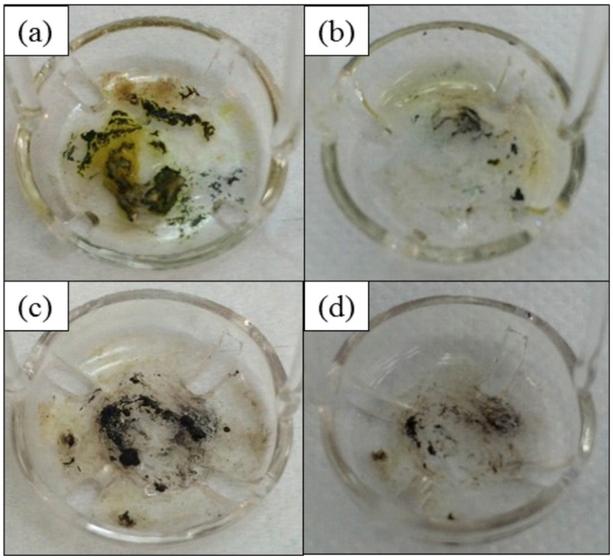

Figure 5. Aspect of quartz holder after sample pellet combustion. Solution of 0.51 mol L^{-1} $K_2Cr_2O_7$: (a) without reflux step and (b) after reflux step; solution of 0.48 mol L^{-1} $KMnO_4$: (c) without reflux step and (b) after reflux step. Experiments were performed using 6 mL of 2 mol L^{-1} HNO_3 as absorbing solution; microwave power of 1400 W, 60 s and 20 bar of oxygen pressure.

In order to evaluate the effect of sample mass on the ignition and combustion times, sample masses ranging from 100 to 500 mg were studied. For this experiment, pelletized samples were positioned on the filter paper and 50 µL of 0.51 mol L^{-1} $K_2Cr_2O_7$ solution was used as igniter. The obtained results are shown in Table 4.

Table 4. Evaluation of ignition and combustion times of whole milk powder using 50 µL of 0.51 mol L^{-1} $K_2Cr_2O_7$ solution as igniter

Sample mass / mg	Ignition time / s	Combustion[a] time / s
100	12.7 ± 2.9	8.0 ± 2.0
200	12.0 ± 3.6	13.3 ± 3.2
300	12.3 ± 3.5	20.3 ± 3.5
400	13.0 ± 2.6	25.0 ± 2.0
500	12.7 ± 2.5	33.7 ± 2.1

[a] Combustion performed using 6 mL of H_2O as absorbing solution, microwave power of 1400 W, 60 s and 20 bar of oxygen pressure; results are the mean and standard deviation, n = 3.

According to results, no significant difference (ANOVA, confidence level of 95%) was observed for the ignition time using different sample masses. Moreover, the time required for ignition when burning 100 to 500 mg of sample was the same obtained using only filter paper (without sample). This result reinforces the statement related to the oxidation action promoted by igniter solution added on the filter paper, which transfer enough energy for starting the combustion reaction in a stable way. Although the ignition time was independent of sample mass, differences in combustion time were observed when higher sample masses were used.

It was possible to observe that ignition reaction started by $K_2Cr_2O_7$ and $KMnO_4$ solutions can be useful as an alternative for MIC, in addition to nitrate solutions previously studied.[23] The obtained results were also important for better understanding the ignition assisted by microwave radiation. It can be observed that the use of oxidizing species (nitrates[23] or other salts with oxidant proprieties, as shown in this work) is necessary to start the combustion reaction in the evaluated conditions for MIC method. With the exception of $KClO_4$ and $K_2S_2O_8$, other compounds can be used as igniters considering their high oxidizing potential, allowing the necessary energy for oxidation of organic matter and further combustion reaction.

Metals determination by ICP OES after MIC

In order to evaluate the applicability of $K_2Cr_2O_7$ as igniter solution, 50 µL of 0.51 mol L^{-1} $K_2Cr_2O_7$ was used for digesting commercial whole milk powder sample and CRMs by MIC. After digestion step, metals determination

Table 5. Results obtained for analysis by ICP OES of certified reference materials[a] and commercial sample of milk powder[a] using microwave-induced combustion (MIC) and $K_2Cr_2O_7$ as igniter solution

Element	Concentration / (µg g^{-1})				
	Commercial whole milk powder	NIST 8435		BCR 151	
		Certified	Found	Certified	Found
Ca	0.893 ± 0.052%	0.922 ± 0.049%	0.954 ± 0.047%	–	–
Cu	0.332 ± 0.021	0.46 ± 0.08	0.44 ± 0.05	5.23 ± 0.08	5.25 ± 0.05
Fe	2.67 ± 0.14	1.8 ± 1.1	1.75 ± 0.09	50.1 ± 1.3	51.4 ± 2.7
Mg	1011 ± 49	814 ± 76	795 ± 55	–	–
Mn	0.410 ± 0.022	0.17 ± 0.05	0.18 ± 0.03	–	–
Mo	0.136 ± 0.015	0.29 ± 0.13	0.30 ± 0.08	–	–
Zn	26.9 ± 1.1	28.0 ± 3.1	29.4 ± 1.9	–	–

[a] 500 mg; results are the mean and standard deviation, n = 3.

was performed by ICP OES and obtained results are shown in Table 5.

It is important to observe that the proposed MIC method allowed quantitative recoveries for elements that were present in a relatively wide range of concentration (from sub µg g^{-1} level up to %) in both samples and CRMs. The values obtained by MIC were in agreement (in the range of 96 to 106%) with certified values for both CRMs evaluated. Despite the use of $K_2Cr_2O_7$ as igniter, which is not obtained in high purity quality, blanks were still low and limits of detection were not significantly affected for the evaluated analytes. Additionally, the RCC was determined in digests after MIC, in order to evaluate the efficiency of sample decomposition when $K_2Cr_2O_7$ was used as igniter solution. According to the obtained results, the values found for RCC were always below 1%, showing that $K_2Cr_2O_7$ solution is suitable for sample ignition and subsequent digestion. Such low values of RCC contributed for avoiding possible interferences during analytes determination. This fact was expected once the RCC is independent of the igniter used for start the combustion process. Thus, using igniter solution of $K_2Cr_2O_7$ in MIC method, it was possible to efficiently digest up to 500 mg of whole milk powder, allowing further determination of Ca, Cu, Fe, Mg, Mn, Mo and Zn by ICP OES.

Conclusions

It was observed a darkening of filter paper by using $KClO_4$ and $K_2S_2O_8$ solution, a clear indication of oxidation, bringing evidence about ignition assisted by microwaves. However, as more concentrated solutions could not be evaluated (due to the restriction of low solubility), it was not observed paper ignition followed by burning when exposed to microwaves. On the other hand, it was observed the filter paper ignition and further burning when more concentrated solutions of $K_2Cr_2O_7$ and $KMnO_4$ were used (e.g., 0.3 mol L^{-1} or higher). Thus, it can be concluded that the ignition process was dependent on the type and concentration of the evaluated igniter solutions. According to the concentration and oxidant species, complete combustion or only partially oxidation of filter paper occurred, which is closely related to the oxidant potential of each compound. In this sense, considering the same salt concentration, less ignition time was required for solutions with higher oxidant potential (e.g., $KMnO_4$). As it was already expected, the time that filter paper remained during combustion was almost the same independent on the solution evaluated. Since only the igniter was changed and paper mass and concentration of oxygen were kept constant, the combustion time was also expected to be constant. On the other hand, it can be concluded that ignition time was independent on the sample mass (from 100 to 500 mg) and, as expected, the higher the sample mass used the longer the combustion time observed. Additionally, obtained results for metals in CRMs after digestion by MIC using $K_2Cr_2O_7$ as igniter solution were in agreement with certified values. In this way, microwave-induced combustion can be performed using solutions of salts, which present oxidant properties, in addition to use nitrates as a new alternative for combustion methods. In spite of the better performance of NH_4NO_3, the use of other igniters could be useful in case of further nitrate determination by, e.g., ion chromatography. Such reagents might be considered as an alternative for groups working in places where the use of nitrates is strictly controlled, being its acquisition quite difficult for science purposes (as in the case of Brazil). On the other hand, depending on the elements to be determined, the use of $K_2Cr_2O_7$ and $KMnO_4$ solutions may impair the determination of K, Cr or Mn, since these elements are present in the igniter solution.

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