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# Use of Factorial Design for Optimization of Microwave-Assisted Digestion of Lubricating Oil

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A eficiência dos procedimentos de digestão em fornos de microondas pode ser afetada por parâmetros experimentais críticos, como massa de amostra, volume da mistura ácida, potência de radiação aplicada e o tempo da digestão. Neste trabalho foi proposta a utilização de um planejamento fatorial completo para a otimização da digestão de amostras de óleo lubrificante em forno de microondas, com recipientes fechados. O teor de carbono residual e a acidez final das soluções foram determinados em todos os digeridos provenientes do forno de microondas, como resposta ao planejamento fatorial. Cálcio, Cu, Mg, P, S e Zn foram determinados nos digeridos ácidos e a exatidão foi checada utilizando-se um material de referência certificado, NIST SRM 1848-Lubricating Oil Additive Package. Os resultados encontrados para as amostras e para o material de referência certificado estão em concordância a um nível de confiança de 95%. Tempo de digestão, potência de radiação aplicada, massa de amostra e as interações entre essas variáveis foram significativas (P < 5%), aplicando-se a análise de variância (ANOVA).

This work proposes the use of factorial design for optimization of microwave-assisted digestion of lubricating oil. The accuracy of digestion procedures is affected by critical experimental parameters, such as sample amount, concentrated acid volumes, microwave radiation applied power, and digestion time. The effects of these key variables on the microwave-assisted digestion efficiency were investigated. The residual carbon content and the acidity were determined in all digestates after microwave-assisted digestion as response of the factorial design. Calcium, Cu, Mg, P, S, and Zn were determined in oil digestates obtained by using two systems: a cavity- and a focused-oven. The accuracy was checked using one standard reference material, NIST SRM 1848 – Lubricating Oil Additive Package. All determined and certified values are in agreement at a 95% confidence level. The digestion time, microwave applied power, sample mass, and the interaction between these variables were significant according to P-values when the analysis of variance (ANOVA) was used.

**Keywords**: factorial design, microwave-assisted digestion, lubricating oil, metals

## Introduction

The proposal of a new analytical method requires the optimization of the experimental variables and its validation. The first one involves the selection of the values of the factors that have an influence on the analytical signal and lead to the best results for the analytical process. The optimization of the proposed method allows us to understand effects that are not explained in a traditional way, such as those in which the analytical response is a multimodal function of the independent variables or when the effects of the variables are not additive and there is interaction among them.[1]

Sample preparation involves digestion or extraction of the analytes before the analysis,[2] so this step is time limiting, requiring up to 60% of the complete analysis time, and is responsible for up to 30% of the total analysis error.[3] Nowadays, the goals are to obtain the best results in the shortest time, with minimal contamination, low reagent consumption, and generation of minimal residue or waste.[4] Microwave-assisted digestion is a well-known procedure for sample preparation of organic and inorganic samples. This strategy is being applied not only in analytical chemistry but also in organic synthesis, inorganic reactions, preparation of catalysts, and other fields with the goal to speed up chemical processes.[5] The association of factorial design and microwave-assisted digestion can

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contribute to accelerate the pretreatment step, improving the accuracy of the results.

The efficiency of the digestion of organic samples is associated with the residual carbon content remaining in the digestates. It is desirable to reach low carbon content in the digestates, otherwise this quantity can seriously interfere in instrumental measurements. Not only anodic stripping voltammetry and related electroanalytical techniques but also spectroanalytical techniques, such as inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS), could also suffer interference by dissolved organic compounds. Organic oxidation products can act as surfactants and the efficiency of pneumatic nebulizers can be changed.[2]

Another important aspect of sample introduction by pneumatic nebulization is related to the acid content of the digestates. Additionally, the quartz torch of ICP OES with axial viewing configuration equipment is specially damaged when it is in contact with solutions containing elevated acid concentrations. Consequently, the quality of a digestate is related to both low levels of residual carbon and acidity for minimizing the dilution factor before introduction by pneumatic nebulization.

Microwave-assisted oil digestion has been proposed to speed up the decomposition reactions in closed-vessels.[6,7] The major component of lubricating oil sample is hydrocarbons, but the most important characteristic is due to the metals added as additives. These additives fall into several groups that may be summarized as anti-oxidants, detergents, anti-wear agents, dispersants, corrosion inhibitors, and viscosity index improvers.[8] The knowledge of trace metal concentration is important to characterize oils from different sources and the deterioration of mechanical parts of machines.[9-11]

Thus, the parameters that affect the digestion process, such as sample amount, concentrated acid volumes, microwave radiation applied power, and digestion time, should be investigated. These operating parameters can be effectively and efficiently optimized using a factorial design approach. Factorial design allows a consideration of over-all number of experiments and possible interactions effects between the variables.[12]

Zhou *et al.* optimized the parameters of a closed-vessel microwave-assisted digestion for determination of trace metals in sediments using orthogonal array design.[13] Orthogonal array design is a chemometric approach combining advantages of both the simplex and factorial design. The parameters studied were: maximum pressure setting, HCl / $HNO_3$ ratio, output applied power, and digestion time. The optimized parameters of the closed-vessel microwave digestion were applied for digesting

certified reference materials of sediments. The results obtained agreed well with certified values.

Martin-Garcia *et al.* applied a fractional factorial design to the determination of tin in lubricating oils by continuous flow hydride generation-atomic absorption spectrometry.[14] Oil samples were digested using a pressurized system equipped with PFA Teflon® vessels. The variables investigated in this work were: $HNO_3$ and $NaBH_4$ concentrations, acetylene, Ar, sample, and $NaBH_4$ flow-rates. Analysis of variance (ANOVA) showed that there were only three variables with a significant (95%) influence on the measurements: $NaBH_4$ concentration, acetylene, and sample flow-rates. Results enabled the proposal of a tailored procedure for determining total tin in lubricating oils.

Martinez *et al.* developed a chemometrically guided sample composition for fast screening of trace metals in water samples.[15] The authors presented an alternative named strategic sample composition (SSC). This approach allows to reliable adjustment of the required time, with costs and facilities being easily automated. It also exhibits excellent robustness characteristics and can be fitted to any particular study by defining the composition matrix.

This work proposes the optimization of a microwave-assisted digestion process applied for lubricating oil samples using a cavity-oven through a two-level full factorial design $2^4$ with 16 runs. The determinations of elements in the digestates were performed using ICP OES. A focused-microwave oven was used to compare the results obtained in cavity-oven, and additionally, a standard reference material (NIST SRM 1848 – Lubricating Oil Additive Package) was used to check the accuracy. The residual carbon content was determined using ICP OES with an axial viewing configuration.[16]

## Experimental

### Instrumentation

Acid digestions were performed in a microwave–oven (ETHOS 1600, Milestone, Sorisole, Italy) equipped with 10 perfluoroalkoxy Teflon® (PFA) closed vessels with calibrated resealing pressure relief mechanisms (maximum operating pressure 110 atm). Six vessels were put on a rotation turntable inside the microwave oven cavity. Before using, the PFA vessels were acid cleaned and rinsed with deionized water.

Axial view simultaneous ICP OES (Vista AX, Varian, Mulgrave, Australia) equipped with solid state detector was used. The operational parameters established for residual carbon content (RCC) and element analysis are listed in Table 1. The RCC was monitored at C I 193.025 nm wavelength. All measurements were carried out using liquid argon to decrease signal blank caused by plasma

gas contamination. The method used in this work was previously described by Gouveia *et al.*[16]

**Table 1.** Instrumental parameters for residual carbon and elements determination using axial ICP-OES

| Instrumental parameter | |
|---|---|
| Power (kW) | 1.3 |
| Plasma gas flow (L min$^{-1}$) | 15.0 |
| Auxiliary gas flow (L min$^{-1}$) | 1.5 |
| Nebuliser gas flow (L min$^{-1}$) | 0.7 |
| Integration time (s) | 1.0 |
| Stabilization time (s) | 15 |
| Reading time (s) | 1 |
| Replicates | 3 |
| Spray chamber | Sturman-Masters |
| Nebulizer | V-groove |
| Analytical wavelengths (nm) | |
| B I | 249.772 |
| C I | 193.025 |
| Ca II | 396.847 |
| Cu I | 327.395 |
| Mg I | 285.267 |
| P I | 177.432 |
| S I | 181.972 |
| Zn II | 202.548 |
| Y II | 371.029 |

*Reagents and solutions*

All solutions were prepared using analytical grade reagents and Milli-Q® distilled and deionized water (Millipore, Bedford, MA, USA). Nitric acid and hydrogen peroxide (Mallinckrodt, Mexico) were used in the microwave-assisted digestions.

Reference solutions containing from 100 to 2500 mg L$^{-1}$ C were prepared using a 5.0% (m/v) C stock solution made of ureia ($CH_4N_2O$, Reagen, Brazil). Reference solutions containing 1000 mg L$^{-1}$ of B, Ca, Cu, Mg, P, S, and Zn were used for preparing multielementar reference solutions.

A 1000 mg L$^{-1}$ yttrium stock standard solution was used as internal standard in all digestates obtained by focused-microwave oven digestion for avoiding transport interferences caused by sulfuric acid.[17]

*Samples and measurements*

One standard reference material NIST SRM 1848 Lubricating oil (National Institute of Standards and Technology, Gaithersburg, MD, USA) was digested in order to check the accuracy of the proposed procedure. A new lubricating oil sample was used in the factorial design for optimizing the digestion process. The residual carbon content and elements in all diluted digestates were determined using ICP OES with an axial view configuration.

*Factorial design experiment*

Considering the microwave-assisted digestion in the cavity oven, a two-level $2^4$ full factorial design with 16 runs (in duplicates) was developed in order to determine the influence of the factors and their interactions on the system. Four factors were studied: sample mass, digestion time, microwave radiation applied power, and volume of oxidant mixture ($HNO_3 + H_2O_2$). Minimum and maximum levels of each factor (Table 2) were chosen according to preliminary experimental data. The factorial design was evaluated using the RCC and final acidity as response.

The heating program investigated in the cavity-oven microwave for oil sample acid digestion is shown in Table 3. The optimization was carried out considering the last step of the heating program, because in this step there is a maximum incidence of the microwave radiation applied power. The experimental sequence of the experiments is shown in Table 4. The experiments were carried out in a random order.

The heating program developed in a focused microwave oven for acid digestion of oil sample for determination of elements is shown in Table 5.

Significances of the effects were checked by analysis of the variance (ANOVA). The effects and significance of the variables in the microwave-assisted digestion system were evaluated using Pareto's charts (Figures 1 and 2).

Oil samples were kept in contact with $HNO_3$ for 4 h at room temperature before digestion for improving safety

**Table 3.** Heating program for oil sample digestion in cavity-oven microwave

| Step | time (min) | Power (W) |
|---|---|---|
| 1 | 2 | 250 |
| 2 | 1 | 0 |
| 3 | 3 | 250 |
| 4 | 4 | 400 |
| 5 | 6 | 600 |
| ventilation | 5 | 0 |

**Table 2**. Factors and levels used in the factorial design experiment

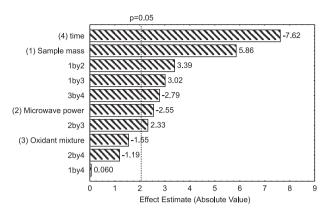| Factor | Higher level (+) | Medium point | Lower level (-) |
|---|---|---|---|
| Sample Mass (mg) | 200 | 150 | 100 |
| Power (W) | 600 | 550 | 500 |
| Oxidant mixture | 4.0 mL HNO$_3$ + 1.0 mL H$_2$O$_2$ | 3.0 mL HNO$_3$ + 0.75 mL H$_2$O$_2$ | 2.0 mL HNO$_3$ + 0.5 mL H$_2$O$_2$ |
| time (min) | 6 | 5 | 4 |

**Figure 1.** Pareto's chart of standardized effects for variables, using the residual carbon content as response.

conditions by previous oxidation of easily oxidable compounds in the oil sample. Without using this strategy, opening and self-resealing of vessels containing higher masses of samples were observed in some experiments at elevated temperatures. This is not critical for safety owing to the proper performance of the vessels, however volatile compounds can be partially lost.

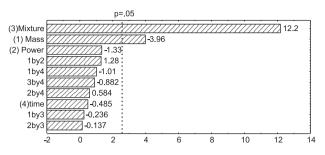After digestions, the volumes were made up to 25.0 mL with water.



**Figure 2.** Pareto's chart of standardized effects for variables using the final acidity as response.

## Results and Discussion

### Factorial design

Factorial design approach is an useful tool to establish and improve analytical procedures. Although it seems more complex than the univariate procedure from the operative point of view, it is advantageous since it makes use of fewer experiments and provides important information on interactions among the studied variables.[18]

A two-level full factorial $2^4$ with 16 runs was carried out in order to determine the main factors of the

**Table 4.** Design matrix and results for residual carbon content and residual acidity

| Experiment | random order | sample mass | microwave power | oxidant mixture | time | % RCC | Acidity (mol L$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 1 | 8 | + | + | + | + | 9.1 9.2 | 1.66 |
| 2 | 1 | + | + | + | - | 17.5 18.0 | 2.08 |
| 3 | 4 | + | + | - | + | 14.7 14.6 | 0.62 |
| 4 | 6 | + | + | - | - | 13.6 14.3 | 0.52 |
| 5 | 11 | + | - | + | + | 11.7 12.0 | 1.58 |
| 6 | 5 | + | - | + | - | 17.9 19.1 | 1.97 |
| 7 | 14 | + | - | - | + | 13.3 15.5 | 0.73 |
| 8 | 10 | + | - | - | - | 11.0 9.8 | 0.622 |
| 9 | 7 | - | + | + | + | 11.7 11.0 | 2.23 |
| 10 | 9 | - | + | + | - | 8.4 9.7 | 1.87 |
| 11 | 3 | - | + | - | + | 4.1 4.8 | 0.93 |
| 12 | 15 | - | + | - | - | 12.4 11.5 | 0.93 |
| 13 | 12 | - | - | + | + | 7.1 7.7 | 2.39 |
| 14 | 17 | - | - | + | - | 14.9 10.4 | 2.49 |
| 15 | 16 | - | - | - | + | 13.7 13.9 | 1.04 |
| 16 | 2 | - | - | - | - | 15.7 18.4 | 1.09 |
| Medium point | 13 | 0 | 0 | 0 | 0 | 18.0 18.2 | 1.45 |

**Table 5.** Heating program for oil sample digestion in focused-oven microwave Initial addition: 5.0 mL $HNO_3$ + 5.0 mL $H_2SO_4$

| Step | $t_{ramp}$ (min) | T ($^{\circ}$C) | $t_{plateau}$ | Reagent (mL) | Aliquot (mL) |
|------|------|------|------|------|------|
| 1 | 1 | 95 | 1 s | 1.0 $HNO_3$ | 1 |
| 2 | 3 | 150 | 1 s | 1.0 $HNO_3$ | 1 |
| 3 | 3 | 220 | 5 min | 3.0 $HNO_3$ | 1 |
| 4 | 2 | 250 | 0 | - | - |
| 5 | 0 | 200 | 10 min | 10.0 $H_2O_2$ | 1 |

microwave-assisted oil digestion in a cavity-oven. Significances of the effects were checked by analysis of variance (ANOVA). In this experiment, a negative value for the effect means an inversely proportional effect on RCC and a positive value means a directly proportional effect on RCC; i.e. negative values are associated with a decrease on residual carbon values and positive values are associated with higher RCC values.

The results considering RCC as response (Figure 1), demonstrated that the most significant variables were: digestion time, sample size, and microwave applied power. Additionally, the interactions of microwave applied power and sample size, microwave applied power and volume of oxidant mixture, sample size and volume of oxidant mixture, and finally volume of oxidant mixture and digestion time were significant and contributed to the reduction of RCC in the digestates.

As it can be seen in Figure 1, a Pareto's chart demonstrated that the increase in digestion time from 4 to 6 min and increase in microwave applied power from 500 to 600 W decreased the RCC, measured as a negative effect of -7.62 and -2.55, respectively. Additionally, the interaction of oxidant mixture and digestion time was also statistically significant. The negative value (- 2.79) of the effect for RCC indicates that the RCC decreased when both factors increased. On the other hand, when the sample size was increased from 0.10 to 0.20 g the RCC also increased, with a positive effect of 5.86. Additionally, the interactions sample size and microwave applied power (3.39), sample size and oxidant mixture (3.02), and microwave applied power and oxidant mixture (2.33) were significant factors because a simultaneous increase of the sample size and decrease in microwave applied power led to high RCC's; an increase of the sample size and a decrease in oxidant mixture volume also increased the RCC, and finally, a decrease of microwave applied power associated with a decrease of oxidant mixture volume caused an increase in the RCC of the digestates. It can also be noted a curvature effect in the results of the factorial design when RCC is used as response. If there were no curvature, then the center point should be equal (within experimental uncertainty) to the average of the points of the design.[19]

The oxidant mixture volume by itself was not a significant factor. It implies that in the studied range, the reagents volume used did not affect the results. However, this parameter could not be increased at will because of the undesirable effect on the acidity of the digestate.

The interpretation of the factorial design by Pareto's chart in Figure 2 using final acidity as response shows that the significant variables to residual acidity were oxidant mixture volume and sample size. The increase of the sample mass led to a higher consumption of the oxidant mixture, and consequently, lower residual acidity. The increase of the volume of the oxidant mixture to 4 mL $HNO_3$ promoted higher acidity values when compared to lower volumes (2 mL $HNO_3$) producing a positive effect (12.2). On the other hand, the increase of the sample size influenced negatively the residual acidity (- 3.96) leading to lower acidity values. These effects are expected and according to Würfels et al.[20] the increase of the sample size generated higher quantities of $NO_2$, resulting in better digestions. There is a direct relation between $NO_2$ formation, concentrated nitric acid volume, and sample amount. As described by Würfels et al.,[20] an increase in the RCC was observed for biological samples when decreasing the mass of sample and keeping constant the acid volume. This effect occurs because of the reduction in $NO_2$ formation due to the lower sample mass.

### Metal determination in oil samples

The inorganic characterization of oil samples is used as a diagnostic of mechanical waste of motor parts. Metals are usually added to oils to improve the lubrication of motor components. Barium, Ca, Mg, P, and Zn are added to new oils as organometallic compounds while Al, Cu, Fe, and Ni are present as products of the gradual degradation of lubricating parts.[8] The elemental concentrations in a new lubricating oil is shown in Table 6. The digestion procedure using a focused-microwave oven was used to compare the values obtained using the developed procedure for cavity-oven microwave. Sulfur was not determined in the digestates obtained using the focused-microwave oven since sulfuric acid was use in the digestion mixture to increase the digestion temperature at normal pressure. The accuracy of the procedure was also checked by digestion of NIST SRM 1848 and the results are presented in Table 7. All determined values are in agreement with certified ones at 95% confidence level, according to a t-Student test.

## Conclusions

The application of factorial design allowed the optimization of parameters that influence the performance

**Table 6**. Elemental concentrations of Ca, Cu, Mg, P, S, and Zn in AGIP lubricating oil (mean ± standard deviation, n = 3)

| Elements ($\mu$g g$^{-1}$) | Cavity oven | Focused oven |
|---|---|---|
| Ca | 47.3 ± 2.4 | 43.5 ± 0.3 |
| Cu | 3.83 ± 0.10 | 2.58 ± 0.33 |
| Mg | 876 ± 14 | 789 ± 2 |
| P | 806 ± 18 | 795 ± 7 |
| S | 5784 ± 34 | – |
| Zn | 870 ± 15 | 836 ± 2 |

**Table 7**. Elemental concentrations of B, Ca, Mg, P, S, and Zn in NIST SRM 1848 (mean ± standard deviation, n = 3)

| Analyte (% m/m) | Certified | Determined | |
|---|---|---|---|
| | | Cavity oven | Focused oven |
| B | 0.137 ± 0.019 | 0.124 ± 0.033 | 0.119 ± 0.006 |
| Ca | 0.359 ± 0.011 | 0.343 ± 0.019 | 0.359 ± 0.012 |
| Mg | 0.821 ± 0.038 | 0.812 ± 0.006 | 0.819 ± 0.016 |
| P | 0.788 ± 0.028 | 0.858 ± 0.038 | 0.756 ± 0.014 |
| S | 2.327 ± 0.004 | 2.369 ± 0.029 | – |
| Zn | 0.873 ± 0.022 | 0.922 ± 0.026 | 0.874 ± 0.018 |

of microwave-assisted acid digestion procedures. Employing the Pareto's charts, it was possible to evaluate the influence of each variable and the combination of variables in the RCC value and acidity of the digestates. It was demonstrated that the most critical parameters for reaching low RCC values are digestion time, sample mass, and microwave applied power and the most important interaction between variables occurred for sample mass and microwave applied power. The cavity-microwave oven offers lower final acidity digestate and blank values, because lower acid volumes are used in the digestion procedure. Since the system is operated under relatively high pressure, only nitric acid can be used. On the other hand, in a focused-microwave oven a higher sample mass can be digested, and the reagents can be introduced at will during the digestion procedure. However, the use of sulfuric acid is mandatory when it is necessary to reach high temperatures. A multivariate adjustment of these parameters allowed the reduction of RCC in oil digestates. On the other hand, the acidity of the digestates was more critically affected by the oxidant mixture volume and the sample mass. The adopted multivariate approach led to a proper adjustment of experimental parameters resulting in a digestate with low RCC and suitable acidity for pneumatic nebulization without extensive dilution.

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