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Comparison of digestion methods for the determination of ruthenium in catalyst materials

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ABSTRACT

A fusion method, an acid digestion method with a high pressure asher (HPA) and two microwave (MW)-assisted acid digestion methods were compared to investigate their suitability for the determination of Ru in catalyst materials. Ru contents in the digested samples were determined with inductively coupled plasma optical emission spectrometry (ICP-OES). Ru powder and three Ru compounds ($RuO_2 \cdot xH_2O$, anhydrous RuO_2 and $RuCl_3$), possibly present in Ru catalysts, were digested and analyzed to compare the digestion efficiencies of the methods. Significant differences among the digestion efficiencies of the methods were observed; the fusion method having the best digestion efficiency for the compounds studied. The methods were applied for the determination of Ru in alumina- and carbon-supported catalysts. No differences among the methods were observed for these samples.

1. Introduction

Ruthenium is a versatile catalyst for various chemical reactions [1]. Ru catalysts have applications, e.g. in Fischer–Tropsch synthesis and ammonia production [2]. Due to active research in the field of Ru catalysts, also the Ru contents in catalyst materials are often determined. However, according to our knowledge there are only a couple of detailed studies with the principal aim of reliable determination of Ru content in catalyst materials. For example, the determinations of Ru in catalytic materials having carbon [3–6], alumina [7,8] or silica–alumina [8] as a support material have been studied. In one of these studies a fusion method employing KOH and KNO_3 was applied [6]. Traditionally, acid digestions on a hot plate have been carried out. For example concentrated HCl and mixtures of HCl and HNO_3 have been used for the digestion of Ru on carbon-supported catalysts [3–5], whereas mixtures of HCl and H_2SO_4 (with the addition of HF in the presence of silica) have been used for the digestion of Ru on alumina and silica–alumina supports [7,8].

It is well known that (metallic) Ru is very resistant to chemical attack [9]. Another problem encountered in Ru analytics is that oxidative conditions during the digestion stage may lead to Ru losses due to formation of volatile RuO_4. It has, for example, been found that Ru volatilizes as RuO_4 from boiling nitric acid solutions after an induction period. The length of the induction period was the shortest with the highest concentration of HNO_3 [10,11]. For this reason the use of a lower amount of nitric acid compared to the *aqua regia* composition (3:1 (v/v) HCl–HNO_3) in Ru digestions has been recommended [3,12]. When the HCl to HNO_3 ratio of 6:1 was used to digest carbon-supported Pt–Ru catalysts in open vessels on a hot plate, slightly higher recoveries and a little more reproducible results compared to *aqua regia* digestion were obtained [3]. On the other hand, Scaccia and Goszczynska [5] obtained similar results when they compared *aqua regia* and hydrochloric acid digestion in the determination of Ru in carbon-supported Pt–Ru catalysts.

Nowadays sample preparation in closed vessels (e.g. microwave-assisted digestion) is strongly favored over open vessel digestions due to the many advantages gained (e.g. digestion times are shortened and a smaller amount of corrosive acid vapors is liberated). Digestions in closed vessels with different acid mixtures have been applied in determinations of low concentrations of Ru and other platinum group elements, e.g. in geological and environmental materials [13–17].

Measurements of the Ru contents in digested catalyst samples have been done by using spectrophotometry [3,4,6], atomic absorption spectrometry (AAS) [5,6,8] and inductively coupled plasma optical emission spectrometry (ICP-OES) [7]. Also X-ray fluorescence spectroscopy (XRF) as a non-destructive analytical method, not requiring sample digestion, is a possible choice for the determination of Ru in catalyst materials. However, a large sample mass (~15 g) is usually needed in XRF analysis. In the

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development stage of catalyst materials the sample masses available for analytical determination may be more than ten-fold lower, thus excluding the use of XRF. The lack of suitable calibration materials may also represent a problem in XRF technique.

In this study different digestion methods for the determination of Ru in catalyst materials were investigated. The aim of this study was to achieve a complete Ru digestion with no losses. The Ru contents in the digested samples were determined with the ICP-OES technique. A fusion method with KOH–KNO_3 mixture and acid digestion methods with various HCl–HNO_3 mixtures were applied for the digestions of Ru in different catalyst materials. Previously these reagent mixtures had been applied for the determination of Ru only in carbon-supported catalysts [3–6]. The effect of experimental variables in microwave (MW)- and high pressure asher (HPA)-assisted acid digestions was tested in order to find the most suitable digestion conditions for Ru catalysts. The use of both MW- and HPA-assisted digestions created the opportunity to use large variations in digestion temperatures and times when studying the effects of these variables. Since no clear information was available on the dissolution properties of Ru from different Ru compounds present in the catalyst materials, the digestion efficiencies of the methods were evaluated by digesting metallic Ru powder as well as selected Ru compounds ($RuO_2 \cdot xH_2O$, anhydrous RuO_2 and $RuCl_3$).

2. Experimental

2.1. Instrumentation

A PerkinElmer Optima 5300 DV ICP-OES (PerkinElmer Inc., Waltham, MA, USA) was used to determine Ru (240.272 nm). The ICP-OES instrument was equipped with an AS-93plus autosampler, a Ryton double-pass Scott-type spray chamber and a Gem Tip Cross-flow pneumatic nebulizer. The instrumental parameters for ICP-OES were as follows: RF power 1.3 kW, nebulizer gas flow 0.8 L min^{-1}, auxiliary gas flow 0.2 L min^{-1}, plasma gas flow 15 L min^{-1} and sample uptake rate 1.5 ml min^{-1}. Normal resolution and axial mode of viewing were used in the measurements.

An HPA-S (Anton Paar GmbH, Graz, Austria) high-pressure asher with 90 ml quartz vessels and a CEM MARS 5X microwave oven (CEM Corp., Matthews, NC, USA) equipped with XP-1500 plus high pressure Teflon® TFM vessels (CEM Corp., 100 ml, maximum pressure 10 MPa and temperature 300 °C) were used in the acid digestions of the samples. The microwave oven was operated in a temperature-controlled mode. A programmable muffle furnace L5/11/B170 (Nabertherm GmbH, Lilienthal, Germany) was used for sample digestions with the fusion method.

2.2. Reagents and catalyst samples

Ultrapure water was purified with a Millipore Gradient (Millipore Corp., Billerica, MA, USA) water purification system. A commercial stock solution containing 1000 mg L^{-1} Ru in 10% HCl (VWR BDH Prolabo) was used for calibration of the ICP-OES. HCl (37–38%, J.T. Baker, Baker Analyzed), HNO_3 (65%, J.T. Baker, p.a.), HF (40%, Merck, p.a.), H_2O_2 (30%, J.T. Baker, Baker Analyzed), KNO_3 (Merck, p.a.), KOH (Merck, p.a.) and $K_2S_2O_8$ (Riedel-de Haën, p.a.) were used in the sample digestions. Ru powder (99.9%, −325 mesh, Alfa Aesar) and the following Ru compounds: $RuO_2 \cdot xH_2O$ (99.99%, Ru 54–58%, Alfa Aesar), anhydrous RuO_2 (99.95%, Ru min. 75.2%, Alfa Aesar) and anhydrous $RuCl_3$ (99.5%, Merck) were used to compare the digestion efficiencies of the digestion methods.

Three commercially available alumina-supported Ru catalysts and one commercially available carbon-supported Ru catalyst were analyzed in this study. The catalysts were 0.5% Ru on 3 mm alumina tablets (Alfa Aesar), 2% Ru on 1/8 in. alumina pellets (Alfa Aesar), 5% Ru on alumina (Aldrich) and 5% Ru on carbon powder (Engelhard). Ru contents of these catalysts are not certified. For the method comparison purposes a sub-sample was taken from each of the catalyst samples and ground prior to analysis, in order to ensure the homogeneity of samples. These sub-samples may, however, not be representative of the original Ru content of the analyzed catalysts. Sample homogenization was accomplished by using an agate mortar for 5% Ru on alumina and 5% Ru on carbon or using a ring rolling mill (Siebtechnik) for 2% Ru on alumina pellets and 0.5% Ru on alumina tablets. The samples were analyzed without drying.

2.3. Microwave digestion methods

Catalyst samples of 50–100 mg, or 5–10 mg of Ru powder or the Ru compounds were carefully weighed into the microwave digestion vessels. Digestions were carried out using two HCl–HNO_3 mixtures, either 6:1 (v/v) or 3:1 (v/v, *aqua regia*). For the digestions, 9 ml of HCl and 1.5 ml of HNO_3 or 7.5 ml of HCl and 2.5 ml of HNO_3 were added to the digestion vessels. The vessels were closed and the samples were digested in the microwave oven with a two-stage program (stage 1 – heating to 180 °C at 15 min; stage 2 – holding at 180 °C for 10 min). The solutions were carefully allowed to cool to room temperature prior to opening the vessels. The solutions were transferred to volumetric flasks and diluted to 50 ml with water. The samples were further diluted and their HCl concentration was adjusted to 2% (v/v) prior to the ICP-OES determination. If an undigested residue was present in the samples (e.g. in the case of carbon-supported catalysts), the residue was allowed to settle on the bottom of the vessel prior to the dilution.

2.4. High-pressure asher (HPA) digestion

For the HPA digestion 50–100 mg of the catalyst samples, or 5–10 mg of Ru powder and the Ru compounds were carefully weighed into the 90 ml quartz vessels. 6 ml of HCl and 1 ml of HNO_3 were added, the vessels were closed, set in the heating block and inserted into the pressure vessel of the HPA. The system was pressurized with nitrogen to 100 bar and a three-stage digestion program was run (program: stage 1 – rapid heating to 100 °C; stage 2 – heating from 100 °C to 300 °C at 30 min; stage 3 – holding at 300 °C for 180 min). After cool-down and depressurizing steps the samples were diluted to 50 ml with water in the quartz vessels. The solutions were further diluted and their HCl concentration was adjusted to 2% (v/v) prior to the ICP-OES determination. If an undigested residue was present in the samples, the residue was allowed to settle on the bottom of the vessel prior to the dilution.

2.5. Digestion by a fusion method

The fusion method was adapted from the article written by Taddia and Sternini [6]. 50–100 mg of the catalyst samples or 5–15 mg of Ru powder or the Ru compounds were weighed to nickel crucibles. Carbon-supported catalysts were ashed in their crucibles by inserting them into a preheated muffle furnace (200 °C) and by heating the furnace to 450 °C in 2 h. Other samples were directly moved to the next stage, where 0.38 g KOH and 0.65 g KNO_3 were added to the crucibles and mixed with the samples. The crucibles were covered by lids and inserted into a cold muffle furnace. The furnace was heated to 450 °C in 60 min and the temperature was further held at 450 °C for 60 min. After cooling down overnight (approximately to 30 °C), 50 mg of $K_2S_2O_8$ was added to stabilize the formed Ru compounds (mainly RuO_4^{2-}) and the melts were dissolved with a minimum amount of ultrapure water. 10 ml of 1 M KOH was added and the solutions were transferred into 50 ml volumetric flasks and filled to the mark with ultrapure water. To convert Ru to a stable chloro-complex ($RuCl_6^{2-}$), 10 ml aliquots of these solutions were taken and slowly dropped (with careful mixing) into 25 ml volumetric flasks containing 5 ml of concentrated HCl. The solutions were diluted to 25 ml with ultrapure water. The solutions were further diluted and their HCl concentration was adjusted to a minimum of 2% (v/v), depending on the calibration used, prior to the ICP-OES determination. When high (more than 150-fold) dilutions of the solutions were not used in the measurements, a suitable amount of the reagent blank solution, obtained by fusion, was added to the calibration standards.

3. Results and discussion

3.1. Use of external calibration in the ICP-OES determination

The calibration standard solutions used in this study were diluted from a commercial Ru stock solution (1000 mg L^{-1}). The sample digestion methods were, however, assumed not to produce exactly similar solutions, when concerning, e.g., the chemical state of Ru in the samples or the matrix of the samples. In order to test the suitability of this external calibration approach, a couple of preliminary tests concerning the calibration of the ICP-OES instrument (Ru 240.272 nm) were run.

A color difference was observed between external calibration standards (orange) and MW-digested sample solutions (pink). Based on this observation, it was assumed that different Ru species existed in these solutions. Therefore, the existence of different behaviors during ICP-OES measurement (e.g. matrix effects during nebulization) was tested by measuring calibration curves using both undigested and MW-digested calibration standards. For that, the calibration standards were digested using *aqua regia*. *Aqua regia* was selected because it has higher oxidizing power when compared to 6:1 HCl–HNO_3 mixture and thus it was expected to have a greater effect on the results. The observed difference between the slopes was only 3%. As there was no statistical difference between the slopes of the linear calibration functions (t-test; t_{calc} 0.66 < t_{crit} 2.78, $p=0.05$), the (undigested) external calibration was well-suited for these analyses.

The samples digested by the fusion method contain high levels of dissolved salts, which may cause matrix effects in the ICP-OES determination. Because of this, matrix-matched calibration standards and aqueous calibration standards containing HCl were compared. The matrix-matched calibration standards corresponding to 3-fold and 100-fold sample dilutions were studied (Fig. 1). The slopes of the matrix-matched calibration curves were 32% and 9% higher than the slopes of the aqueous calibration curves. A statistically significant difference in the slopes of the linear calibration functions was observed using a t-test (t_{calc} 21.56 and 12.25 > t_{crit} 2.45, $p=0.05$). Thus, the results showed that it is important to match the matrix of the calibration solutions and samples if high dilutions (approximately greater than 150-fold) cannot be used.

3.2. Investigation of the microwave-assisted acid digestion method using a factorial design

A 6:1 mixture of HCl and HNO_3, previously used by Balcerzak et al. [3,4] in the open vessel digestions of Ru in carbon-supported catalysts, was selected as a basis for the microwave digestion experiments. Due to the use of closed Teflon vessels, mixtures of sulfuric acid (high boiling point), used by Fabec and Ruschak [7,8] for digestions of Ru in alumina- and silica–alumina-supported catalysts, were not considered as a choice as they might have damaged the MW digestion vessels. The effects of selected experimental variables, expected to have the largest effects on the Ru recovery with the MW digestion method, were studied with a full two-level factorial design (2^4). For example, an increased recovery of several elements in the digestion of catalyst materials was observed earlier when the digestion temperature was increased [18]. As ground 0.5% Ru on alumina was used as a sample material in the experiments, HF was included in the reagent mixture to enhance the digestion of the alumina support (to ensure that all Ru is extracted from the support material). H_2O_2 was added to increase the oxidizing nature of the acid mixture in order to test if Ru volatilizes as a tetroxide during MW digestions. Volatile RuO_4 might possibly escape when the vessels are opened. The factors and their levels are summarized in Table 1. The total volume of HCl–HNO_3 mixture used for all of the digestions was 10.5 ml (9 ml HCl + 1.5 ml HNO_3). The ramp time from room temperature to digestion temperature was also held constant (15 min).

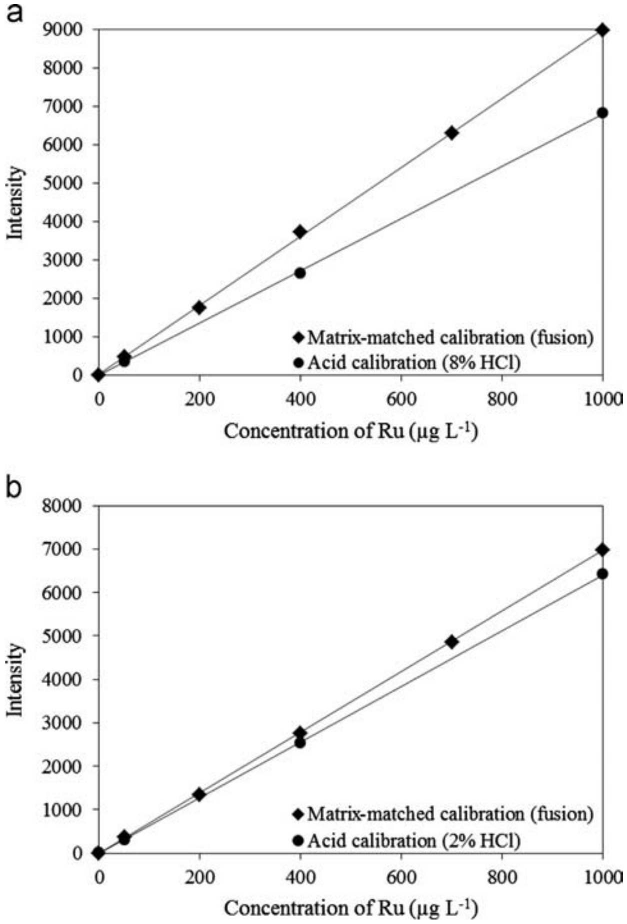

Fig. 1. Calibration curves obtained with matrix-matched standards (fusion method using KOH–KNO_3) and aqueous calibration solutions (HCl) corresponding to (a) 3-fold and (b) 100-fold sample dilutions. The calibration equations are (a) $y=8.98x+13.30$ for matrix-matched calibration and $y=6.81x-19.91$ for acid calibration, and (b) $y=6.98x-15.35$ for matrix-matched calibration and $y=6.42x-10.37$ for acid calibration.

The Ru content of the digested samples varied between 0.45% and 0.48%. No significant differences in the determined Ru contents between the digestion conditions were observed. For further digestions a temperature of 180 °C was selected. The digestion time was held at minimum (10 min) in order to maximize the advantage of the rapidness of the MW digestion method. HF was not used since it was not proven to have any significant influence

Table 1
Factors and their levels in the used 2^4 full factorial design.

Factor	Level		
	Low	Medium	High
Temperature (°C)	140	170	200
Time (min)	10	20	30
HF (ml)	0	0.25	0.5
H_2O_2 (ml)	0	1	2

Table 2
Recoveries obtained for different Ru compounds (%, ± sd) using various digestion methods ($n=3$).

Compound	Digestion method			
	Fusion	HPA, 6:1 HCl–HNO_3	MW, 6:1 HCl–HNO_3	MW, *aqua regia*
$RuO_2 \cdot xH_2O$	94 ± 2[a]	97 ± 1	100 ± 2	98 ± 1
Anhydrous $RuCl_3$	96 ± 4[b]	84 ± 8	< 1	< 1
Ru powder	93 ± 4[a]	24 ± 2	< 1	< 1
Anhydrous RuO_2	94 ± 2[a]	< 1	< 1	< 1

[a] $n=4$.
[b] $n=7$.

on the results. The results also indicated that the volatilization of Ru is not a concern with MW digestions, as no volatilization losses were observed even if H_2O_2 was used. However, it is possible that H_2O_2 may not have had an expected influence on the oxidation efficiency of the acid mixture, because its rapid decomposition may have occurred in contact with Ru [19].

3.3. Comparison of the digestion methods for Ru compounds

In the absence of certified reference materials, different Ru compounds, expected to be present in catalyst samples, were used to investigate the digestion efficiencies of the different methods. The Ru compounds were selected according to the results of Li et al. on their X-ray photoelectron spectroscopic (XPS) characterization of Co_3O_4-supported Ru catalysts [20]. The selected compounds were hydrous ruthenium oxide ($RuO_2 \cdot xH_2O$), anhydrous RuO_2, metallic Ru and anhydrous $RuCl_3$. The compounds were digested using all of the described digestion methods: fusion method, HPA method and two MW methods.

The recoveries of the Ru compounds (Table 2) were calculated by assuming the Ru contents of the samples to be 55.86% for $RuO_2 \cdot xH_2O$ (manufacturer's certificate of analysis), 48.72% for $RuCl_3$, 100% for Ru powder and 75.2% for anhydrous RuO_2 (manufacturer's certificate of analysis). The studied methods appeared to have different digestion efficiencies as only $RuO_2 \cdot xH_2O$ was fully digested by all of the methods. The recoveries obtained with the fusion method were good also for the other Ru compounds, whereas the recoveries obtained with HPA or MW methods were significantly lower. In addition, clear undigested residues were observed after HPA and MW digestions.

$RuCl_3$, Ru powder and anhydrous RuO_2 were not digested to a significant extent with the MW-assisted methods. The digestion efficiency of the HPA method was better when compared to the MW methods, as $RuCl_3$ and Ru powder were partially digested and only anhydrous RuO_2 was completely resistant to the HPA digestion. When the 6:1 HCl–HNO_3 mixture was used in MW and HPA digestions, the results indicated that elevating the digestion temperature from 180 °C to 300 °C and extending the digestion time from 10 min to 180 min favored the digestion of these Ru compounds.

The results also indicate that problems may be encountered if the Ru content of a catalyst sample is analyzed after the catalyst has been annealed to a high temperature (e.g. to activate the catalysts). In such a case, amorphous $RuO_2 \cdot xH_2O$ might convert (at least partially) to crystalline RuO_2 [21]. This transformation might lead to incomplete dissolution of Ru in catalyst samples with MW (or HPA) techniques. However, it should be noted that the particle size of the Ru compounds in catalyst samples is probably smaller than that in the Ru compounds digested in this study, which might favor the dissolution of these resistant compounds in catalyst samples. It has also been stated that the dispersion of Ru on the surface of a support material favors the dissolution of Ru [12].

3.4. Comparison of the digestion methods for catalyst materials

Ruthenium contents in three alumina-supported catalysts and in one carbon-supported catalyst were determined using all of the digestion methods studied. When ruthenium contents of unground samples were determined, it was noted that the repeatability was poor, with RSDs varying from 13% to 40%, indicating sample inhomogeneity. Thus, to ensure the comparability of the results between the digestion methods, the determinations of Ru in these catalysts were made from ground (homogenized) subsamples taken from the original samples.

The results obtained for the homogenized sub-samples using the different digestion methods are in good agreement with each other (Table 3). When compared to the results obtained for the pure Ru compounds (Table 2), these results indicate that Ru in the catalyst samples was mainly in an easy-to-dissolve chemical form, such as $RuO_2 \cdot xH_2O$. However, the determined Ru contents were lower than expected. This indicates that, due to the sample homogenization step performed prior to the digestions, the subsamples analyzed were probably not representative of the original samples. In addition, the catalyst samples may have contained low amounts of Ru species resistant to the digestion methods studied, although the results in Table 2 showed that the digestion efficiency of the fusion method was good for all of the studied Ru compounds.

When the digestion method for a particular set of Ru catalyst samples is selected, the fusion method would seem to be an obvious choice due to its high digestion efficiency. On the other hand, MW digestion is much faster and appeared to give good recoveries for the studied catalyst samples and $RuO_2 \cdot xH_2O$. Furthermore, both acid mixtures in MW digestions gave similar results, indicating that both of them are equally suitable for digestion of the studied catalyst materials. However, prior to applying MW digestion to unknown catalyst materials, a reliable reference method should be used to test the completeness of the Ru dissolution.

3.5. Method performance

The instrumental limit of detection (LOD) for the ICP-OES determination of Ru in acidic solutions, based on blank values measured at different days (3s, $n=14$), was 8 μg L^{-1}. Similarly, LOD for the determination of Ru in matrix-matched (fusion) solutions was 10 μg L^{-1} (3s, $n=5$). Consequently, dilution of the samples prior to the analysis was possible in order to reduce the acid concentration as well as the amount of concomitants in the sample solutions. The calibration curve was linear at least up to 50 mg L^{-1}.

To the best of our knowledge, there is no suitable certified reference material for the determination of Ru in catalyst materials. Thus, the accuracies of the methods were calculated using the

Table 3
Ru found (%, ± sd) in catalysts using different digestion methods ($n=3$).

Sample	Digestion method				
	Fusion[a]	HPA, 6:1 HCl–HNO_3[a]	MW, 6:1 HCl–HNO_3[a]	MW, *aqua regia*[a]	Un-ground, MW, 6:1 HCl–HNO_3
0.5% Ru on alumina	0.46 ± 0.01	0.46 ± 0.01	0.45 ± 0.04	0.49 ± 0.01	0.55 ± 0.07
2% Ru on alumina	1.59 ± 0.04	1.52 ± 0.09	1.65 ± 0.05	1.62 ± 0.01	1.6 ± 0.6[b]
5% Ru on alumina	2.6 ± 0.1	2.96 ± 0.03	2.76 ± 0.04	2.71 ± 0.06	4.0 ± 0.5[b]
5% Ru on carbon	4.06 ± 0.07[c]	4.2 ± 0.2[c]	4.1 ± 0.2	4.06 ± 0.08	–

[a] In order to ensure the homogeneity of analyzed samples, a sub-sample was taken from each of the catalysts and ground. The homogenized sub-samples may not be representative of the original Ru content of the catalysts.

[b] $n=2$.

[c] $n=4$.

recoveries obtained for Ru in the digestions of $RuO_2 \cdot xH_2O$ (Table 2). The recoveries of Ru from this compound were between 92% and 97% for the fusion method ($n=4$), between 97% and 98% for the HPA digestion ($n=3$) and between 98–101% and 97–100% for the MW digestion methods ($n=3$), 6:1 HCl–HNO_3 and *aqua regia*, respectively. Thus, acceptable Ru recoveries were obtained with all the studied methods when $RuO_2 \cdot xH_2O$ was digested. Furthermore, the results indicate (Table 2) that by the fusion method the accuracy is acceptable also for other Ru compounds ($RuCl_3$, Ru powder and anhydrous RuO_2).

Repeatabilities for the different digestion methods were calculated (as RSDs) on the basis of the results obtained for the catalyst samples (Table 3) and $RuO_2 \cdot xH_2O$ (Table 2). In the case of the catalyst samples repeatability was estimated to be 3% for the fusion method, 4% for the HPA digestion, and 5% and 2% for the MW digestion methods, 6:1 HCl–HNO_3 and *aqua regia*, respectively. The inhomogeneity of the sample material, however, may have had an influence on these values. Another estimation was made with $RuO_2 \cdot xH_2O$ as it was the only Ru compound fully digested by all of the methods. In this case repeatability was estimated to be 3% for the fusion method, 1% for the HPA digestion and 2% for both the microwave digestion methods. Based on these values, repeatabilities of the methods are adequate.

4. Conclusions

The studied MW-assisted digestion methods (HCl–HNO_3 mixtures, 6:1 (v/v) and 3:1 (v/v, *aqua regia*)) are well-suited for the sample preparation of catalyst materials analyzed in this study. However, the suitability of the MW-assisted methods may depend on the chemical form of Ru in the catalyst samples. The results showed that MW-assisted acid digestion was the least efficient among the tested methods in the digestions of anhydrous $RuCl_3$, Ru powder and anhydrous RuO_2. Good recoveries for these compounds were obtained only by using the fusion method (KOH–KNO_3). Thus, according to our results, careful consideration is needed when selecting the digestion method for Ru in catalyst materials.

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