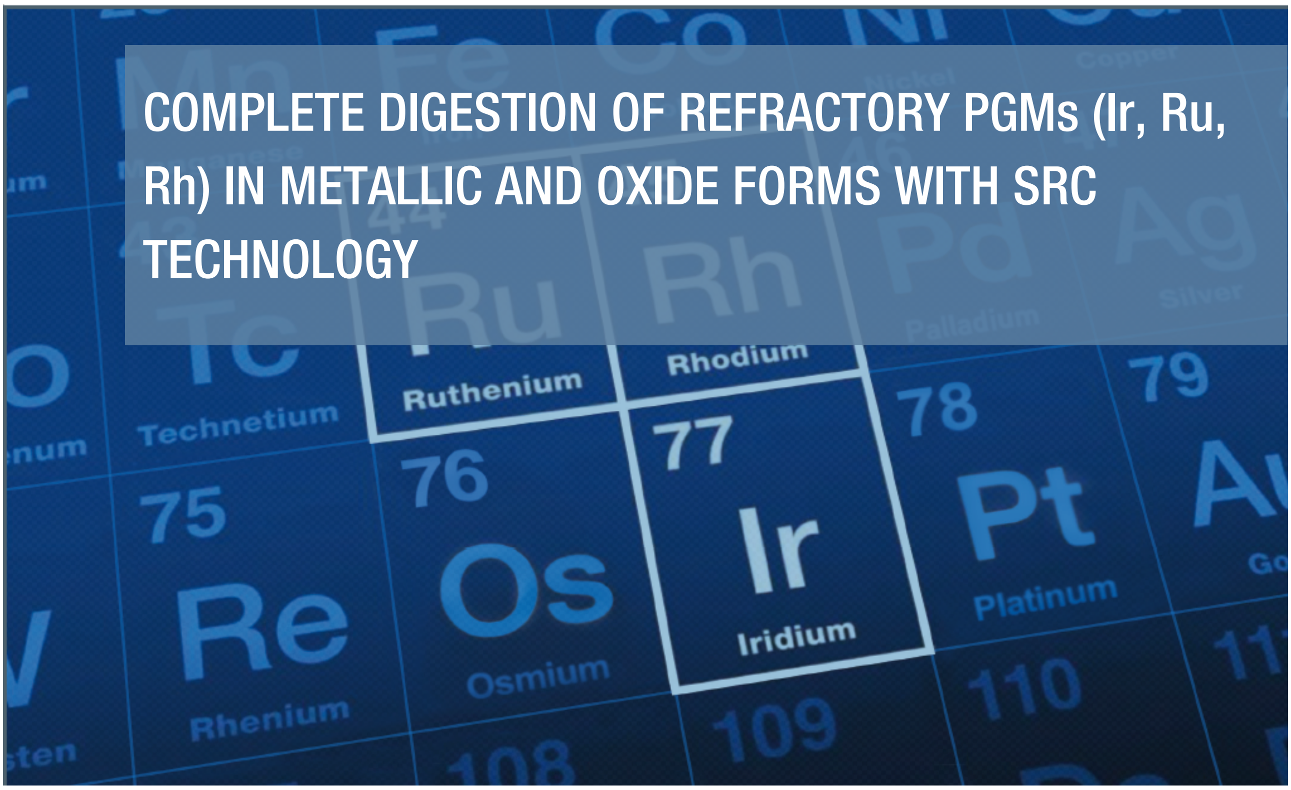
COMPLETE DIGESTION OF REFRACTORY PGMs (Ir, Ru, Rh) IN METALLIC AND OXIDE FORMS WITH SRC TECHNOLOGY



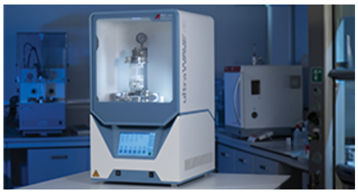
Advanced digestion of Iridium, Ruthenium, and Rhodium, including oxide forms, requires extreme and corrosive acid conditions. ultraWAVE 3 SRC technology delivers complete dissolution >99% with high durability, safety, and reproducibility

| INTRODUCTION

Platinum group metals (PGMs) – specifically Iridium (Ir), Ruthenium (Ru), and Rhodium (Rh) – are critical to high-value industries such as catalysis, electronics, high-performance coatings, and electrochemical applications. Their rarity, value and exceptional stability make them indispensable, but these properties make them extremely challenging to dissolve for chemical analysis.[1]

Both metallic and oxide forms of Ir, Ru, and Rh display extraordinary chemical inertness, with oxides being particularly refractory. [2] Dissolving these materials requires aggressive acid mixtures, such as concentrated hydrochloric and perchloric acids, which are highly corrosive to standard digestion equipment. Operating safely and effectively under such conditions demands an advanced and exceptionally robust system, capable of maintaining long-term performance while withstanding chemical attack. [3]

Milestone's ultraWAVE 3 with Single Reaction Chamber (SRC) technology provides these capabilities in a single, high-capacity platform. [4] By combining precise control of temperature, pressure, and atmosphere, the ultraWAVE 3 can reach up high temperature and pressure, enabling complete dissolution of Ir, Ru, and Rh while ensuring low procedural blanks. Its advanced design and chemically resistant construction allow it to operate reliably under highly aggressive acid conditions, maintaining performance and durability over extended use.



This application report details the optimized digestion method for PGMs, including oxide reduction strategies, demonstrates >99% dissolution efficiency, and explores alternative acid mixtures for laboratories with restricted access to perchloric acid.

EXPERIMENTAL

DIGESTION INSTRUMENT

Milestone ultraWAVE 3 system equipped with:

- Magnetic stirring
- High-purity nitrogen gas (grade 5.0) for reactor pressurization
- Cooling chiller, 1000 W capacity
- 5-position rack with 100 mL QS-100 quartz vials
- Quartz covers
- Magnetic stirring bars, Ø 10 × 20 mm

Accessories for alternative oxidizing agents (H_2O_2 and $KClO_3$)

- 6 mL borosilicate glass vials
- TFM Stirring bars (cross shape) Ø 12/33 mm

HYDROGENATION SETUP

When Iridium or Ruthenium samples are present in oxide form, a pre-reduction step using hydrogen is required to convert them into their metallic state prior to acid mineralization.

- Tubular muffle furnace for hydrogenation
- Quartz boats for sample containment
- Gas cylinder supplying a 1.5% H_2 / 98.5% N_2 mixture, connected to the furnace

REAGENTS

- HCl, hydrochloric acid, 37%, ACS reagent (Sigma-Aldrich)
- $HClO_4$, perchloric acid, 70%, ACS reagent, technical grade (Sigma-Aldrich)
- H_3PO_4, orto-phosphoric acid, 85%, ACS reagent (Sigma-Aldrich)
- H_2O_2, Hydrogen peroxide, 30%, ACS reagent (Sigma-Aldrich)
- $KClO_3$, Potassium Chlorate, ACS reagent >99.0% (Sigma-Aldrich)
- Deionized water

MICROWAVE METHOD

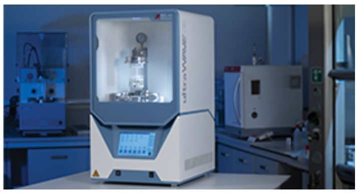
Below are reported the setting for the microwave program with UW3:

Step	Time (min)	Power (W)	T1 (°C)	T2 (°C)	P (bar)
1	2	1500	120	60	90
2	6	1500	200	60	90
3	12	1500	260	60	130
4	45	1500	260	60	130

Stirrer speed	90%
N_2 Load	60 bar
Cooling valve opening	> 25 °C
Release pressure	< 50 °C
Stirrer	90%

QUANTIFICATION

Digestion efficiency was determined using a gravimetric approach, a method recognized for its accuracy and reliability in



quantifying residual solids after mineralization. This procedure requires dedicated laboratory equipment, including:

- Vacuum filtration system for 47 mm membranes
- Electric diaphragm vacuum pump
- Sartorius cellulose nitrate membrane filters, 0.45 µm pore size
- Analytical balance with 5-digit capability (0.00000 g); for better readability of the results, all weights in this document will be expressed in milligrams (mg).

RESULT AND DISCUSSION

For this study, different Ir, Rh and Ru samples were used, coming from two different suppliers and aged differently.

For confidentiality, the actual company names will not be disclosed; instead, they will be referred to as:

- Supplier A
- Supplier B

Iridium and Ruthenium samples:

- Lot A1: sample form producer A
- Lot A2: sample form producer A but different production batch
- Lot B1: sample form producer B
- Lot B2: oxide forms of samples from producer B

Rhodium samples:

- Lot A1: Sample from producer A unknown sample difficult to fully dissolve with unknown composition
- Lot A2: Sample from producer A but freshly produced with known composition
- Lot B2: oxide forms from producer B

To test these sample a QS-100 quartz vials were used adding 15 mL of hydrochloric acid (HCl, 37%) and 0.5 mL of perchloric acid ($HClO_4$, 65%) in each vial. Magnetic stirring bar is used in all the test performed in this study.

Below a table to summarize the results of tests

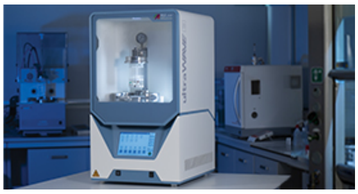
Table 1. Gravimetric results and digestion efficiency using $HClO_4$ (Protocol A)

Samples	Sample ID	Initial sample amount (mg)	Residue on filter (mg)	Digestion efficiency (%)
Iridium	Lot A1	267.08	< 0.01	> 99.9
	Lot A2	251.36	< 0.01	> 99.9
	Lot B1	262.54	0.32	99.8
Iridium Oxide	Lot B2	244.60	236.58 (0.03) [a]	3.3 (> 99.9) [a]
Ruthenium	Lot A1	265.30	< 0.01	> 99.9
	Lot A2	255.30	< 0.01	> 99.9
	Lot B1	249.93	< 0.01	> 99.9
Ruthenium Oxide	Lot B2	259.29	256.21 (0.10) [a]	1.2 (> 99.9) [a]
Rhodium	Lot A1	695.30	442.9	36.3 [b]
	Lot A2	704.89	< 0.01	> 99.9
Rhodium oxide	Lot B2	237.69	3.12	98.7

[a] Results obtained with pre-hydrogenation step

[b] See the next session for more details on how to achieve complete dissolution for such sample

As shown in Table 1, the tested digestion protocol enabled complete dissolution of Ir, Rh, and Ru in their metallic form, but not in



their oxide form. For oxide species, a preliminary hydrogenation step is required prior to acid digestion in the ultraWAVE 3. Table 1 clearly demonstrates that when this reduction step is applied to convert the oxide into its metallic state, complete dissolution of the target element is achieved.

In this study, we also propose an alternative approach to the use of perchloric acid ($HClO_4$), as its handling and storage can present significant challenges for some laboratories. Furthermore, due to the extreme chemical resistance of these metals, not all metallic forms exhibit the same reactivity under identical conditions. This variability is typically influenced by the production process and by the natural aging of the material itself. For this reason, an alternative reagent mixture is proposed, which can be applied when the primary protocol does not achieve complete dissolution.

Defining the $HClO_4$ based procedure as *Protocol A*, the following alternative reagent mixtures are proposed:

- *Protocol B:* 20 mL HCl + 1.5 g $KClO_3$
- *Protocol C:* 20 mL HCl + 3 mL H_2O_2

Both protocol B and C require the addition of $KClO_3$ or respectively H_2O_2 into a small test tube which is then placed into the QS-100 quartz vial.

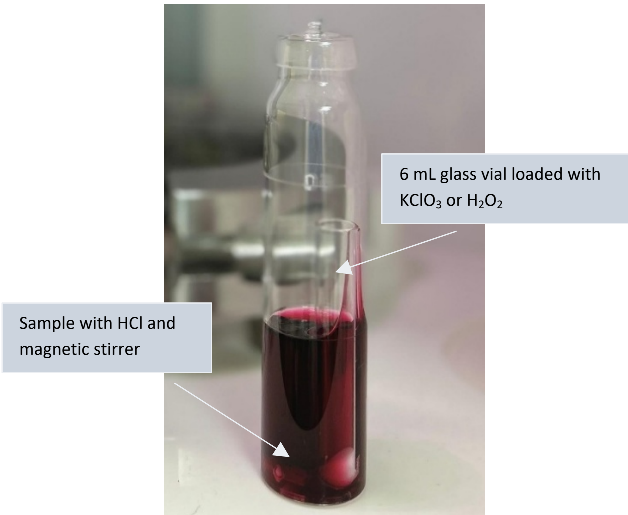


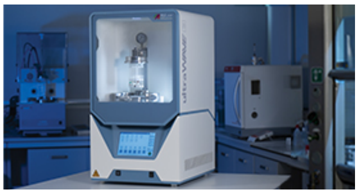
Table 2. Gravimetric results and digestion efficiency using $KClO_3$ (Protocol B)

Samples	Sample ID	Initial sample amount (mg)	Residue on filter (mg)	Digestion efficiency (%)
Iridium	Lot A1	242.59	< 0.01	> 99.9
Ruthenium	Lot A1	260.12	< 0.01	> 99.9
Rhodium	Lot A2	496.97	< 0.01	> 99.9

As reported in Table 2, the use of $KClO_3$ could be a valide alternative to $HClO_4$. Clearly, analytical consideration on the scope of the analysis must be taken into account since using $KClO_3$ enrich the digested solution of K^+ and generally $KClO_3$ is not pure as the $HClO_4$.

Table 3. Gravimetric results and digestion efficiency using H_2O_2 (Protocol C)

Samples	Sample ID	Initial sample amount (mg)	Residue on filter (mg)	Digestion efficiency (%)
Iridium	Lot A1	249.22	17.93	92.8
Ruthenium	Lot A1	255.27	49.64	80.6
Rhodium	Lot A1	506.77	< 0.01	> 99.9
	Lot A2	498.32	1.02	> 99.9
	Lot A2	718.07	6.29	99.1



Result obtained using the mixture HCl/H_2O_2 were shown in Tabel 3, with the evidence that this mixture can be highly effective for some type of Rhodium sample, enabling high dissolution yield while avoiding the use of $HClO_4$. This approach can also allow the digestion of higher sample amounts (up to 700 mg).

CONCLUSION

In this study, digestion was considered complete only when at least 99% of the sample mass was brought into solution. Using the optimized ultraWAVE 3 *Protocol A*, complete dissolution was achieved for Iridium, Ruthenium, and Rhodium in their metallic forms. The recommended sample masses for these metals are: Ir – 250 mg, Ru – 200 mg, and Rh – 500 mg. For Rhodium oxide, 200 mg is suggested, with the essential requirement of a pre-reduction step to the metallic form prior to digestion.

Table 4. Maximum sample size for each metal

Type of sample	Sample amount
Iridium[a]	250 mg
Ruthenium[a]	200 mg
Rhodium	500 mg
Rhodium oxide	200 mg

[a] Oxide forms require a reduction step before digestion

For alternative digestion methods (*Protocol B and C*), the recommended quantities are the same. The choice of the appropriate reagent depends not only on the type of sample being processed (as demonstrated in the case of Rhodium), but also on the specific needs and operational context of the laboratory. Important to consider that the H_2O_2 was not proven to be effective for Iridium and Ruthenium samples.

See the below table for a fast check of which type of chemical approach was effective vs sample type.

Table 5. Reagents successfully used for digestion of different metal samples

Type of sample	HClO4	$KClO_3$	H_2O_2
Iridium[a]	✓	✓	-
Ruthenium[a]	✓	✓	-
Rhodium	✓	✓	✓
Rhodium oxide	✓	-	-

[a] Oxide forms require a prior reduction step before digestion

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