Determination of Rhodium in Catalyst Oil and Aqueous Samples Using the Agilent 710 ICP-OES

Application Note

Energy and Fuels

Author

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Introduction

A series of oil catalyst samples and an unknown aqueous sample were supplied for analysis. The rhodium content in these samples was determined using the Agilent 710 ICP-OES axially viewing ICP-OES. The oil catalyst samples were prepared using microwave digestion.

The axially viewing ICP-OES was selected for measurement as the expected rhodium content was low, and this system provides better sensitivity than that achieved by the radially viewed configuration, independent of the complexity of the sample medium [1]. The improvement in sensitivity with the axially viewed configuration is typically up to a 20 fold improvement in detection limits [1,2].

Instrumentation

All sample measurements were performed on a Agilent 710 ICP-OES axially viewing ICP-OES with simultaneous CCD detection.

The Agilent 710 ICP-OES is a simultaneous ICP-OES featuring an Echelle polychromator and a megapixel CCD detector, which provides the benefit of simultaneous measurement and continuous wavelength coverage over the range from 177 to 785 nm. The polychromator can be purged with a low flow of either argon or nitrogen for improved detection capability when measuring emission lines at low UV wavelengths.

The system is supplied as standard with a 3-channel peristaltic pump and manual pressure control of the nebulizer gas flow. The standard sample introduction system consists of a glass concentric nebulizer (Conikal) and a glass cyclonic spray chamber. Agilent ICP Expert II software was used for instrument operation. The operating parameters of the system are listed in Table 1.

Table 1. Instrument Operating Parameters

Condition	Setting
Power	1.15 kW
Plasma gas flow	16.5 L/min
Auxiliary gas flow	1.5 L/min
Spray chamber type	Glass cyclonic (single-pass)
Torch	Standard one piece axial torch
Nebulizer pressure	200 kPa
Nebulizer type	Conikal
Replicate read time	5 s
Auto-integration	On
Number of replicates	3
Stabilization time	15 s
Pump tubing	Sample: white-white (1.05 mm ID) Waste: blue-blue (1.65 mm ID) Buffer/Reference element: black-black (0.76 mm ID)
Sample uptake delay time	15 s
Pump speed	15 rpm
Rinse time	10 s
Fast pump	On
Background correction	Fitted

Sample Preparation and Instrument Conditions

All chemicals and reagents used were of high purity grade.

- HNO_3, Ultrapure, 60%, Merck.
- 40 and 100 mg/L Rh standard solutions as supplied by the client.
- Milli-Q water with resistivity less than 18 Mohm–cm^{-1}.

The oil catalyst samples were prepared using a microwave digestion system with temperature and pressure control (Shanghai EU Microwave Chemistry Technology Co. Ltd. model WX-4000).

0.3 g of sample was accurately weighed and placed into a digestion vessel. The digestion vessel was heated on a conventional hot plate at 80 °C for approximately 20 minutes. The aim of this sample pre-treatment was to remove the volatile organic components from the sample. The digestion vessel was removed from the hot plate and allowed to cool.

This solution was quantitatively transferred into a microwave digestion vessel and 4 mL of nitric acid (HNO_3) was added. The digestion vessel was sealed and placed into the microwave digestion system. The microwave digestion method used is summarized in Table 2.

Table 2. Microwave Digestion Settings

Step	Temperature (°C)	Pressure (atm.)	Time (min.)
1	130	10	5
2	160	16	5
3	180	20	5
4	200	25	5

The digestion vessels were removed from the microwave digestion system and left to cool to room temperature. The digest was transferred to a volumetric flask and diluted on a mass basis. A summary of the initial sample weights, the final weights after dilution and observations on the digest obtained are summarized in Table 3.

As the expected concentration of rhodium in the aqueous sample was around 60 mg/L, no preparation was required for analysis. The aqueous sample was measured directly.

All the prepared samples were analyzed directly for rhodium.

Table 3. Actual Sample Weights Used for Digestion Together with Observations on the Samples Before and After Microwave Digestion

No.	Sample ID	Sample type	Expected Rh concentration	Observations	Sample weight (g)	Weight of predetermined volume (g)	Digest obtained
1	Q22321 2007-08-04	Oil catalyst	Very low	Light yellow, transparent oil sample with pungent odor	0.3033	23.8461	Clear
2	Q22321 2007-08-05	Oil catalyst	Very low	Light yellow, transparent oil sample with pungent odor	0.3260	27.5567	Clear
3	Q22321 2007-08-06	Oil catalyst	Very low	Light yellow, transparent oil sample with pungent odor	0.3442	23.2292	Clear
4	Q22321 2007-08-07	Oil catalyst	Very low	Light yellow, transparent oil sample with pungent odor	0.3386	22.7784	Clear
5	Q22321 2007-08-08	Oil catalyst	Very low	Light yellow, transparent oil sample with pungent odor	0.3043	24.2429	Clear
6	Q22321 2007-08-09	Oil catalyst	Very low	Light yellow, transparent oil sample with pungent odor	0.3380	24.9658	Clear
7	Q22321 2007-08-10	Oil catalyst	Very low	Light yellow, transparent oil sample with pungent odor	0.3025	22.2151	Clear
8	Q21011 2007-08-06	Oil catalyst	Est. 100-200 mg/L	Yellow, transparent oil sample with pungent odor	0.3096	52.3151	Light yellow color, but basically clear
9	Rhodium acetate solution	Aqueous solution	Est. 60 mg/L	Light yellow, transparent sample	N/A	N/A	N/A

Calibration Solutions

Conventional aqueous Rh standard solutions of 40 and 100 mg/L were provided by the client together with the samples.

For the determination of the aqueous sample, which was expected to be at a concentration of 60 mg/L, these standard solutions were used directly to calibrate the instrument.

For the determination of the digested oil samples, for which the Rh content was expected to be low, these standard solutions were diluted by a factor of 10 to concentrations of 4 and 10 mg/L respectively.

Results and Discussion

The calibration graphs obtained are shown in Figures 1 and 2.

The weight/dilution corrected sample results are listed in Table 4. These results have been converted back to report the actual rhodium content contained in the original samples. This takes into account the sample weight used for digestion and the applied dilution ratio during preparation.

The measured concentrations for rhodium in a number of the samples were close to the calibration blank solution. Accordingly, these results have been reported as “Not Detected” (ND).

Signal traces for the measured solutions where the Rh content could be quantified are included in Figures 3 to 5.

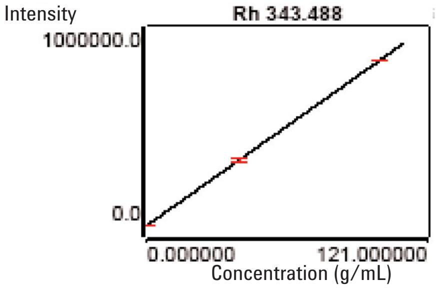

Figure 1. Calibration graph used for the determination of the aqueous sample at the Rh 343.488 nm emission line.

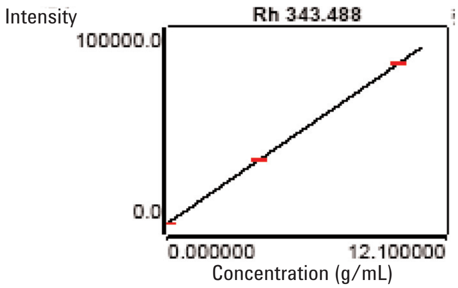

Figure 2. Calibration graph used for determination of the digested oil catalyst samples at the Rh 343.488 nm emission line.

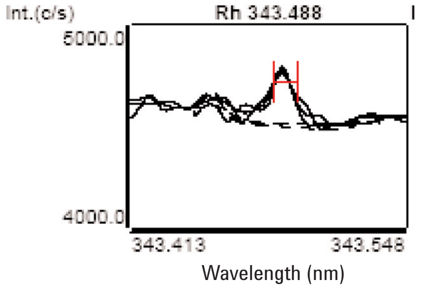

Figure 3. Signal trace for oil sample Q22321 2007-08-07.

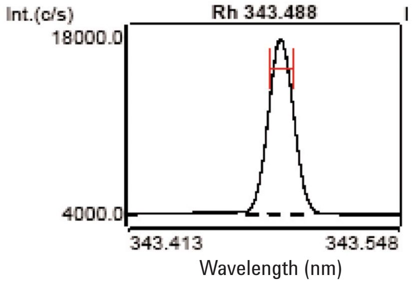

Figure 4. Signal trace for oil sample Q21011 2007-08-06.

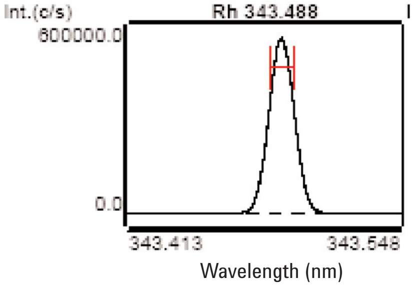

Figure 5. Signal trace for the rhodium acetate aqueous solution.

Table 4. Measured Rhodium Concentrations in Each of the Samples

Sample Type	Sample ID	Expected Rh Concentration (mg/L)	Measured Rh Concentration (mg/L)	Precision (% RSD)
Oil samples	Q22321 2007-08-04	Very low	ND	N/A
	Q22321 2007-08-05	Very low	ND	N/A
	Q22321 2007-08-06	Very low	ND	N/A
	Q22321 2007-08-07	Very low	3.08	4.15
	Q22321 2007-08-08	Very low	ND	N/A
	Q22321 2007-08-09	Very low	ND	N/A
	Q22321 2007-08-10	Very low	ND	N/A
	Q21011 2007-08-06	Est. 100–200 mg/L	216.20	0.197
Aqueous samples	Rhodium acetate	Est. 60 mg/L	55.26	0.842

Conclusion

Using the Agilent 710 ICP-OES axially viewing ICP-OES, it was possible to determine the rhodium content in both the oil catalyst and the aqueous samples without interferences. The oil catalyst samples were prepared using a microwave digestion system with temperature and pressure control. The digests obtained were clear, confirming complete digestion. The method demonstrated good results, although the Rh concentration in most samples was not detectable.

The results demonstrate this method can be readily applied to the routine determination of rhodium in oil catalyst and aqueous samples.

References

1. F.V. Silva, L.C. Trevizan, C.S. Silva, A.R.A. Nogueira and J.A. Nobrega, Evaluation of inductively coupled plasma optical emissions spectrometers with axially and radially viewed configurations, Spectrochim. Acta, 2002, 57B, 1905.
2. I.B. Brenner and A.T. Zander, Axially and radially viewed inductively coupled plasmas – A critical review, Spectrochim. Acta, 2000, 55B, 1195.

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