Application Note

Limits of Detection Obtained by ICP-OES in 10 g/L Rhodium

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1 Introduction

The analysis of impurities in Rhodium samples requires an instrument with high resolution to avoid inter-element correction and obtain low detection limits. For this reason the ULTIMA was used. This Application Note reports the wavelengths that were used in this difficult matrix and the detection limits obtained.

2 Principle

2.1 Technique used

The elemental analysis of solutions was undertaken by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The sample is nebulized then transferred to an argon plasma. It is decomposed, atomized and ionized whereby the atoms and ions are excited. We measure the intensity of the light emitted when the atoms or ions return to lower levels of energy. Each element emits light at characteristic wavelengths and these lines can be used for quantitative analysis after a calibration.

2.2 Wavelength choice

The choice of the wavelength in a given matrix can be made using the "profile" function, or by using Win-IMAGE, which is rapid semi-quantitative analysis mode using multiple wavelengths. The principle is the same in either case: record the scans of analytes at low concentration, and of the matrix. By superimposing the spectra, we see possible interferences.

2.3 Limits of detection estimation

The limits of detection are calculated using the following formula:

$$LOD = k \times BEC \times RSD_0$$

With:
LOD = limits of detection,
k= 3 for the normal 3-sigma values,
BEC = Background equivalent concentration,
RSD_0 = relative standard deviation of the blank.

To calculate the LOD, a calibration curve is constructed using two points, 0 ppm and 5 ppm, or some concentration where the calibration is linear; this gives the BEC. The RSD_0 is evaluated by running the blank ten times.

3 Sample Preparation

The samples were prepared in HCl giving a $RhCl_3$/HCl matrix.

4 Instrument specification

The work was done on a ULTIMA.The specifications of this instrument are listed below in Tables 1 and 2.

Table 1: Specification of spectrometer

Parameters	Specifications
Mounting	Czerny Turner
Focal length	1m
Nitrogen purge	Yes
Variable resolution	Yes
Grating number of grooves	2400 gr/mm
Order	2nd order

Table 2: Specification of RF Generator

Parameters	Specifications
Type of generator	Solid state
Observation	Radial
Frequency	40.68 MHz
Control of gas flowrate	by computer
Control of pump flow	by computer
Cooling	air

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In order to measure at high resolution (5 pm) and to measure the entire spectral range (160 - 800 nm), two gratings were used. The first one covers the 160 - 420 nm range with a resolution of 5.5 pm. The second one covers the rest of the spectral range, up to 800 nm.

5 Operating conditions

The operating conditions are listed in Table 3 below.

Table 3: Operating conditions

Parameter	Condition
RF Generator power	1100 W
Plasma gas flowrate	12 L/min
Auxiliary gas flowrate	0 L/min
Sheath gas flowrate	0.2 L/min 0.8 L/min for Na, K
Nebulizer flowrate	3 bars
Sample uptake	1 mL/min
Type of nebulizer	Meinhard
Type of spray chamber	Cyclonic
Argon humidifier	Yes
Injector tube diameter	3.0 mm

6 Wavelength selection and analytical conditions

The limits of detection were determined using the following parameters:

Mode of calculation: Mode maximum
Entrance slit: 20 µm
Exit slit: 15 µm
Integration time: 4 s

7 Limits of Detection

Three standards were used STD1, STD2 and STD3. The concentrations are listed in Table 4 below in mg/kg.

Table 4: Standard concentration

Element	STD1	STD2	STD3
Ag	7		207
Al	5	505	
As	0		600
Au	0	250	
B	12	262	
Bi	0		250
Ca	35	300	
Cd	0		270
Co	0		260
Cr	15	275	
Cu	2	252	
Fe	20	270	
Ir	40		400
K	10	510	
Mg	20	270	
Mn	0		200
Mo	5		270
Na	110	410	
Ni	5	250	
Pb	0	505	
Pd	3	503	
Pt	0	500	
Ru	0	250	
Sb	0		500
Se	0		260
Si	100		600
Sn	110	610	
Te	4		240
Ti	5	255	
Zn	10		260
Zr	**0**		**100**

The limits of detection were determined using the formula given in section 2.3 and are given in Table 5.

Table 5: Limits of Detection

Element	Wavelength (nm)	BEC (mg/kg)	LOD (mg/kg)
Ag	338.289	17.7	0.31
Al	167.020	24.8	1.19
Al	396.152	45.5	1
As	189.042	42.7	0.92
Au	174.050	217	5.4
Au	208.209	33.8	0.95
Au	242.795	18.4	0.14
B	249.678	8.91	0.11
B	249.773	24.6	1.08
Bi	206.170	1400	36.9
Bi	223.061	21.6	0.46
Ca	393.366	0.203	0.004
Cd	214.438	2.58	0.049
Cd	226.502	3.84	0.054
Co	237.862	12	0.14
Co	238.892	6.1	0.1
Cr	205.552	12.4	0.24
Cr	267.716	9.91	0.26
Cu	324.754	5.21	0.08
Fe	238.204	11.8	0.2
Fe	240.488	5.45	0.052
Fe	259.940	10.2	0.23
Ir	171.760	1410	36.5
Ir	204.419	426	17.5
Ir	224.268	372	6.27
Ir	292.479	405	16
K	766.490	17.3	0.25
Mg	279.553	1.89	0.035
Mn	257.610	2.23	0.025
Mo	202.030	15.4	0.36
Na	589.592	23.8	1.48
Ni	221.647	5.37	0.09
Ni	231.604	4.68	0.053
Pb	220.353	35.6	0.73
Pd	340.458	14.2	0.084
Pt	172.313	498	19.1
Pt	299.797	44.3	0.6
Pt	306.471	25.8	0.22
Ru	240.272	25	0.63
Sb	217.581	28	0.76
Se	196.026	71.8	1.46
Si	251.611	189	5.3
Sn	189.989	2620	20.7
Sn	235.484	89.8	1.91
Sn	283.999	64.3	1.22
Te	170.000	288	10
Te	170.158	296	8.24
Te	214.281	54.9	2.28
Ti	323.452	6.73	0.11
Ti	334.941	6.06	0.07
Zn	202.551	8.93	0.16
Zn	206.191	18.5	0.4
Zr	343.823	3.62	0.07

8 Conclusion

HORIBA Scientific ICPs have the ability to analyze very difficult samples, such as those with high salt content, in part due to the large 3 mm ID injector. In addition, the use of the sheath gas device, originally patented by HORIBA Scientific, enables analysis without clogging of the injector tube and provides the capability of running samples up to 300 g/L salt content.

The flexibility of the ULTIMA configuration enables you to choose the gratings depending on the applications, such as the dual grating (4320 and 2400 gr/mm), which provides high resolution and low LOD, in the 200 - 400 nm region. This is particularly useful for the analysis of impurities in rare earths and precious metals.

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