

COMPARISON OF ULTRA LAMP FLAME ATOMIC ABSORPTION AND ICP-OES MEASUREMENT SYSTEMS FOR THE DETERMINATION OF PRECIOUS METALS IN AUTOCATALYST SAMPLES

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ABSTRACT

A study was completed comparing the analysis of precious metals in a wide variety of automobile catalyst materials using Flame Atomic Absorption equipped with the Varian Ultra lamp system to Inductively Coupled Plasma Optical Emission. Ultra lamps are high intensity discharge lamps, which can be used instead of conventional hollow cathode lamps. The study has shown that the Ultra Lamp system provides superior quality precious metal analytical data on automobile catalyst materials. The study has also indicated a much wider application of the Ultra Lamp system in our laboratory.

INTRODUCTION

With the exception of x-ray fluorescence, there are normally two different approaches when analyzing automobile catalysts. The first option would be to totally digest the sample matrix and to determine the precious metals within the sample by reading them against matrix matched standards containing all of the major matrix components of the samples. This approach can be tedious as the variety of different catalyst formulations means that matrix matching can become a very complex exercise. In addition, it is very difficult to correctly matrix match when the laboratory does not have a thorough knowledge of all the components in the catalyst materials. The second approach and the one that SGS Minerals Services, Lakefield Laboratory employs is to totally breakdown or destroy the sample matrix and to isolate the precious metals from the substrate and any other interfering elements. This allows for a generic, one size fits all approach. The catalyst material is subjected to an alkaline fusion at a controlled temperature. The melt is dissolved in water and then acidified. Tellurium chloride is added to quantitatively precipitate the platinum, palladium and rhodium by reduction of tellurium chloride to tellurium metal using stannous chloride. The resulting tellurium compounds are filtered and dissolved with aqua regia.

For this study a wide variety of automobile catalyst samples and standards were analyzed comparing atomic absorption spectrophotometry equipped with a Varian UltraAA lamp system to Inductively Coupled Plasma (ICPOES). The objective of the investigation was to examine the applicability of the Varian flame atomic absorption system equipped with the UltraAA Lamp system for the final measurement of platinum and palladium from the Lakefield Lab's tellurium collection method.

Rhodium was not included in the study as no UltraAA Lamp was available from Varian at the time of the study. Finally the paper examines the co-precipitation of base metal and rare earths present in automobile catalysts.

SUMMARY OF COLLECTION METHOD

Automobile catalyst samples of 1 to 3 grams are mixed with excess sodium peroxide in alumina crucibles. The mixtures undergo fusion in a temperature controlled muffle furnace.¹ After cooling, the crucibles are leached in deionized water and then acidified with hydrochloric acid. When the melt has dissolved, the crucibles are removed with a stirring rod and thoroughly rinsed with water. Tellurium chloride is added to the solution followed by

additions of stannous chloride. Platinum, palladium and rhodium are quantitatively precipitated as tellurium compounds.² The tellurium precipitate containing the noble metals is filtered onto a fiber fax pad, and rinsed thoroughly to remove excess sodium salts. The pad containing the tellurium and precious metals is dissolved in aqua regia. Any nitric acid present in the solutions is removed by repeated evaporations with hydrochloric acid. The platinum, palladium and rhodium are determined by either ICPOES or atomic absorption equipped with an UltraAA lamp system.

INSTRUMENTATION: WHICH TO CHOOSE?

ICPOES and Flame AAS are both viable instruments for the determination of platinum, palladium and rhodium in solutions prepared using the Te Collection method. ICPOES has better detection limits for the precious metals, especially Pt, but this is not an issue when determining the noble metals

present in automobile catalyst samples as they are typically found in high concentrations. AAS has a larger sample throughput than ICPOES for two elements, even if the elements are determined simultaneously by ICPOES. In order to achieve the best possible precision when analyzing catalyst samples by ICPOES, multiple replicates with extended read times and long rinse times between samples are necessary. This effectively lengthens the ICPOES run time beyond the time required to analyze two elements by AAS. ICPOES does have the advantage of better automation and true unattended operation. Most labs are not comfortable leaving open flames burning on AAS in an unattended fashion. Chemical and ionization interferences are relatively non-existent by ICPOES and can be minimized or eliminated by AAS with chemical modifiers. Ionization interferences can be found in samples that contain very high concentrations of sodium. However, optimizing the plasma viewing height can minimize these. Spectral interferences are rare by AAS and can be overcome by ICPOES by selecting multiple wavelengths for the Pt, Pd and the internal standard. Physical interferences are more prevalent by ICPOES than AAS but these can be minimized with the use of an internal standard. Short-term instrument precision is critical for the analysis of precious metals in catalyst samples and is better by AAS (0.1-1%) than by ICPOES (0.3-2%).

PT, PD (AND RH) ANALYSES BY ICPOES

In order to achieve the best possible precision when analyzing catalyst samples, multiple replicates with extended read times and long rinse times between samples are necessary. Five 10 second replicates are taken for each analysis. A stabilization time of 45 seconds is applied before analysis to ensure stable readings and a rinse time of 25 seconds is applied between samples to minimize carry over.

Samples are analyzed against a Scandium internal standard to correct for physical interferences. Both the sample and internal standard are pumped rather than aspirated to improve precision and accuracy by minimizing viscosity

effects. The internal standard solution is 1 mg/L Sc in 10 % HCl containing 0.1% Triton-X-100 nonionic surfactant which acts as a rinsing agent minimizing the formation of droplets in the spray chamber and carry over to subsequent samples.

The analytes of interest and the internal standard are each analyzed at two different wavelengths to check for any spectral interference which may exist. Table 1 below lists the wavelengths used at the Lakefield Lab; the preferred wavelength is marked accordingly.

Table 1 Preferred ICPOES Wavelengths

ELEMENT	WAVELENGTH IN NM
Pd	340.458 (preferred)
Pd	324.27
Pt	265.945 (preferred)
Pt	214.424
Rh*	343.488 (preferred)
Rh*	369.236
Sc	361.383 (preferred)
Sc	335.372

* Not included in the study

All ICPOES data was obtained on a radial Varian Vista-Pro ICP spectrometer with simultaneous CCD. The instrument operating conditions are listed in Table 2.

Table 2 Varian Vista ICPOES Instrument Operating Conditions

ITEM	SETTING
Power	1.30 kW
Plasma Gas Flow	16.5 L/min
Auxiliary Gas Flow	0.75 L/min
Nebulizer Gas Flow	0.80 L/min
Viewing Height	10 mm
Pump Rate	20 rpm

PT, PD (AND RH) ANALYSES BY AAS-ULTRAA LAMP

With precision and accuracy the main objective when determining precious metals, multiple replicates with extended

read times are also necessary by AAS. The standard practice of the Lakefield Lab is to use three ten second readings with manual resloping.

The quality of the AA system is limited by the performance of the hollow cathode lamp. The use of UltraAA lamps provides improved stability and increased sensitivity over conventional lamps. Unlike conventional lamps, these boosted lamps employ a second discharge, electrically isolated from the sputtering discharge, to excite the sputtering atoms.

Samples are determined using lanthanum as a releasing agent with matrix matched standards. Table 3 below provides the preferred wavelengths used by the Lakefield Lab.

Table 3 Preferred AAS Wavelengths

ELEMENT	WAVELENGTH IN NM
Pd	340.5
Pt	265.9
Rh	343.5

All AAS data was obtained on a Varian SpectrAA 220 spectrophotometer equipped with an UltraAA lamp system. The AAS instrument operating conditions are listed in Table 4.

Table 4 Varian SpectrAA 220 Instrument Operating Conditions

ELEMENT	FLAME	LAMP CURRENT MA	SLIT	BACKGROUND
Pt	Air/Acetylene	10	0.5	On
Pd	Air/Acetylene	5	1	On
Rh*	Air/Acetylene	4	0.5	On

*no ultra lamp available

Table 5 Palladium Experimental Data-Live Samples (Samples analyzed in triplicate)

SAMPLE	Pd by ICPOES	RSD ICPOES	Pd by AAS	RSD AAS
	%	%	%	%
1A	0.8272	0.3	0.8379	0.1
1B	0.8369	0.4	0.8356	0.3
1C	0.8335	0.2	0.8372	0.2
2A	0.4689	0.2	0.4718	0.6
2B	0.4717	0.4	0.4726	0.5
2C	0.4691	0.4	0.4736	0.4
3A	0.0211	1.1	0.0202	0.6
3B	0.0202	2.0	0.0205	0.1
3C	0.0201	0.8	0.0203	0.1
4A	0.0305	0.2	0.0305	0.2
4B	0.0307	0.5	0.0306	0.5
4C	0.0306	0.3	0.0307	0.2
5A	0.4418	0.4	0.4407	0.6
5B	0.4419	0.7	0.4405	0.1
5C	0.4389	0.3	0.4415	0.6

Table 6 Palladium Experimental Data-Reference Materials (Samples analyzed in triplicate)

STANDARD	CERTIFIED VALUE	Pd by ICPOES	RSD ICPOES	Pd by AAS	RSD AAS
	%	%	%	%	%
SGS-328 Pd Inhouse Standard	3.2857 ± 0.0328	3.2839	0.4	3.2846	0.2
CAT-2E Inhouse Standard	0.1200 ± 0.0024	0.1186	0.2	0.1195	0.1
NIST2557	0.0233 ± 0.0004	0.0232	0.2	0.0234	0.2

ANALYTICAL DATA

Analytical data received from live samples and certified reference materials analyzed in the study are presented below.

CO-PRECIPITATION OF BASE METALS AND RARE EARTHS

An addendum to the main precious metal analytical study was conducted to determine the presence of base metals and rare earth elements found in typical tellurium precipitates from automobile catalysts. Five random samples of prepared automobile catalyst were scanned by ICPOES to determine elements that may have co-precipitated along with the tellurium and precious metals. The main elements found in the precipitate were aluminum, sodium, and tin. All other elements were found to be under 1 mg/L in the final solution for measurement. See Table 9 for the analytical data.

SYNTHETIC STANDARDS + CO-PRECIPITATES VS. SYNTHETIC STANDARDS

A synthetic set of precious metal standards containing tellurium, aluminum, sodium and tin in the same quantities as in Table 9, were compared and overlaid against a set containing just the precious metals in 10% HCl. See Table 10 for the data.

Table 7 Platinum Experimental Data-Live Samples (Samples analyzed in triplicate)

SAMPLE	Pt by ICPOES	RSD (ICPOES)	Pd by AAS	RSD (AAS)
	%	%	%	%
1A	0.1821	0.3	0.1812	0.2
1B	0.1833	1	0.1813	0.5
1C	0.1823	0.2	0.181	0.4
2A	0.1985	0.2	0.1987	0.1
2B	0.1998	0.2	0.1989	0.4
2C	0.1988	0.3	0.1984	0.1
3A	0.0137	1.1	0.0136	1.0
3B	0.0134	1.2	0.0138	0.8
3C	0.0141	1.4	0.0137	0.6
4A	0.0166	0.5	0.0163	0.5
4B	0.0164	0.7	0.0164	0.4
4C	0.0167	1.0	0.0164	0.7
5A	0.2096	0.2	0.21	0.1
5B	0.2117	0.2	0.2113	0.1
5C	0.2112	0.2	0.2107	0.1

Table 8 Platinum Experimental Data-Reference Materials (Samples analyzed in triplicate)

STANDARD	CERTIFIED VALUE	Pt by ICPOES	RSD ICPOES	Pt by AAS	RSD AAS
	%	%	%	%	%
SGS/ Pt IA Inhouse Standard	1.7000 ± 0.034 ±	1.7092	0.3	1.7115	0.4
CAT-2E Inhouse Standard	0.2025 ± 0.004	0.2023	0.4	0.2029	0.1
SGS/ Pt3C Inhouse Standard	0.3117 ± 0.006	0.3131	0.2	0.3107	0.1
NIST2557	0.1131 ± 0.002	0.1127	0.5	0.1136	0.4

Table 9 Co-precipitation of Base Metals with Precious Metals

SAMPLE	Al mg/L	Sn mg/L	Na mg/L	Te mg/L
Sample A	9.8	17.6	17.8	1184
Sample B	4.8	12	12.9	1169
Sample C	12.4	19.7	21.8	1172
Sample D	8.4	20.3	20.6	1199
Sample F	11.7	9.6	19.7	1145

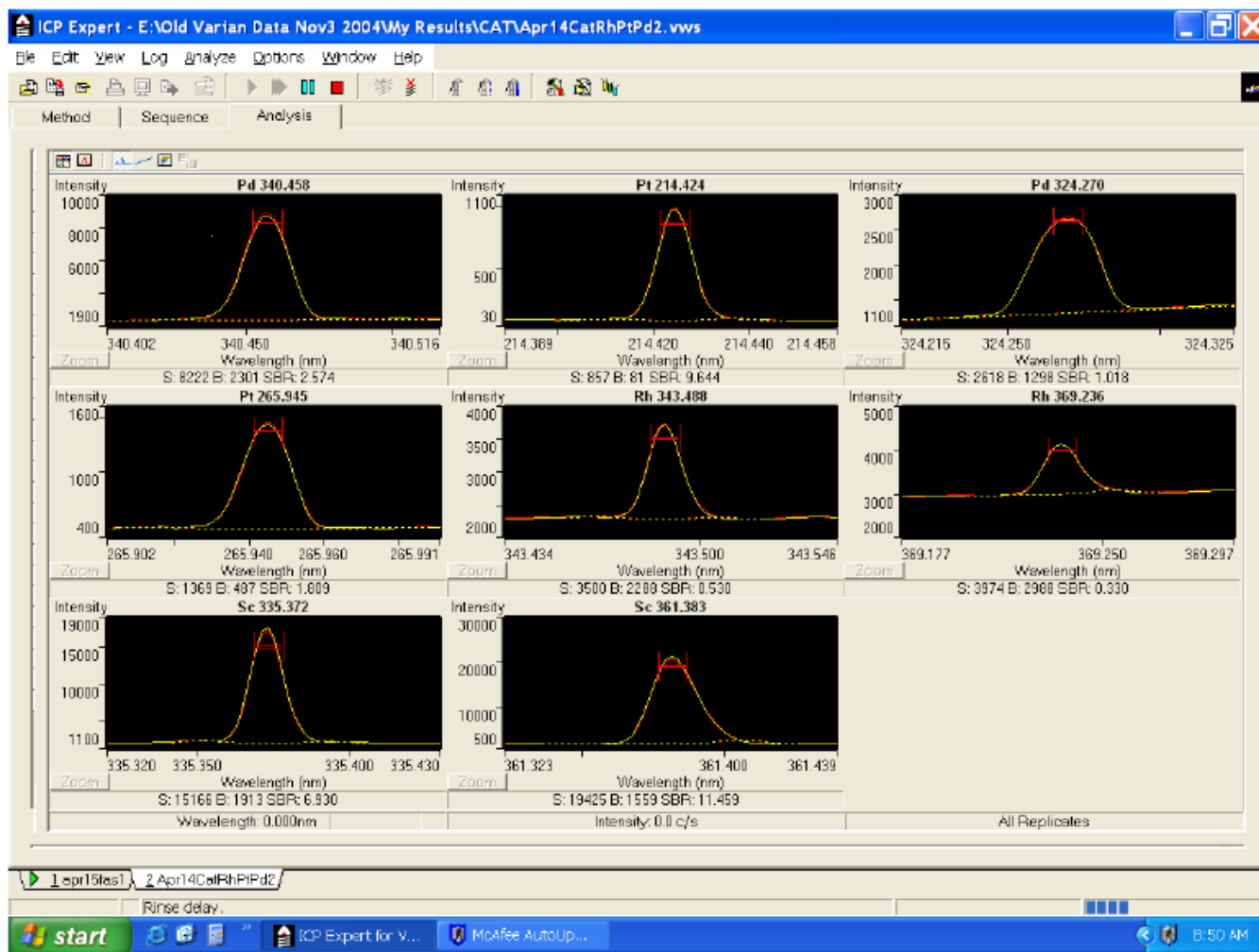
DISCUSSION

The data presented in Tables 5 and 6 above compare actual triplicate automobile samples run by both measurement techniques. The relative standard deviations were derived from five separate measurements per individual sample by ICPOES and three separate measurements by the AAS UltrAA lamp system. Overall the RSD's obtained from the UltrAA lamp system was found to be between (0.1% to 0.6%) for palladium and (0.1% to 1.0%) for platinum. The ICPOES RSD's were slightly higher with palladium running between (0.2% to 2.0%) and platinum running between (0.2% to 1.4%).

The standard reference analytical data presented in Tables 7 and 8 is from actual inhouse catalyst standards prepared by the Lakefield Lab. Accepted values for these standard materials were determined using a roundrobin exercise involving multiple commercial and manufacturing labs. The only exception to this is the NIST 2557 standard, which is a certified spent catalyst. The data achieved on all standards was well within accepted values; again the RSD's were lower using the AAS UltrAA lamp system.

Table 9 illustrates the level of co-precipitate aluminum, sodium, tellurium and tin. It is evident from Table 10 that the co-precipitates do not lead to spectral interferences. The standards containing high sodium from the peroxide fusions showed approximately 5% higher counts than those in 10 % HCl possibly due to the ionization effect from the sodium. SGS Lakefield Lab compensates for this effect by matrix matching all ICPOES and atomic absorption standards with a blank substrate passed through the entire procedure.

Table 10 Co-precipitate Modified Synthetic Standards



CONCLUSION

The data contained in this report verifies that the UltraAA Lamp AAS system is equal to or slightly better than the data achieved by ICPOES. Both measurement methods produced excellent results, however slightly better RSD's were obtained by the AAS ultra lamp

system. The ability to have alternate measurement systems available for such precise analyses, allows for verification of complex samples or possible interferences by the second technique. Two reliable independent methods allow laboratories the ability to defend data used for "party / umpire" work. Moreover, the lack of certified

reference materials is of great concern to the commercial laboratory, with ever changing catalyst formulations the days of the NIST 2256 and 2257 only serve as a reference of what was and do not adequately represent the catalyst formulations labs are currently analyzing.

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