Quantitative Analysis of Polypropylene by LA-ICP-OES

Introduction

Laser ablation is a proven tool for the qualitative analysis of virtually any solid material and, with appropriate standards, will provide quantitative results which rival traditional, solution based standardization and analysis. In this application, a total of 10 standards were provided, which were characterized for Magnesium (Mg) by digestion and solution analysis by ICP-OES. Additionally 5 unknown samples were to be analyzed. All samples were made of Polypropylene but differed in appearance and translucence due to the addition of other additives. The purpose of this application was to determine if Laser Ablation ICP-OES (LA-ICP-OES) could be used to generate a suitable calibration curve. The unknown samples were to be analyzed against that curve and results compared to those derived by digestion and nebulization technique. The use of LA-ICP-OES would eliminate the rather aggressive digestion techniques typically required for plastics. In this application all data were collected and integrated using the ICP-OES system-software to demonstrate that Laser Ablation can be run without off-line data reduction or internal standardization - an attractive feature for high volume sample analysis.

Instrumentation

The CETAC LSX-213 Laser Ablation System was used for these analyses. The CETAC LSX-213 is state of the art laser ablation system designed to ablate the widest range of solid samples. The LSX-213 is an integrated system that is controlled from the host ICP computer. The DigiLaz213™ software integrates the video from the sample area into the main control screen which runs side by side with the host ICP software so that the two units act as a single instrument. The DigiLaz213™ features a variety of flexible methods giving the user full control over every aspect of the ablation process.

The ICP used was a PerkinElmer Optima 3500 DV. This ICP-OES gives the flexibility of axial or radial viewing (axial viewing was used in this case) and uses a unique background correction algorithm to minimize spectral overlap. Both the ICP software and the laser software, DigiLaz213™, are run on the same computer.

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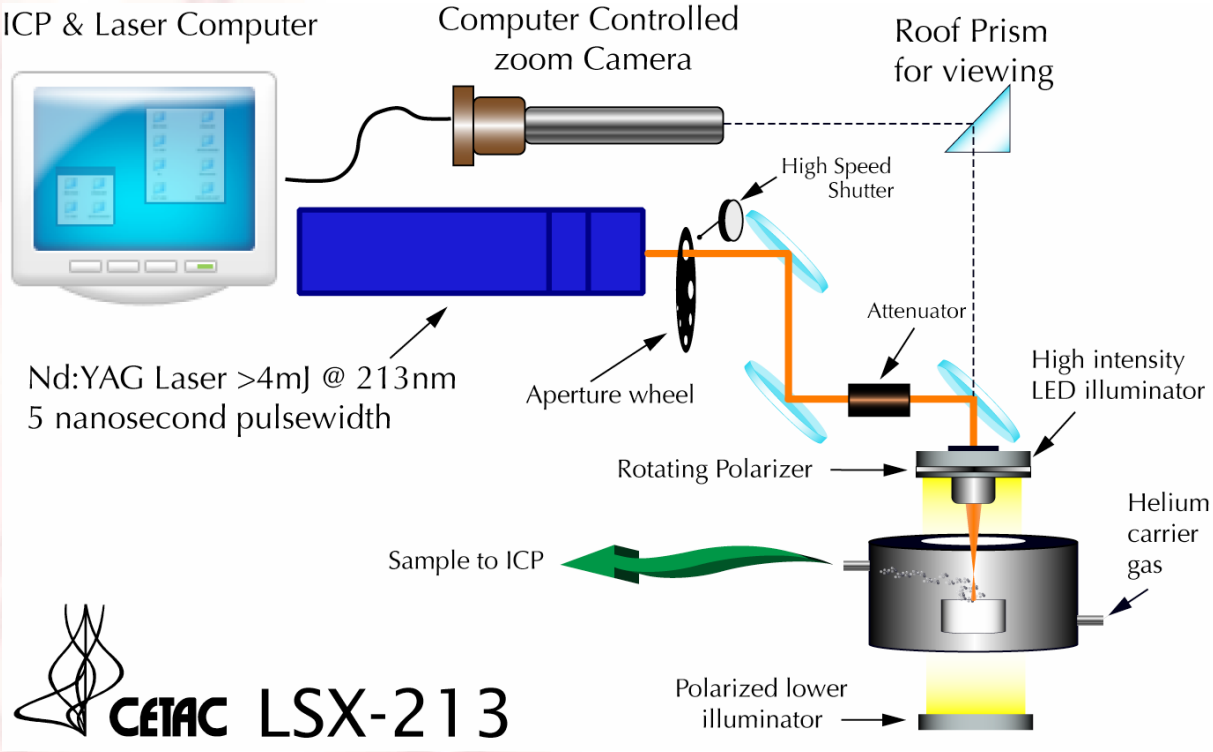


The ICP parameters were set to the following:

Forward Power:	1350W (axial)
Plasma Gas:	15 L/min
Aux Gas:	0.4 L/min
Neb (carrier) gas:	0.8 L/min Argon
Integration time:	Auto set between 1-5 sec (5 replicates / reading)

The LSX-213 was set up to run a line scan with the following parameters:

Energy:	100%
Shot Frequency:	20 Hz
Spot Size:	200 µm
Scan Rate:	20 µm/sec
Scan length:	Variable due to Auto Integration feature of ICP (≈1-4mm)
Helium:	0 mL/min

These laser settings were optimized to give the highest signal and stability whilst using Argon as carrier gas. Line scans were performed on these disks in order to get a long, stable signal. Scanning at 20µm/sec gave the best performance. This setting also allows a 90% overlap so the scans are quite deep which ensures that the majority of the material ablated is below the surface minimizing any surface contamination contribution to the signal.

Methods & Samples

As mentioned previously, one of the impediments to producing quality quantitative analysis with LA-ICP is the relative scarcity of commercially available standards for some materials. In this instance, the problem was overcome by collecting a variety of samples which have been analyzed multiple times by a number of dissolution methods enough times to give a suitable degree of confidence in the elemental concentrations. In this case the producer was in a position to produce their own standards using this process.

Because Laser Ablation uses such a small amount of sample during analysis, the 50mm diameter disks produced will provide many calibrations. The homogeneity of sample also allows for steady state signal integration instead of the transient signals seen frequently with Laser Ablation. This greatly simplified the data collection and analysis process by allowing the ICP software to manage all of the data. Magnesium is the analyte of interest. The samples, polypropylene based disks, differed in physical and visible characteristics and are described below:

Std #	Appearance	Mg ppm
1	smooth yellow	1.7
2	smooth yellow	3.8
3	spotted white	7.4
4	spotted white	12.7
5	spotted white	18
6	larger spots white	25.4
7	smoother white	32.3
8	mottled white	47
9	larger spots white	72.5
10	larger spots white	100

Unknowns:

1u	white, hard, clear
2u	white, hard, clear
3u	yellow smooth
4u	clear soft
5u	clear soft

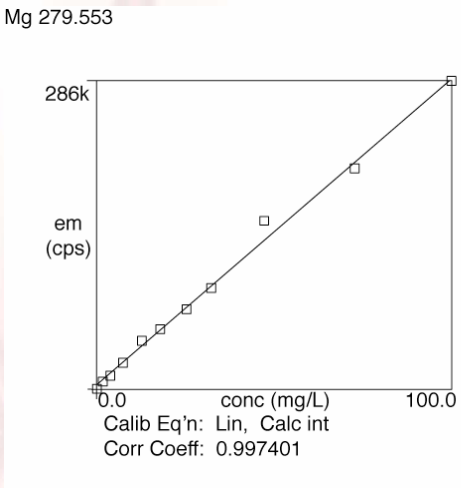
Analysis

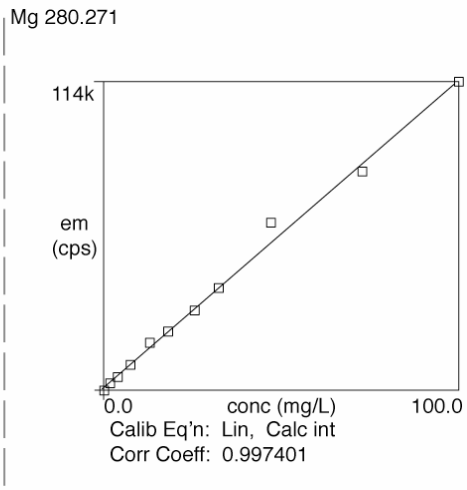
Emission lines were based on maximum sensitivity and low signal/noise ratio. Standardization and analyses were based on two Mg lines in the UV, 279.553nm and 280.271nm. A two point background correction was used. The 100 ppm standard was used for optimization of the ICP axial x-y viewing position, nebulizer (= carrier) gas flow and the z-position of the torch prior to analysis. For a blank, a gas blank was run prior to calibration.

The gas blank reading was taken with the sample in place but without the laser firing as is typical for blank determination in laser ablation. Each standard/sample was then run sequentially with each analysis taking under a minute. The calibration intensities are shown below, each an average of 5 replicates measured at two wavelengths for comparison.

From this table it is clear that the 279.553nm wavelength is about twice as sensitive and marginally more stable. The %RSD values all fall within typical limits for laser ablation (2-8%). From this data, the following calibration was derived, as linear, passing through the gas blank.

Std #	Mg ppm	Wavelength	Intensity	%RSD
gas	0	279.553	316.0	12.89%
		280.271	151.7	19.61%
1	1.7	279.553	6946.2	4.21%
		280.271	2793.5	5.55%
2	3.8	279.553	12511.9	1.55%
		280.271	5014.5	2.61%
3	7.4	279.553	24070.0	2.57%
		280.271	9556.1	2.75%
4	12.7	279.553	44693.9	7.92%
		280.271	17787.2	7.82%
5	18	279.553	55474.2	6.04%
		280.271	21910.0	4.47%
6	25.4	279.553	74335.3	2.96%
		280.271	29707.1	3.31%
7	32.3	279.553	93707.8	5.02%
		280.271	38061.4	5.28%
8	47	279.553	155775.2	2.38%
		280.271	62143.7	2.42%
9	72.5	279.553	204155.0	7.13%
		280.271	81096.8	6.48%
10	100	279.553	285570.5	3.40%
		280.271	113689.9	3.68%

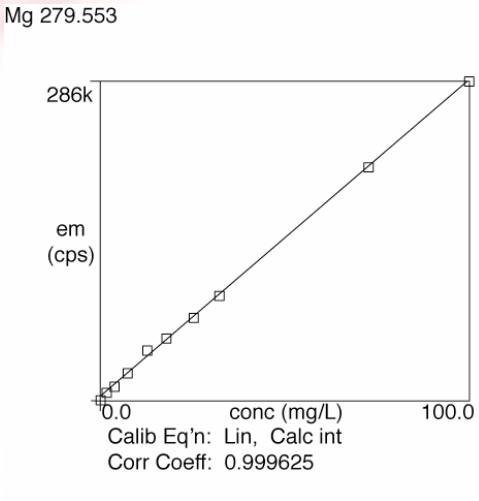


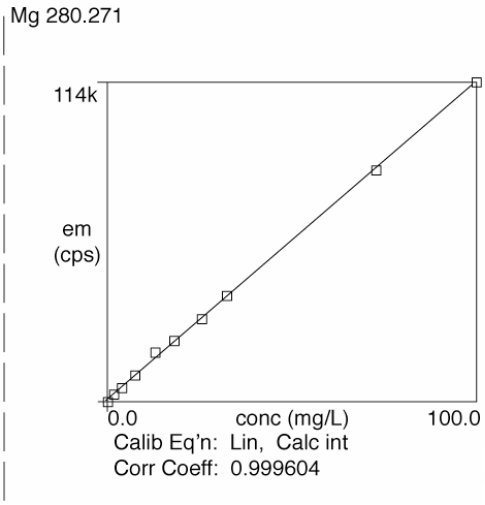


Using this curve, the results for the unknown samples were as follows:

Sample ID	Wavelength	Intensity	%RSD	Mg ppm	Mg Avg
1u	279.553	17039.0	3.22%	4.58	4.56
	280.271	6796.0	4.02%	4.53	
2u	279.553	29481.6	2.13%	9.08	9.13
	280.271	12056.8	1.79%	9.18	
3u	279.553	7973.9	14.32%	1.40	1.4
	280.271	3248.1	25.09%	1.40	
4u	279.553	19015.6	3.08%	5.28	5.27
	280.271	7611.7	3.24%	5.25	
5u	279.553	18487.7	2.60%	5.09	5.06
	280.271	7346.0	3.49%	5.02	

There is good agreement in linearity and stability for both wavelengths, indicating that there is no significant interference at either wavelengths and the calculated concentrations agree quite well between wavelengths. However, looking at this curve it appears that standard 8 is the standard which is most deviant from the curve whether calculated as linear, linear through zero or quadratic. As an additional exercise, these samples were reprocessed with a standard curve that did not include Std 8 in the event that the provided concentration for this standard was in error. The following curve was calculated with Std 8 omitted:





This calibration curve appears much better with a correlation coefficient of 0.9996 which is what would be expected from such an extensive calibration. Sample #3 was run as a quality check too. Reprocessing the sample results with the above curve gave the following results:

Sample ID	Wavelength	Mg ppm	Mg Avg	Mg expected
1u	279.553	4.94	4.91	5.0
	280.271	4.89		
2u	279.553	9.49	9.54	9.5
	280.271	9.59		
3u	279.553	1.71	1.72	1.6
	280.271	1.72		
4u	279.553	5.64	5.63	5.5
	280.271	5.62		
5u	279.553	5.45	5.42	5.4
	280.271	5.38		
Std 3	279.553	7.46	7.43	7.4
	280.271	7.40		

Reprocessing gave concentrations of the samples a nominal increase of 0.4ppm. Because all of the samples were in the lower region of the concentration calibration, the results above certainly benefited from the removal of STD 8 from the curve. All values were very close to the expected results. These results demonstrate the uniform coupling of the 213 nm laser beam into these polymers samples, which were quite different due to various additives as evidenced by the differing color and plasticity. The deviation of standard 8 is to be investigated further.

Detection Limit Calculations:

Detection limits were calculated for both wavelengths based on 3σ of the standard deviation of the gas blank with Standard 2 for concentration equivalence. The calculation is given in the table below.

Wavelength	Blank SD cps	3σ cps	Std 2 cps	Std 2 ppm	Cps/ppm	DL ppm
279.553	40.73	122.19	12511.9	3.8	3292.6	0.04
280.271	29.75	89.25	5014.5	3.8	1319.6	0.07

The obtained detection limits are very good using LA-ICP-OES with detection limit on the order of 50 ppb. As Magnesium is very sensitive in ICP-OES, the detection limits in LA-ICP-OES for other elements are likely to be reflected by the sensitivity difference in ICP-OES.

Conclusion:

Standards and samples gave high signal intensities. A good calibration for Magnesium (especially after removal of Std 8) suggests similar performance for other elements, whereby the obtainable detection limits would depend on the sensitivity of the different elements in ICP-OES. For this analysis, the laser was set to maximize the signal which leaves flexibility for the development of other laser methodology if smaller spots, single spot analysis or faster scan rates are desired. The linearity of the calibration curve is very good as has been shown on the large number of standards provided. The laser coupled easily with the plastics. It is very likely that analysis would be equally accurate using fewer standards.

The LSX-213 is an ideal tool for this type of analysis due to the fact that the standards and samples, while all polypropylene, did vary significantly in their physical characteristics. The LSX-213 generally has less matrix dependence and a positive effect on sensitivity compared to a 266nm laser. Signal stability is a good indicator of sample homogeneity. The clear differences in some of the samples, which range from hard-white to hard-yellow and soft translucent, did not affect the calibration curve. This indicates that the additive which imparts a yellow color to the material did not affect the Mg response based on the linearity of the curve.

The LSX Laser Ablation System handled these samples easily and quickly. While Mg was the only analyte measured in this study, the ablation characteristics and stability of the signal indicate that the same method is applicable to other elements of interest. The amount of sample consumed in the analytical process is very small; a line-scan 200µm wide, 1µm deep and between 1-5mm long. This tiny area would allow hundred of calibrations when using a 5mm disc. Overall, the LSX-213 performed equally well as digestion/liquid standardization techniques without very little sample preparation. This application shows that LA-ICP-OES is an easy, valid method for sample analysis and that it can be used in a manner analogous to liquid standardization using the steady state signal afforded by these samples.