



Analysis of Lead-Based Paint using the Teledyne Leeman Labs Prodigy High Dispersion ICP

INTRODUCTION

Lead-based paints have been used extensively for painting the interior and exterior surfaces of homes. These paints were applied to almost any surface; however, they were most commonly found on interior and exterior woodwork including: doors, window frames and windowsills, cupboards and interior moldings. Almost all of the homes constructed before 1970 contain some lead-based paint. Until 1950, some of these paints contained up to 50% lead (500,000 ppm) and by the late 1960s, paints containing more than 1% (10,000 ppm) were still being used.

One of the most common uses of lead in paint is in pigments. Lead (II) chromate (PbCrO_4) creates a color commonly known as “chrome yellow” and a “white lead” color is created using lead (II) carbonate (PbCO_3). Lead is also added to improve the general performance of the paint by increasing the speed with which the paint dries after application, improving its durability and increasing its resistance to moisture and mildew corrosion.

Lead is also used in the toy manufacturing process and can be particularly concentrated in those toys made out of plastic. Painted toys sometimes contain lead-based paint which gives them a durable, brightly colored outer surface. Plastic toys contain additional amounts of lead to increase the flexibility of the material and to make it more resistant to warping from heat and sunlight.

When the paint is in good condition, homes and toys pose little or no health risk. The concern arises when these lead-based paints peel or crack as they age and deteriorate or when a painted surface is scraped, sanded or heated. Exposure to lead could be a risk if the paint chips are ingested, or if dust from the paint is inhaled.



In 1978, the U.S. Consumer Product Safety Commission (CPSC) set the maximum allowable lead content in paint for residential use to 0.06% (600 ppm) as outlined in 16 C.F.R. § 1303.1. As of August 14, 2009, the maximum allowable lead content will drop to 0.009% (90 ppm). While lead has been banned from all paint used for domestic purposes, the use of lead in plastics is still permitted.

This application note will demonstrate the ability of the Teledyne Leeman Labs **Prodigy** High Dispersion ICP to analyze lead-based paints. The sensitivity and large linear dynamic range of the instrument in the axial view mode will be used to determine a wide range of lead concentrations in several different paint samples.



Experimental

Instrumentation

A **Prodigy** High Dispersion Inductively Coupled Plasma (ICP) Spectrometer equipped with a dual view torch was used to generate the data for this application note.

The **Prodigy** is a compact bench-top simultaneous optical emission instrument featuring an 800 mm focal length Echelle optical system and a mega-pixel Large Format Programmable Array Detector (L-PAD). At 28 mm², the active area of the L-PAD is significantly larger than that of all other solid-state detectors currently used in optical emission spectrometers.

The long focal length, combined with the large array detector, create a solid-state detection system that provides continuous wavelength coverage from 165 to 1100 nm. Well-resolved analytical signals can be measured and background corrected in a single instrument reading, a feature unseen in other emission spectrometers with solid-state detectors.

An additional benefit of the L-PAD is its charge injection device (CID) design which allows random access to each pixel in the detector array and non-destructive readout of its stored charge. These features prevent detector saturation and image distortion (“blooming”) over a linear working range that can cover 6 orders of magnitude.

The **Prodigy** uses a 40.68 MHz free running, water-cooled oscillator which produces a robust plasma that is stable with the most challenging sample matrices. An efficient sample introduction system produces and transports a constant, steady aerosol to the plasma which is reflected in stable emission signals.

The **Prodigy’s** innovative Image Stabilization system uniquely integrates the sample introduction components into the optical system which further improves signal stability. In this system, the torch is rigidly attached to the spectrometer and, thus, becomes part of the optical path.

In this work, the sample introduction system consisted of a cyclonic spray chamber, single-piece quartz, dual view torch and a Glass Expansion Conical nebulizer. The instrument was equipped with an 88 position autosampler. All analytical data presented were collected using the autosampler.

Operating Parameters

For all analytes of interest, background correction was performed simultaneously with the peak measurement, resulting in improved detection limits. All data was generated using the instrument operating conditions listed in *Table 1*.

Parameter	Setting
Coolant Gas	19 L/min
Auxiliary Gas	0 L/min
Nebulizer Gas	36 psi
RF Power	1.2 kW
Pump Rate	1.3 mL/min

Table 1. Plasma Operating Conditions

Method

Sample Prep

Two paint reference materials were digested and analyzed, along with two real paint samples. The certified reference materials included Trace Metals in Paint Chips (RTC CRM013-050, lot# AW13) and NIST Powdered Paint Nominal 200 mg/kg Lead (SRM 2582). Both certified reference materials were digested without further grinding. Real paint samples included paint chips scraped from the back porch of a local house and from a yellow-painted toy car. Paint chips from the back porch and toy car were ground with a mortar and pestle prior to being weighed for digestion. The certified reference materials were weighed and digested as received.

All paint samples were digested using a MARS5 closed vessel microwave system (CEM Corporation, Matthews, North Carolina) according to the procedure outlined in EPA Method SW846 3051A. Briefly, 0.3-0.5 g of material was weighed directly into a Teflon vessel and the exact mass of the material was recorded. To this vessel, 10 mL of concentrated nitric acid was added and was immediately sealed and heated according to the microwave heating program listed below.

Step	Power (W)	Ramp (°C/min)	Temp (°C)	Hold (mins)
1	600	5.5	175	5.0

Once cool, the seals on the vessels were broken and allowed to sit inside a fume hood until nitric acid fumes were no longer visible. The contents of each vessel were then filtered through 0.4 µm filter paper directly into a 100 mL volumetric flask and brought to volume with deionized water. It should be noted that 5 mL of HNO₃ was used to digest the NIST Powdered Paint standard and the final volume was brought to 50 mL to avoid diluting the sample below the concentration of the lowest calibration standard and to maintain the same acid concentration as that in the calibration standards.

Calibration Standards

Calibration standards were made from single element **Teledyne Leeman Labs Plasma Pure®** ICP standards containing either 1000 or 10,000 ppm Pb. The final acid concentration in all standards was 10% HNO₃ to match the acid concentration in the digested samples. The concentrations used for calibration are listed in *Table 2*. The instrument was calibrated over a wide range to accommodate the expected Pb concentrations in a wide variety of lead-based paints.



Elements	Std 1 (ppm)	Std 2 (ppm)	Std 3 (ppm)	Std 4 (ppm)	Std 5 (ppm)	Std 6 (ppm)
Pb	0	1	10	50	100	200

Table 2. Calibration Standards (in 10% HNO₃)

Wavelength Parameters

The **Prodigy** uses a 3 x 15 pixel subarray, centered on the wavelength of interest, to collect data for each analyte. The analytical peaks and background correction points are defined in each subarray with pixel position and width values. The wavelength and background correction points used in this method are outlined in *Table 3*. For background correction points that were more than 1 pixel wide, the background position indicates the starting position for the set of pixels used. The starting position and pixel width used for the analytical peak was 7 and 3, respectively. For the analyte of interest, background correction was performed simultaneously with the peak measurement. Additionally, all pixel data are saved which allows for future data recalculation.

Element	Wavelength (nm)	Left Background Pixel Position	Left Background Width	Right Background Pixel Position	Right Background Width	Simultaneous Integration Time (s)
Pb	220.353	1	5	None	---	5

Table 3. Wavelengths, Background Correction Points and Integration Times Used

An example of the data collection that takes place in each subarray is illustrated graphically in *Figure 1*. This figure represents the data collected for Std 2 at the Pb 220 nm line. In *Figure 1*, the left background correction point is illustrated at pixel position 1 with a width of 5. No background correction was used on the right side of the peak due to a noisy baseline observed in the paint samples. The pixels used for integrating the analytical peak are at pixel positions 7, 8 and 9. The thin black line that runs across the subarray underneath the peak illustrates the calculated background based on the background correction points chosen.

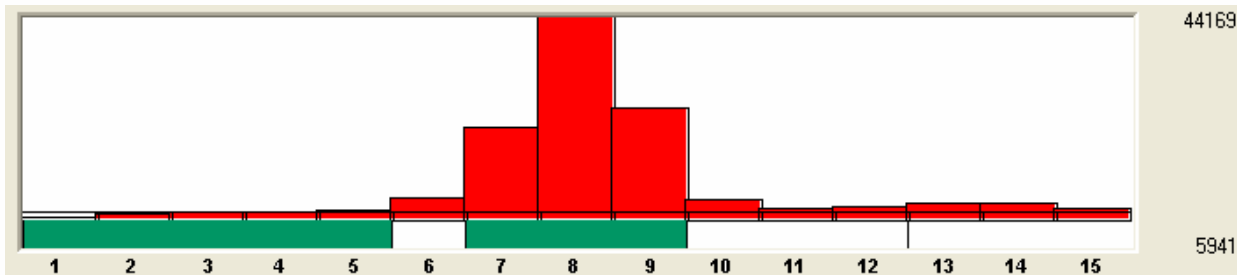


Figure 1. Graphical Representation of the Pb 220 nm Subarray for Std 1

An example of a typical calibration curve is illustrated in Figure 2. The figure is based on calibration data for the Pb 220 nm line and demonstrates typical precision and linearity for the range of concentrations included in the calibration.

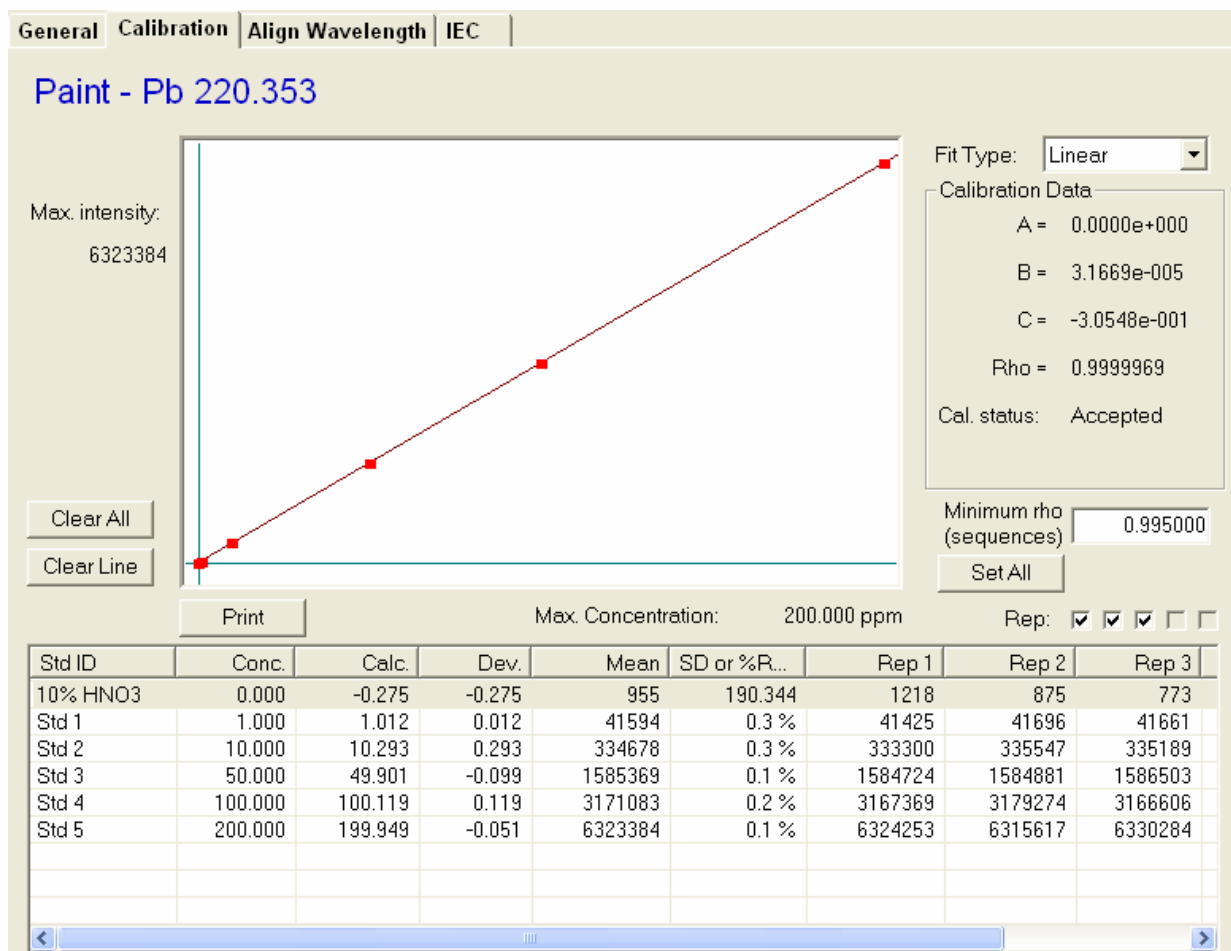


Figure 2. Typical Calibration Curve for Pb 220.353 nm

Results and Discussions

After igniting the plasma and allowing 15 minutes for the instrument to warm up, the instrument was calibrated using the calibration blank and standards listed in Table 2. Following calibration, the standard reference materials were analyzed. Results for the NIST and RTC standards are presented in Tables 4 and 5, respectively. The NIST standard was prepared and analyzed in duplicate and the % difference between each sample preparation was calculated. The RTC standard was also prepared in duplicate,

however, the results from both sample preparations were averaged together to compensate for sample inhomogeneities due to the fact that the standard was comprised of paint chips of varying colors, textures and sizes.

Element	Wavelength (nm)	Measured Pb Conc (mg/kg)	St Dev (mg/kg)	% RSD	Certified Conc (mg/kg)	% Difference Between Result and Duplicate Prep
Pb	220.353	209.5	2.8	1.3	208.8 ±4.9	1.2

Table 4. Results For the Analysis of NIST SRM 2582

Element	Wavelength (nm)	Avg Measured Conc (mg/kg)	Avg. % RSD	Certified Conc (mg/kg)	Acceptable Conc Range (mg/kg)
Pb	220.353	638.5	0.4	643 ±129.4	513.6-772.4

Table 5. Results For the Analysis of RTC #CRM013-050

This method, as applied to the analysis of real samples, is illustrated below. Results for the analysis of Pb in paint scraped from the back porch of a local house and from paint scraped from a plastic toy are presented in Tables 6 and 7, respectively. Note that the results in Table 6 are listed in units of elemental wt % and the results in Table 7 are listed in units of mg/kg. Since no detectable Pb was measured in the real samples, 10 ppm Pb was spiked into the samples to verify that Pb could be measured at relatively low concentrations in that sample matrix. As Table 7 indicates, both spikes were measured within ±10% of the spiked concentration.

Element	Wavelength (nm)	Measured Pb Conc (wt %)	St. Dev. (wt %)	% RSD	% Difference Between Result and Duplicate Prep
Pb	220.353	5.56	0.01	0.2	1.2

Table 6. Results For the Analysis of Paint Chips From a Local Back Porch

Sample ID	Wavelength (nm)	Measured Pb Conc (mg/kg)	% RSD	Spike Conc (µg/mL)	Spike Rec (%)	% RSD
Toy paint, prep 1	220.353	None detected	---	10.0	102.6	0.2
Toy paint, prep 2	220.353	None detected	---	10.0	102.7	0.4

Table 7. Results For the Analysis of Paint Scraped From a Plastic Toy



Conclusions

The analysis of Pb in a variety of lead-based paints has been successfully performed using the Teledyne Leeman Labs **Prodigy** High Dispersion ICP. The sensitivity of the instrument in the axial view mode, combined with its long linear dynamic range, allowed the instrument to be calibrated over a wide concentration range to accommodate samples containing Pb at concentrations ranging from 100 ppm to 6% in a single instrument method.

The image stabilized plasma and the simultaneous data collection of both peak and background data combine to provide exceptionally precise and stable results.