Field Turbidity Method for the Determination of Lead in Acid Extracts of Dried Paint

William B. Studabaker,*[a] Michelle McCombs,[a] Kristen Sorrell,[a] Cynthia Salmons,[a] G. Gordon Brown,[a] David Binstock,[a] William F. Gutknecht,[a] and Sharon L. Harper[b]

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Lead, which can be found in old paint, soil, and dust, has been clearly shown to have adverse health effects on the neurological systems of both children and adults. As part of an ongoing effort to reduce childhood lead poisoning, the U.S. Environmental Protection Agency promulgated the Lead Renovation, Repair, and Painting Program (RRP) rule requiring that paint in target housing built prior to 1978 be tested for lead before any renovation, repair, or painting activities are initiated. This rule has led to a need for a rapid, relatively easy, and an inexpensive method for measuring lead in paint. This paper presents a new method for measuring lead extracted from paint that is based on turbidimetry. This method is applicable to paint that has been collected from a surface and extracted into 25% (v/v) of nitric acid. An aliquot of the filtered extract is mixed with an aliquot of solid potassium molybdate in 1 M ammonium acetate to form a turbid suspension of lead molybdate. The lead concentration is determined using a portable turbidity meter. This turbidimetric method has a response of approximately 0.9 NTU per µg lead/mL extract, with a range of 1–1,000 Nephelometric Turbidity Units (NTU). Precision at a concentration corresponding to the EPA-mandated decision point of 1 mg of lead/cm^2 is <2%. This method is insensitive to the presence of other metals common to paint, including Ba^{+2}, Ca^{+2}, Mg^{+2}, Fe^{+3}, Co^{+2}, Cu^{+2}, and Cd^{+2}, at concentrations of 10 mg/mL or to Zn^{+2} at 50 mg/mL. Analysis of 14 samples from six reference materials with lead concentrations near 1 mg/cm^2 yielded a correlation to inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis of 0.97, with an average bias of 2.8%. Twenty-four sets of either 6 or 10 paint samples each were collected from different locations in old houses, a hospital, tobacco factory, and power station. Half of each set was analyzed using rotor/stator-25% (v/v) nitric acid extraction with measurement using the new turbidimetric method, and the other half was analyzed using microwave extraction and measurement by ICP-AES. The average relative percent difference between the turbidimetric method and the ICP-AES method for the 24 sets measured as milligrams of lead/cm^2 is −0.63±32.5%; the mean difference is −2.1±7.0 mg lead/cm^2. Non-parametric and parametric statistical tests on this data showed no difference in the results for the two procedures. At the federal regulated level of 1 mg of lead/cm^2 paint, this turbidimetric method meets the performance requirements for EPA's National Lead Laboratory Accreditation Program (NLLAP) of accuracy within ±20% and has the potential to meet the performance specifications of EPA's RRP rule.

Introduction

Studies have shown that chronic exposure to even low levels of lead can result in impairment of the central nervous system and behavioral disorders. Although young children are at the greatest risk, adults may also suffer harmful effects. Lead in paint continues to be a major source for this exposure.[1] Lead in paint at or above 0.5% by weight or 1 mg of lead/cm^2 must be controlled or removed according to Title X of the Housing and Community Development Act.[2] These federal regulated levels must now be applied in the renovation and repair industry according to the U.S. Environmental Protection Agency's (EPA's) Lead Renovation, Repair, and Painting Program (RRP) rule.[3] The performance requirements for the Rule are no more than 5% false negative results at levels greater than the federal regulated level and no more than 10% false positive results at levels less than the federal regulated level. The renovation and repair industry is in need of a method that will meet these performance requirements, but will also be easy to perform, inexpensive, and take less than 1 hour for each sample. Two methods available for directly measuring lead in paint in situ are field-portable X-ray fluorescence (FPXRF) and portable laser-induced breakdown spectroscopy (LIBS), both of which require extensive training and are relatively expensive.[4] The measurement requirements are more likely to be met using a quantitative, portable chemical test kit. This quantification will most likely be based on a quantitative reaction with solubilized lead using, for example, electrochemistry, complexation (colorimetry), or precipitation (gravimetry or turbidimetry).

In a previous paper,[4] we describe a field deployable method used to collect paint samples from surfaces and extract them directly using nitric acid. In this paper, we present a novel procedure for determining the concentration of lead in those extracts. This new method based on turbidimetry is inexpensive, easy to perform, and is not subject to interference from the metal ions commonly associated with paints, pigments, and substrates.

Background

Development of a field method for measurement of lead in paint that achieves the performance requirements of the RRP rule is challenging because this level of performance is usually only associated with laboratory-based equipment. The electrochemical technique of anodic stripping voltammetry

(ASV)[5-8] has the potential to meet the previously listed bias requirements, but it is moderately expensive per sample and shows negative bias for some samples.[9] The Hach LeadTrak™ Fast Column Extraction, Colorimetric method (Hach Company, Loveland, CO) is one method that is available for measuring lead in the field based on complexation. This 8-step analysis, which requires separating the lead from other metals, is not simple and costs approximately $10 per sample, which is similar to the cost of ASV analysis with the Hach ASV Analyzer System, which uses a one-time-use electrode array.[10] The DirectDetect (Seattle, WA) Nano-Band™ Explorer II uses the same electrode for each ASV analysis, but this electrode must be routinely polished to maintain accuracy.[11] In light of these issues of relatively high cost and lack of simplicity, we initiated the development of a new measurement method.

The first step in method development was to identify chemistries and detection methods that were adaptable to the sample collection and extraction method previously described,[4] and that were consistent with the objectives of field portability and analytical accuracy. Color-forming reactions of lead with a variety of reagents have been described in the literature, including, historically, rhodizonic acid and dithizone, as well as more recently described methods, including 2-(2-thiazolylazo)-p-cresol,[12] malachite green,[13] phenanthraquinone monophenyl thiosemicarbazone,[14] pyridine-2-acetaldehyde salicyloylhydrazone,[15] resazurin,[16] 4-(2-pyridylazo)-resorcinol (PAR),[17] 2,2'-dipyridyl-2-pyridylhydrazone (DPPH),[18] and 5,10,15,20-tetra-(4-N-sulfoethylpyridinium)porphyrin.[19] A drawback to using methods that utilize these reagents is that other metal cations such as Zn^{2+}, which are also likely to be present in paint, paint pigments, plaster, or drywall, also react with the color-forming reagent and would lead to unacceptable increases in the false positive rate. In addition, acid-extractable pigments in the paint may increase the background signal, thereby producing false positives.

Other candidate reagents identified to stronglybind/precipitate Pb^{2+} ion were hexathiocyanato-chromate(III),[20] metavandadate, orthovanadate, molybdate,[21] and ethyl xanthate.[22] Of these candidates, the hexathiocyanatochromate(III) was not available commercially and could not be successfully synthesized. The ethyl xanthate was eliminated because of its extremely unpleasant odor. One report indicated that Pb^{+2} reacts quantitatively with the molybdate anion to form an insoluble complex, without interference from a variety of metal cations or oxo anions that were present.[23] On the basis of this report by Kaza and Vaidya,[23] the reaction between molybdate and lead was considered as a primary candidate.

Experimental

Prelimimary Tests

During initial screening experiments with molybdate, the approach followed by Kaza and Vaidya was simplified and adapted to use with paint extract. Solutions of lead in 25% (v/v) nitric acid, which was the extraction medium used in the recently reported extraction method,[4] were added to solutions of excess potassium molybdate in 1 M ammonium acetate, yielding a white precipitate. Solutions of other metals (e.g., Zn^{+2}, Cd^{+2}) mixed with the molybdate were found to be unreactive under the same conditions. However, the need for a fast, inexpensive, field-usable method ruled out a gravimetric determination such as that reported by the original authors, so alternative means of quantifying the reaction were explored.

Small, lightweight, battery-powered turbidimeters that are suitable for field use are readily available for applications (e.g., the measurement of suspended particulates in water) and cost approximately the same as portable spectrophotometers. Although quantitative turbidimetry is more commonly a component of flow injection analysis methods,[24] and is a well-established method in clinical applications, such as immunoassays[25], turbidimetric determinations may be performed using portable devices.[26] The reaction previously described produced what appeared to be a colloidal dispersion that remained stable long enough to obtain reproducible measurements of its opacity. Thus turbidimetry was chosen as a means to follow the reaction of lead and molybdate. A Hach 2100P (Hach Co., Loveland, CO) portable turbidimeter was used for subsequent experiments.

Method Development

Preliminary experiments employing turbidiy involved mixing various amounts of 12 millimolar (mM) lead standard, 25% (v/v) nitric acid, 100 mM potassium molybdate, 5 M ammonium acetate, and deionized water in the turbidimeter cell for a total of 15 mL of solution. Based on earlier work at RTI International (RTI), ammonium acetate was selected as the buffer.[27] After the reagents were placed in the cell of the turbimeter, it was capped immediately, inverted three times to mix the reagents, and timing was started. The turbidimetry value in Nephelometric Turbidity Units (NTU) was read periodically for approximately 2 hours.

Tests at different pHs (adjusted with ammonium acetate plus potassium hydroxide [KOH]) indicated that a pH of approximately 5 gave the greatest amount of reaction product (i.e., the greatest turbidity). At a lower pH, Pb^{2+} species remain partly or fully soluble in the presence of molybdate. At neutral or alkaline pH, precipitation of other metals that may be present (e.g., Zn^{+2}) may be expected to interfere with specific detection of Pb^{2+}. A standard turbidimetric curve was generated over the range of 0 to 2 mg of lead/mL, and very good linearity was attained ($r^2 = 0.999$). Another experiment was performed to determine the effect of time on the turbidity measurements because it is known that formation of the particles may continue for some time with the time of reaction being related to the concentration of the lead. Six replicate aliquots of lead standard solution (plus one blank) were mixed with stoichiometric amounts of molybdate in 1 M ammonium acetate; this lead concentration is equivalent to a 1 mg of lead/cm^2 paint sample dissolved in 3 mL of 25% (v/v) nitric acid. The precision of the values was observed to be very

poor, but the reaction seemed to be complete after approximately 20 minutes. These results indicated that molybdate does not react with Pb^{2+} ion with sufficient strength to react 1:1 (i.e., quantitatively precipitate all of the lead present).

Next, the molybdate concentration was increased to 10 mM and then to 100 mM. Figure 1 shows the results of this increase to 100 mM on sensitivity and development time as measured by turbidity. The turbidity values for each sample level off or are at a maximum after approximately 5 minutes. The linearity of the response is much improved (correlation coefficient = 0.978), and the turbidity values for replicate samples are much closer in value for each reaction time. Replicate analyses of a solution of 1.67 mM Pb^{+2} yielded a relative standard deviation of <2%. The limit of detection is ~0.1 mM Pb^{2+}.

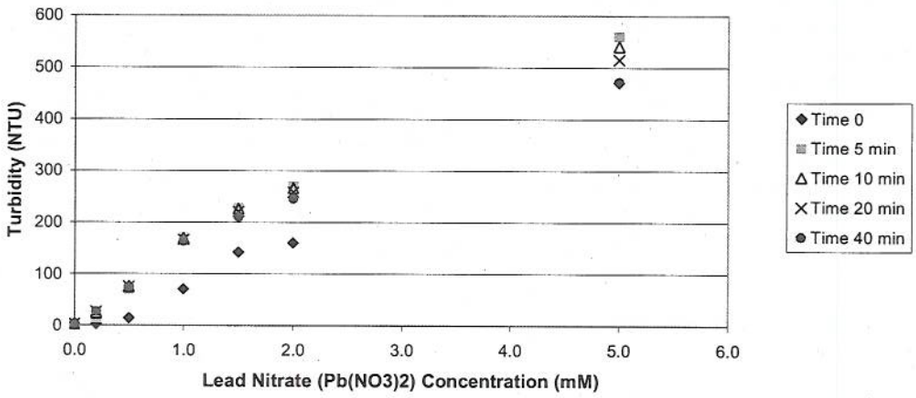


Figure 1. Turbidity values versus lead concentrations.

Note: 15 mL test solution final volume, 100 mM in molybdate, pH 5.5 – buffered with 1M ammonium acetate, and lead test standard samples varying in concentration from 0 to 5.0 mM. (Note: 1.6 mM is equivalent to 1 mg of lead in the test sample.)

At this point, another test for reactions of molybdate was performed to verify selectivity. Using the reaction system, acetate buffer plus molybdate, equivalent concentrations of different metal species (Ba^{+2}, Fe^{+3}, Cu^{+2}, Co^{+2}, Zn^{+2} and Pb^{+2}) were added. None of the species, other than lead, produced a precipitate.

Determining the optimum reaction conditions required selection of reagent and sample volumes sufficient to fill the turbidimeter cell, a buffer species and concentration, and a sample volume sufficient to achieve the desired sensitivity. At a low pH (<4), lead will be solubilized with loss of sensitivity, whereas at high pH (>7), other metals will precipitate and interfere. As development proceeded, it was determined that 15 mL 1 M ammonium acetate (sufficient to fill the turbidimeter cell) was sufficient to buffer a range of volumes of both standards and sample extracts to a final pH of 5.5 to 6.0, where apparent maximum turbidity (i.e., precipitation) of lead molybdate was observed.

During this early part of the method development, we observed that previously prepared solutions sometimes yielded turbidity values lower and more variable than expected. That is, the reactivity of potassium molybdate solutions in water or in sodium or ammonium acetate deteriorated over a matter of hours. This observation suggests that as potassium molybdate dissolves, its initial, kinetically formed hydration product is the most reactive species, which must undergo some transformation to a less reactive species. The solution chemistry of the molybdate oxo anion itself is complex. In an alkaline solution, the primary species present is the tetrahedral monomer, MoO_4^{2-}. As the pH is lowered, hexahedral hydrates are formed, followed by polymerization first to an oxo-bridged dimer, then to paramolybdate $Mo_7O_{24}^{6-}$ and octamer $Mo_8O_{26}^{4-}$, with the equilibrium position dependent on pH.[28] Experiments using other molybdate species yielded ambiguous results. A commercial solution sold as the molybdate "dimer," as a 10% aqueous solution of the ammonium salt, was tested as a reagent and was found to give only approximately 25% of the turbidity yielded using monomer (as the solid potassium salt) with an equivalent amount of lead. Ammonium paramolybdate, which was added as a solid, was slow to dissolve in ammonium acetate. Although the solution was reactive with lead, the reagent solubility characteristics precluded a direct comparison with the solid monomer. Therefore, potassium molybdate (K_2MoO_4) was determined to be the reagent of choice, and for the reasons described above, it needed to be added to the reaction vessel as a solid. As development moved into evaluation of field samples, we suddenly found that the test response of standard lead solutions was lower and became more variable. After ruling out other factors (e.g. pipettor function), we started testing molybdate reagent from different

lots and vendors. While tests using reagent from some lots yielded results consistent with previous observations, material from other lots exhibited the same problems of reduced sensitivity and precision. Furthermore, some lots that gave good results initially were found to deteriorate over time, with changes in test precision, indicated by higher RSDs typically being the initial signal of a change in the reagent performance. Conducting all weighing and dispensing operations in a rigorously dry environment (glove box) was needed to avoid reagent deterioration. Ultimately, we found that potassium molybdenum oxide from Alfa Aesar (anhydrous, 99.9% metals basis) worked reliably in the test. Other sources may be used but lots must be pre-screened. The reasons for what appears to be a sensitivity to atmospheric moisture, and possible dependence on manufacturing processes, are not obvious, and understanding would require additional investigation. To obtain consistent results, anhydrous potassium molybdenum oxide must be purchased with reported purity of 99%, must be kept totally dry while in storage, must be packaged into packets for individual measurements, and must be checked for acceptability before use.

Evaluation of the New Method with Reference Materials

The turbidimetric method was next evaluated using the target matrix, which was 25% (v/v) nitric acid extracts of aged paint samples. First, aliquots of a low-lead (<20 μg/g), real world reference paint material from the American Industrial Hygiene Association (AIHA) Environmental Lead Proficiency Analytical Testing (ELPAT) program[29] were extracted using the stator/rotor grinding/extraction method (25% (v/v) nitric acid)[4]. Extracts were filtered using a one-piece syringeless filter. (Syringe tip-style filters were found to be susceptbible to blockage.) The aliquots of the ELPAT material extract were combined to yield 500 mL of "blank" (low lead) authentic, real world paint extract, which provided potential interferences from the paint matrix for the subsequent experiments. Aliquots of this blank were spiked with known amounts of lead standard. These samples were analyzed using the pre-optimized conditions described above (add 0.75 mL extract to 15 mL buffer, add 357 $\pm$ 10 mg K_2MoO_4, shake, incubate 5 minutes). There was generally good agreement (within ± 10%) between the turbidity values for the same lead concentrations in the two different matrices – water and "blank" authentic, real world paint extract. In a second experiment, aliquots of the "blank" paint extract were spiked with lead standard and then diluted serially with blank extract 1 to 1 six times; with an initial concentration of 4.83 mM and a final solution concentration of 0.075 mM. The turbidity decreased in the same ratio except for the lowest concentration; it may be that a longer reaction time (> 5 min.) was needed at this low concentration to achieve maximum turbidity. The correlation coefficient was 0.993.

As a further test of the turbidimetric method, we determined the reproducibility of the turbidimetric standard response curve. Two, seven-point standard curves were generated on each of seven different days from two different sets of solutions prepared by spiking the low-lead paint extract with standard lead solutions. The values for each standard were calculated from the equation for the fitted curve. Table 1 presents the results of this effort, which show that the relative standard deviations for the concentration values are excellent, all being less than 7% across all 7 days, except for the zero concentration.

Table 1. Reproducibility of Standard Turbidimetric Curves on Seven Different Days

Original Lead Conc. (mM)	Average Realculated Concentration Value Determined from each of 7 Standard Curves (mean±SD(RSD))
0	0.050±0.014(27%)
0	0.050±0.014(27%)
0.15	0.206±0.013(6.3%)
0.15	0.207±0.013(6.1%)
0.3	0.362±0.010(2.9%)
0.3	0.367±0.011(2.9%)
0.6	0.645±0.011(1.7%)
0.6	0.644±0.011(1.7%)
1.2	1.140±0.015(1.3%)
1.2	1.135±0.021(1.9%)
2.4	2.139±0.058(2.7%)
2.4	2.126±0.096(4.5%)
4.83	4.963±0.061(1.2%)
4.83	4.926±0.052(1.1%)

Following the experiment using spiked, low-lead extracts, we analyzed six National Institute of Standards and Technology (NIST) Reference Material (RM) 8680 lead-containing paint-on-fiberboards[30] using the rotor/stator grinding/extraction method.[4] The extracts were analyzed for lead using the new turbidimetric method. The extracts were also measured for lead using inductively coupled plasma-atomic emission spectroscopy (ICP-AES).[31] Table 2 lists the results of this effort, which show that the turbidimetric and ICP-AES values agree well, with a statistical comparison having a slope of 1.084 and a correlation coefficient of 0.927. Table 2 also shows that there is no statistical difference between the NIST expected values and the turbidimetric values; for example, for sample RM KB2, the expected lead value is 1.25±0.35 mg/cm^2 and the turbidimetric average lead value is 1.10±0.04 mg/cm^2. Sample RM HA3 apparently has a great deal of variability from place to place on the board; however, the turbidimetric and ICP-AES values for the individual aliquots agree very well.

Table 2. Results of Turbidimetric Analysis of Six NIST RM 8680 Lead-Containing Paint on Fiberboards with Additional Aliquot Measurements for Lead by ICP-AES

NIST RM Board Sample #	Turbidimetric Value (mg/cm^2)	ICP-AES Value (mg/cm^2)	NIST RM Value (mg/cm^2)
KB2-1	1.13	1.38	
KB2-2	1.10	1.14	
KB2-3	1.04	1.12	
KB2-4	1.12	1.19	
	Average 1.10±0.04(3.7%)	Average 1.21±0.12(9.8%)	1.25±0.35
TD5-1	1.58	1.55	
TD5-2	1.40	1.46	
TD5-3	1.38	1.45	
TD5-4	1.36	1.44	
	Average 1.43±0.10(7.1%)	Average 1.48±0.05(3.4%)	1.21±0.38
DG2-1	1.11	1.18	
DG2-2	1.14	1.2	
DG2-3	1.01	1.08	
DG2-4	1.02	1.06	
	Average 1.07±0.06(6.1%)	Average 1.13±0.07(6.2%)	1.14±0.32
HA3-1	1.42	1.46	
HA3-2	1.65	1.68	
HA3-3	1.00	1.14	
HA3-4	0.78	0.85	
	Average 1.21±0.39(33%)	Average 1.29±0.36(28%)	1.31±0.34
MD2-1	0.86	0.98	
MD2-2	1.08	1.18	
MD2-3	0.96	1.06	
MD2-4	1.00	1.12	
	Average 0.98±0.09(9.4%)	Average 1.09±0.09(7.9%)	1.10±0.30
JH1-1	1.64	1.65	
JH1-2	1.48	1.62	
JH1-3	1.62	1.45	
JH1-4	1.49	1.57	
	Average 1.56±0.08(5.4%)	Average 1.57±0.09(5.6%)	1.29±0.40

Table 3. Results of Rotor/Stator-Turbidimetric Analysis of Powdered Real World Paints: NIST SRM 2581 and Five ELPAT Samples

Sample ID	Turbidimetric Value (%)	ICP-AES Value (%)	RM Value (%)
NIST 2581	0.42	0.43	0.449±0.011
NIST 2581	0.44	0.44	0.449±0.011
ELPAT 39P3	0.52	0.53	0.461±0.035
ELPAT 40P2	0.47	0.50	0.506±0.032
ELPAT 51P3	0.47	0.48	0.558±0.039
ELPAT 51P1	2.52	2.18	2.22±0.13
ELPAT 51P2	1.58	1.47	1.51±0.11
Blank	0.02	<0.0001%	0.00

Next, powdered real world paints were used. NIST Standard Reference Material (SRM) Paint 2581 at nominally 0.5% lead[32] and five powdered ELPAT paint materials were extracted using the rotor/stator grinding/extraction method[4] and the extracts analyzed for lead using the new turbidimetric method and also ICP-AES. The results presented in Table 3 show very good agreement between the turbidimetric values, the ICP-AES values, and the NIST and ELPAT nominal values (The ELPAT values are determined as the average results determined by the reference laboratories in AIHA's ELPAT Program.)

Testing the New Method for Ruggedness

A method that is to be used in the field may be subjected to variations both in environmental conditions and sample types/matrices that could give rise to bias or imprecision. A series of tests were performed to determine the effects of temperature, paint color, and plaster paint substrate.

Effects of Temperature

As a test of temperature ruggedness, duplicates of each of three different levels of lead solution were used to generate turbidimetric data on a loading dock at 31°C–33°C. At these temperatures, the turbidity values reached a maximum in approximately 1 minute. The values read at 1 minute matched very well with those predicted from previous calibration data. The turbidity values showed a decline at the highest concentration (3.06 mM) of approximately 10% over 20 minutes; this change was only approximately 3% at the lowest concentration (1.02 mM). Visually, it appeared that the precipitate was coagulating at this temperature. Subsequently, duplicates of each of these two levels of lead solution were used to generate turbidimetric data in a cold room at 4°C; the standard procedure was followed again. At this temperature, the turbidity values reached a maximum in approximately 10 minutes. Figure 2 shows the turbidity values for each temperature versus reaction time for a 1.02 mM Pb^{2+} solution. We see that the values for the room and high temperature reach a maximum immediately, but that with the low temperature, the reaction requires approximately 10 minutes to reach a maximum. At 3.06 mM lead, we observed evidence of the coagulation of the lead molybdate particles (as previously described) at both the room and high temperatures. Based on these tests, the time range recommended for taking readings is 5 to 10 minutes.

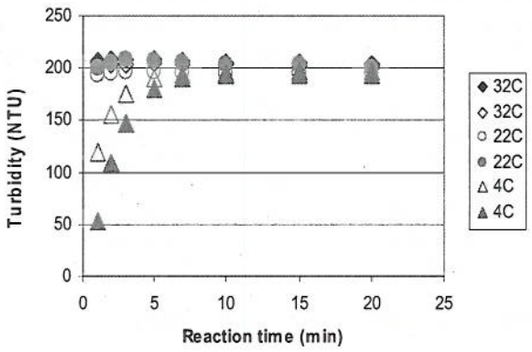


Figure 2. Temperature dependence of reaction rates.

Note: 1.02 mM Pb^{2+} in "blank" paint extract.

Effects of Paint Color

Most authentic paint samples tested initially were white or light in color. To test the effects of color on the method, eight real world colored paints were removed from the RTI archives. (It should be noted that the NIST RM 8680 fiberboards have lower layers that are colored, and as such, provided some test of the effects of color.) The archive paint samples were analyzed using the rotor/stator-turbidimetric method; ICP-AES was used to measure lead in additional sample aliquots of the rotor/stator paint extracts. The results of these tests are shown in Table 4. It is important to note that the samples analyzed for each color were not identical due to the variations found in paint; therefore, they cannot be considered duplicates. We see that the colors of these paints had no major effect on the results. The correlation coefficient for these pairs is 0.976. It is also important to note that the turbidity value for Sample 20035-1 reached saturation at 1,000 NTU, which most likely explains why the rotor/stator-turbidimetric value for this sample is less than the ICP-AES value. If data for 20035-1 are eliminated from the group, then the correlation coefficient is 0.993. With these data eliminated, the average relative percent difference between the turbidimetric method and the ICP-AES method is +4.5%; the mean difference is −0.17 mg of lead/cm^2. Equivalency of the methods is further indicated by the turbidity values being higher than the ICP-AES values for 8 of 16 samples while the ICP-AES values are higher than the turbidity values for 7 of 16 samples.

Effects of Plaster

Another ruggedness issue is the effect of plaster on the turbidimetric measurement. Plaster has caused interference with other lead sensors, such as rhodizonate-based test kits[33, 34, 35] In an experiment to test for this effect, authentic, real world samples that were partially or wholly plaster were submitted to the rotor/stator-turbidimetric method, and then an aliquot of the extract was analyzed by ICP-AES. First, several grab samples of three materials were analyzed using the new method.

Table 4. Results of the Rotor/Stator–Turbidimetric Analysis of Eight Different Colored Paint Samples with Additional Aliquots Measured for Lead by ICP-AES

Sample ID	Paint Color	Extract Color	Turbidity Value (mg/g)	ICP-AES Value (mg/g)
20033-1	Silver	Clear	1.0	1.7
20033-2		Clear	2.24	1.52
20147-1	Reddish	Yellow	10.8	12.4
20147-2		Yellow	5.18	4.98
20151-1	Gray-blue	Light yellow	0.69	0.50
20151-2		Light yellow	0.76	0.53
20114-1	Black	Light yellow	2.09	2.00
20114-2		Light yellow	0.18	0.09
20035-1	Light blue	Light yellow	19.8*	27.5
20035-2		Light yellow	12.2	13.7
20078-1	Bright red	Light pink	10.9	12.1
20078-2		Light pink	13.9	15.1
20075-1	Gray-blue	Light yellow	19.8	18.5
20075-2		Light yellow	22.7	21.8
20072-1	Light gray-blue	Yellow	0.22	0.22
20072-2		Yellow	0.21	0.28

* Turbidity reading was saturated at 1,000 NTU.

Only the first material, P1156 (painted plaster), contained measurable lead; the lead levels found with the samples taken were near or above the measurable range for the test (a turbidity reading of "> 1000 NTU"). ICP-AES measurements showed very high levels of lead in this material. Materials EG-16 (wallboard substrate only) and EG-16 (paint with wallboard substrate) showed essentially no lead by turbidimetry or ICP-AES. The extracts for two samples of P1156 were serially diluted and re-analyzed by both turbidimetry and ICP-AES. In this case, very good agreement was achieved, 4.8 mg per 1 mL for turbidimetry versus 5.0 mg per 1 mL for ICP-AES for one sample and 9.6 mg per 1 mL for turbidimetry versus 9.8 mg per 1 mL for ICP-AES for the other. As a further test of plaster interference, extracts of P1156, EG-16 (wallboard substrate only) and EG-16 (wallboard substrate with paint), were diluted, and then spiked with standard amounts of lead solution. The concentrations were adjusted so that either (1) the spiked concentrations were approximately twice the un-spiked or original amounts or (2) the spikes resulted in easily measurable lead concentration. Table 5 lists the results of the spiking experiments, which show that all values are within 10% of expected, except for one outlier at 183% (turbidity saturated). Finally, the rotor/stator-turbidimetric measurement was performed on plaster scraped and chipped off the back of the P1156, which consisted of a thin layer of paint on 1 to 2 mm's of plaster. As shown in Table 6, samples of the plaster test material resulted in turbidity values >1000 NTU. These results clearly show that lead from paint can penetrate into substrate. When the extracts were diluted, the agreement between the turbidimetric

and ICP-AES values was very good. We conclude from these tests that plaster does not interfere with the rotor/stator-turbidimetric method.

Table 5. Results of Rotor/Stator-Turbidimetric Analysis of Plaster Sample Extracts Spiked with Known Quantities of Lead

Sample ID	Measured Turbidity (NTU)	Calculated Lead (mg) in 3.0 mL	Expected Lead Turbidity* (NTU)	Recovery Based on Expected Turbidity (%)
1.61 mM Pb^{2+}	578	1.78	564	102
P1156-2	510	12.6	474	108
P1156-3	577	3.55	546	106
P1156-4	1,000*	6.12	546	183
EG-16-1	282	0.88	282	100
EG-16-2	290	0.91	283	103
EG-16-3	296	0.92	283	105
EG-16-4	268	0.84	283	95
EG-16-5	284	0.89	283	100
EG-16-6	289	0.90	283	102

* Based on a standard curve.

Table 6. Results of Rotor/Stator-Turbidimetric and ICP-AES Analyses of Plaster Substrate Samples

Sample ID	Turbidity	Calculated Lead (mg) in 3.0 mL	ICP-AES Lead (mg) in 3.0 mL
P1156-1	1,000	3.06	4.88
P1156-2	1,000	3.06	4.18
Sample ID	**Turbidity, Sample Diluted**	**Calculated Lead (mg) in 3.0 mL**	**ICP-AES Lead (mg) in 3.0 mL**
P1156-3	757	4.64	4.88
P1156-4	876	5.36	5.53
P1156-5	647	3.97	4.04

Performance of the New Turbidimetric Method with Authentic, Real World Samples

The final turbidimetric procedure included the following steps:

Step 1. Add premeasured potassium molybdate (347-367 mg) to a turbidimetric vial

Step 2. Add 15 mL of 1 M of ammonium acetate to the vial

Step 3. Cap and shake the vial vigorously for 30 seconds

Step 4. Add 0.75 mL of standard or filtered unknown lead solution in 25% nitric acid (v/v) to vial; mix by inverting it two times.

Step 5. Start the timer and read turbidity after 5 minutes of reaction time.

It is important to note that when samples yielded a saturated turbidity value (i.e., ≥1,000 NTU), the procedure was to dilute an aliquot of the original extract in 25% (v/v) of nitric acid; the order of dilutions performed until a suitable turbidity value was achieved was usually 1:5, 1:50, and 1:100.

Real world paint samples were collected from many sites in Raleigh and Durham, North Carolina. The samples were collected from the surfaces using either a modified drill bit or a chisel as described in an earlier publication.[4] The paints were collected from wood, metal, brick, and plaster substrate. The extractions of these paints were performed using the rotor/stator (grinding/extraction), 25% (v/v) nitric acid method described in this same paper.[4] Generally, five samples were collected in one location for the rotor/stator extraction and turbidity measurement and five samples were collected for extraction using EPA Microwave Method 3051A[36] and measurement by ICP-AES. The first set of samples was taken from wood substrate found in older, empty houses in Durham, NC. The samples were analyzed in situ by FPXRF,[4] and then were collected and extracted using the rotor/stator-turbidimetric methods and EPA Microwave Method 3051A and measurement by ICP-AES. The results listed in Table 7 show good agreement between the methods. It should be noted that the ranges, which show the variability in the analysis of real world samples, overlap in every case.

Table 7. Results of FPXRF, Rotor/Stator-Turbidimetric Method, and EPA Microwave Method 3051A-ICP-AES Analyses of Paint Samples for Lead Collected from Wood Substrate in Old Houses

Substrate–Location	XRF (mg/cm^2)	Value	Rotor/Stator-Turbidity, n=5 (mg/cm^2)	Method 3051A-ICP-AES, n=5 (mg/cm^2)
Houses				
Wood–ST1a	0.26	Mean±SD	0.239±0.056	0.202±0.029
		Range	0.18-0.33	0.165-0.230
Wood–ST1b	5.8	Mean±SD	5.49±0.97	5.15±0.69
		Range	4.88-7.18	4.43-5.97
Wood–ST2a	10.0*	Mean±SD	4.49±1.67	5.94±0.68
		Range	2.59-6.72	5.32-6.95
Wood–ST2b	29	Mean±SD	46.4±8.1	38.6±6.8
		Range	35.8-55.6	29.1-47.7
Wood–ST3a	19.5	Mean±SD	18.8±2.8	22.4±1.3
		Range	14.9-21.6	21.2-24.5
Wood–ST3b	4.9	Mean±SD	4.34±1.54	4.79±1.32
		Range	1.59-4.34	2.89-6.22
Wood–ST3c	0.5	Mean±SD	0.385±0.205	0.148±0.054
		Range	0.149-0.693	0.080-0.209

* Note: In this case, XRF did not overlap with other values.

Following this work, sets of either 6 or 10 real world paint samples were collected from various substrates in an old hospital, an old tobacco factory, and an old power station. The samples were removed from the substrate either with a modified drill bit or a chisel[4], and the samples taken for the two methods were generally within a few centimeters of each other. Replicate samples from each sampling location were analyzed using the rotor/stator-turbidimetric method and EPA Microwave Method 3051A with measurement by ICP-AES. FPXRF was performed as a screening method in the field. The results of these analyses are illustrated in Figure 3. The range of concentration values for the turbidimetric and ICP-AES methods is evidenced by the error bars, that show how widely lead levels can vary even within a small area, an effect that is magnified with thick, high lead concentration paint samples because of the many layers. This variability has been reported in other studies.[37, 38] Figure 3 illustrates the generally good agreement between the values for areal concentration (mg of lead/cm^2) for the turbidimetric and ICP-AES methods.

A simple statistical analysis compared the results obtained with the rotor/stator-turbidimetric method to the EPA Microwave Method 3051A with measurement by ICP-AES. The limitation of this analysis is that no two samples in any of the sets are equivalent because of real world paint sample variability. The average relative percent difference between the turbidimetric method results and the ICP-AES method results for the 24 sets measured as mg of lead/cm^2 is −0.63±32.5%; the mean difference in areal concentration is −2.1±7.0 mg lead/cm^2. Analysis was also performed with the percent (%) concentration data acquired with 17 of the sets. The average relative percent difference between the turbidimetric method and the ICP-AES method for these sets measured as percent lead is −6.9±56.5%; the mean difference is −2.5±4.2 %. Additional statistical analysis included non-parametric and parametric tests.

Non-parametric test of equality of means

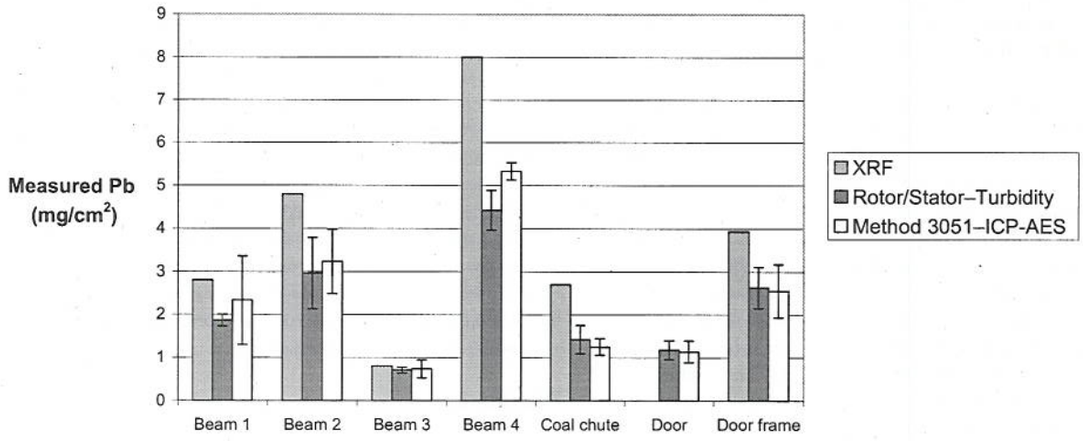
The mean measures of mg lead/cm^2 for the 24 samples were compared between the two methods for each sample. If both methods are producing estimates with the same mean, then it is expected that the mean for EPA Microwave Method 3051A with measurement by ICP-AES will be greater than the mean for rotor/stator-turbidity on 12 out of the 24 samples. Based on the data, the mean for EPA Microwave Method 3051A with measurement by ICP-AES exceeded the mean for rotor/stator-turbidity on 13 out of the 24 samples. Assuming that the samples are statistically independent, then the binomial distribution can be used to calculate a p value for the null hypothesis of equality of means. This test has a corresponding p value of 0.85, which implies that the null hypothesis of equality of means should not be rejected; that is, the two methods cannot be considered to produce different results.

Parametric tests of equality of means

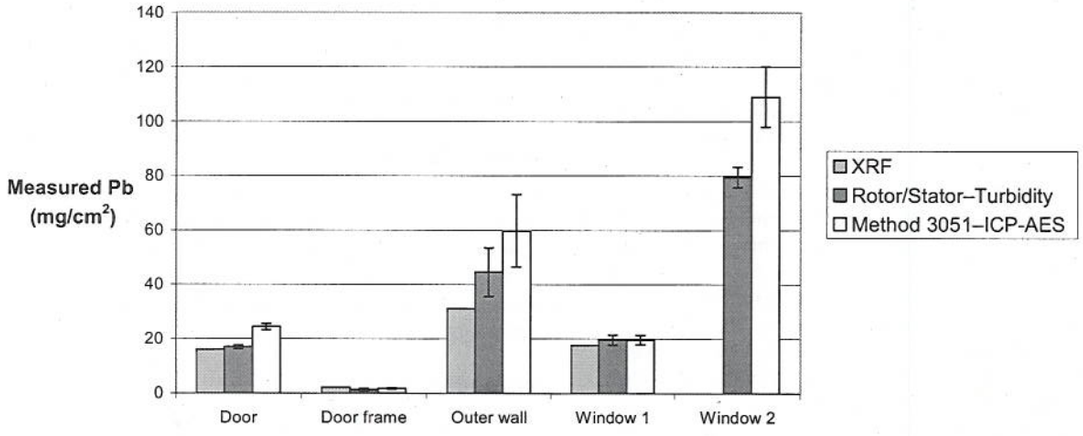
Regression models were used to examine differences of the expected areal concentrations (mg lead/cm^2) and mass concentrations (% lead) between the two methods. The null hypothesis in both cases is that both methods yield the same expected value. The only variable in the model was the method, which was coded as 1 for EPA Microwave Method 3051A/ICP-MS and 2 for rotor/stator-turbidity. The results from the model estimate the difference between the expected mg/cm^2 or the expected percentage. All inference is based on this difference; specifically, it is used to test the null hypothesis that the two methods have the same expected value.

Figure 3. Results of Analysis of Paint Samples for Lead from a Hospital, Tobacco Factory, and Power Station Using FPXRF, the Rotor/Stator-Turbidimetric Method, and EPA Microwave Method 3051A and measurement by ICP-AES*.

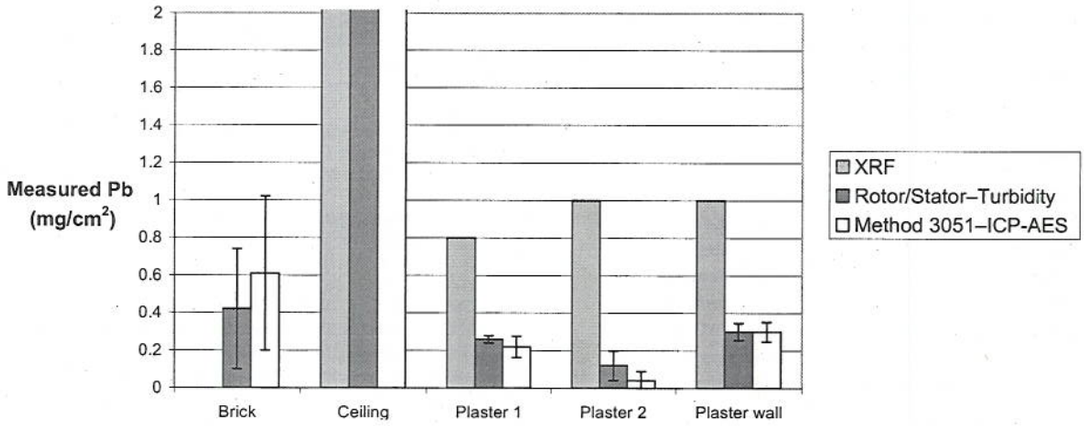
(a) Metal substrate



(b) Wood substrate



(c) Other substrate** (values for ceiling sample all >10 mg)



* Most XRF measurements involved fewer than three replicates, so error bars are not shown for this method.

** Measurements for the ceiling sample were all > 10 mg/cm², and values for R/S-T and 3051-ICPAES were statistically equivalent.

A potential problem with these data is a high level of heteroskedasticity. The variance is increasing as the expected value of mg/cm^2 increases. A similar pattern is noted for the percent lead values. Failure to account for heteroskedasticity can result in poor inference from regression models. There are several possible solutions, two of which were explored for this study. The first solution is to transform the data so that the variance appears to be constant across all likely values of the outcome. This was performed by using the log transformation for the mg lead/cm^2 measurements. No such transformation was conducted for the percent lead values. The second solution is to create a regression model that treats the variance as a function of the expectation. Specifically, variance functions were explored that allowed the variance to increase as the expected values increase. The three functions that were considered were the variance as a linear function of the expectation, a quadratic function of the expectation, and an exponential function of the expectation. The function that produced the lowest Akaike's Information Criterion (AIC) was the one that was used in the final model.

The 24 samples were treated as random. In effect, they were taken as a random sampling of possible samples from the locations being investigated. The measurements within samples were treated as correlated, whereas measurements between samples was treated as statistically independent. We used PROC NLMIXED from SAS© to construct the regression model because it allows both random effects and the ability to model the variance.

For mg Pb/cm^2, the best fitting regression model had the variance as an exponential function of the expectations, which is very similar to a log transformation. The final result was an expected difference of −0.81 mg/cm^2, with standard error of 4.69 mg/cm^2. The p value for this hypothesis of interest was 0.86, implying no significant difference. For the log transformation, the estimated difference was −0.027 (standard error [SE] = 0.078) and had a p value of 0.729. This also implies that there is not a statistical difference between the expected value of the two methods. Finally, the difference in the expected percent was explored. Here, the expected value was a probability, p. The variance was then modeled using the function $p(1\text{-}p)$. The expected difference in the percentages was −2.30 (SE = 2.46) with p value of 0.3551. Therefore, the expected percentage for the two methods does not appear to be statistically significant.

Conclusions

The new method presented here for lead in paint is based on a very selective reaction between lead and molybdate to form a fine lead molybdate particulate that can be measured using turbidity. There is no statisical difference between the expected lead values and those measured by the turbidimetric method for lead-in-paint RMs. Comparisons of analysis results obtained with authentic, real world samples collected locally that were performed with non-parametric and parametric statistical procedures also indicate no difference in the results obtained with the two different procedures (i.e., rotor/stator-turbidity versus EPA Microwave Method 3051A with measurement by ICP-AES).

Therefore, the rotor/stator-turbidimetric method meets the performance requirements for measuring lead in paint according to EPA's National Lead Laboratory Accreditation Program Laboratory Quality System Requirements, Revision 3.0 (July 5, 2007),[39] which requires an accuracy of 20%. The method is rapid, requiring only approximately 10 minutes per sample, assuming the reagents are already prepared, and the total analysis cost is approximately $6.00 per sample with a majority of that cost from the syringe-less sample filtration device and the one-time use of laboratory gloves.

This method also has the potential to meet the performance specifications of the EPA RRP rule[3] at the federal regulated level of 1 mg of lead/cm^2. Further development of this method for use by non-technical personnel will require simplification of the process, including pre-packaging of the reagents for stability and placement of all the components needed for analysis in the field in a travel case.

Disclaimer

This work has been reviewed in accordance with EPA's peer- and administrative-review processes and approved for presentation and publication. It has been subjected to the Agency's peer and administrative review. Any mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Notes and References

[a] *RTI International, P.O. Box 12194, Research Triangle Park, NC, 27709, USA Country. Fax: 919-316-3567; Telephone: 919-541-8046; E-mail: wstudabaker@rti.org*

[b] *U.S. Environmental Protection Agency, National Exposure Research Laboratory, U.S. EPA Mail Room, Mail Code D205-05, Research Triangle Park, NC, 27711, USA. Fax: 919-541-3527; Telephone: 919-541-2443; E-mail: harper.sharon@epa.gov*

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