Journal Pre-proof

Lead-based paint detection using perovskite fluorescence and X-ray fluorescence

Alexander van Geen, Lukas Helmbrecht, Eric Ritter, Ernest Kouassi Ahoussi, Petanki Soro, Maeva Koné, Medy Nongbé, Jacques Gardon, Willem Noorduin

PII: S0003-2670(24)00419-7

DOI: https://doi.org/10.1016/j.aca.2024.342618

Reference: ACA 342618

To appear in: *Analytica Chimica Acta*

Received Date: 22 December 2023

Revised Date: 10 April 2024

Accepted Date: 15 April 2024

	XRF Pb	
	>500 mg kg^{-1}	500 mg kg^{-1}
Green fluorescence	40	2
No green fluorescence	2	32

Lead-based paint detection using perovskite fluorescence and X-ray fluorescence

[1]Alexander van Geen*, [2]Lukas Helmbrecht, [3]Eric Ritter, [4]Ernest Kouassi Ahoussi, [4]Petanki Soro, [5]Maeva Koné, [5]Medy Nongbé, [6]Jacques Gardon, and [2, 7, 8]Willem Noorduin.

[1]Lamont-Doherty Earth Observatory, Columbia University, Palisades, New York, USA
[2]Lumetallix b.v., Science Park 104, 1098 XG Amsterdam, The Netherlands
[3]Spirochaete Research Labs llc, 690 RTE 25a STE3, East Seatuket, NY, 11733, USA
[4]UFR of Earth Sciences and Mineral Resources, University Felix Houphouet Boigny, Cocody Abidjan, Ivory Coast
[5]Laboratoire National D'Essais de Qualité, de Métrologie et d'Analyses (LANEMA), Abidjan, Ivory Coast
[6]HydroSciences Montpellier, University of Montpellier, CNRS, IRD, Montpellier, France
[7]AMOLF, Science Park 104, 1098 XG Amsterdam, The Netherlands
[8]Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, Amsterdam 1090 GD, The Netherlands

Highlights

- Fluorescence-based Pb detection kit tested on variety of liquid and dry paint samples
- High sensitivity and specificity indicated by comparison with two other methods
- Widespread use of kit could enhance efforts to reduce child exposure to Pb in paint

Graphical Table of Content

	XRF Pb	
	>500 mg kg^{-1}	500 mg kg^{-1}
Green fluorescence	40	2
No green fluorescence	2	32

Abstract

Background: Ingestion of flakes of Pb-based paint by infants remains a global health hazard with life-long consequences. Pb-based paint was banned for residential use in the US and Western Europe decades ago but is still sold in many countries. This study evaluates the performance of a new kit for detecting exposed Pb-based paint relying on the formation of Pb-halide perovskite that fluoresces bright green under a UV flashlight after spraying a non-toxic reagent.

Results: Tests with the Lumetallix kit were conducted in parallel with X-fluorescence and inductively-coupled plasma atomic emission analysis upon acid digestion using paint currently sold in Ivory Coast and samples of older US paint. Comparison of the three different methods indicates a detection limit for the Lumetallix kit of approximately 500 mg kg^{-1} Pb in paint, with a sensitivity of 95% and selectivity of 94% relative to that threshold (n=76). This detection limit is an order of magnitude below the US definition of Pb-based paint of 0.5% Pb by weight.

Significance: Because the kit is easy to use, exposed paint posing a risk could reliably be screened at scale by the general public. Any follow-up for confirmation and mitigation based on XRF measurements will need to consider that Pb-based paint covered with low-Pb paint will not respond to the kit but will be detected by XRF through the overpainted layer.

1. Introduction

Blood-lead (Pb) levels reflecting the exposure of the general population in 36 countries have documented the order of magnitude decline in Pb exposure that resulted from the gradual banning of Pb additives in gasoline [1]. In the United States, for instance, where blood-Pb surveys have been conducted most systematically, the proportion of children under six with blood-Pb concentrations >5 ug Pb/dL declined from >99% to <1% in 40 years [2, 3]. For children, such a dramatic reduction in Pb exposure reduced the likelihood of diminished intellectual function, learning and behavioral difficulties at school, and even juvenile detention [4, 5]. For adults, the reduction in Pb exposure prevented a substantial loss in income, hypertension, as well as cardio-vascular disease [6, 7].

Despite the ban on lead additives in gasoline, blood-Pb levels have not declined to the same level in all countries [8]. The US banned sales of Pb-based paint for residential use in 1978, yet the proportion of children under six with blood-Pb levels >5 ug/dL living in older, poorly maintained housing in 2005-15 was still as high as 20-40%, often a factor of ten higher than in wealthier neighborhoods nearby [9]. Cases of exposure from drinking water supplied by Pb pipes attributable to faulty corrosion control have been well documented [10, 11]. On the whole, however, ingestion of Pb-based paint or house dust and soil contaminated with Pb-based paint are probably the more typical remaining routes of child exposure. This applies to North America and Western Europe where the selling of Pb-based paint has been banned for decades, but especially in dozens of countries across Africa, South America, and Asia where Pb-paint is still sold or was banned only recently [12-14]. The need to identify Pb-based paint and the advantages of involving the general public in such testing motivated this study.

X-ray fluorescence, especially since the advent of portable XRF units, has become the most practical way of identifying Pb-based paint [15, 16]. However, portable XRF instruments are expensive and require training for safe handling. The US Environmental Protection Agency tested a number of field kits designed to screen for Pb-based paint 10-15 years ago, but only three are currently approved and this only to confirm the absence of Pb-based paint [17]. None were deemed sufficiently reliable to confirm the presence of Pb-based paint. One of these kits, the 3M LeadCheck swab, relies on sodium rhodizonate to produce a red color when rubbed on Pb-based paint but is no longer produced. There are a number of newer kits that rely on sodium rhodizonate, but none of them have been approved or evaluated systematically.

One kit approved by the US EPA that relies on the formation of Pb-sulfide is more complex to use and, probably for that reason, is not widely sold in hardware stores.

The present study evaluates a new kit marketed by the Dutch start-up Lumetallix that sprung out of research on the properties of Pb-halide perovskite to improve solar panels [18]. The method was optimized for visual detection to produce an intense green fluorescence using methylammonium bromide (CH_3NH_3Br) in isopropanol in the presence of Pb regardless of its oxidation state [19]. The Lumetallix reagent directly converts Pb into a light-emitting perovskite in a wide selection of specimens ranging from plastics and paints, to glazing and glass. The Lumetallix reagent can be applied by dripping, spraying, rubbing or brushing the reagent onto a sample, but for most applications a spray dispenser to coat the specimen is most practical. The constituents of the reagent, isopropanol and methylammonium bromide, are flammable and corrosive, respectively, but neither is toxic. With proper instructions, the kit can therefore safely be used by the general public. The performance of the Lumetallix reagent is evaluated here specifically in the case Pb-based paint relative to XRF and laboratory analysis using samples of old paint obtained from the US as well as new paint still sold today in West Africa.

2. Materials and methods

A total of 45 cans of paint were purchased from various shops in Abidjan, the capital of Côte d'Ivoire, in January 2022, February 2023, and September 2023. Most of the paint came in the original can labeled with a recent manufacturing date, while a subset were purchased from informal roadside shops and mixed from undocumented sources. All but one of these samples were solvent-based rather than water-based.

The Abidjan paint samples were analyzed for Pb in up to five different ways. All 68 samples were tested by applying the Lumetallix reagent and recording the level of green fluorescence under UV light, in most cases without prior knowledge of XRF readings. The fluorescence was recorded in a partially darkened setting by only one but always the same observer. The beam of the UV flashlight was swept back and forth over the sample to maximize the chances that any fluorescence was overlooked.

The paint from Abidjan was tested with a handheld XRF analyzer after applying the paint with a brush to either a 1-cm thick plank of wood or a set of 3-mm thick wooden tongue depressor and letting it dry. The XRF instrument (InnovX, later Olympus, Delta Premium with a Au tube anode) was used in the so-called soil mode, as calibrated by the manufacturer, set to three sequential 20 s readings at different incident energy levels. A subset of 23 liquid paint samples from Abidjan were also analyzed by entirely filling a scintillation vial, capping it tightly with a single layer of cling film, and placing the 1.5-cm diameter opening upside down on the detector of the InnovX instrument for analysis again in the soil mode. A National Institute of Technology and Standards soil reference material was included with each series of measurements on a given day. The concentration of Pb in soil standard NIST2711a over the course of the study averaged 1,240±60 mg kg^{-1} (n=9), which corresponds to 88% of the certified value of 1,400±10 mg kg^{-1} [20]. The cause of the somewhat lower InnovX readings is unclear and concentrations were not adjusted. Fifteen of the liquid paint samples were also analyzed in a similar fashion on a second XRF instrument, a Niton XL3t set to the soil mode, in Abidjan. The text hereon refers to analysis using the InnovX instrument unless specified, however.

The samples tested by XRF in liquid form were also sent for analysis to Complete Environmental Testing, Inc. in Stratford, Connecticut, which participates in the National Institute for Occupational Safety & Health (NIOSH) Environmental Lead Proficiency Analytical Testing (ELPAT) program for soil, paint chips, and air cassettes. CET, Inc. follows EPA method 3051a for microwave-assisted digestion [21] and EPA method 6010c for analysis by inductively-coupled plasma atomic emission spectroscopy (ICP AES) [22], including prescribed quality control protocols.

A subset of 13 paint samples from Côte d'Ivoire tested in liquid form were ashed at LANEMA for 4 hours at 750°C, after which 0.1-0.2 g of the ash was micro-wave digested for 45 min in 7 mL of nitric acid and 3 mL of hydrofluoric acid. The digest was then taken up in 50 mL of 1% nitric acid for analysis by inductively-coupled plasma mass spectrometry (ICP-MS) on an Agilent 7850 instrument.

Another 23 paint samples were obtained as paint chips in scintillation vials by a team of investigative reporters at Reuters from families living in poorly maintained housing on US military bases [23, 24]. The US paint chips were analyzed by XRF by placing the chip samples, some small and not covering the entire detector window, on a single layer of cling film on top of the same inverted XRF analyzer in its benchtop stand.

A serial dilution experiment was conducted using a vintage can of Dutch Boy Lead White to constrain the detection limit of the Lumetallix kit. The paint was almost dry and therefore thinned with linseed oil from a can of the same brand in a scintillation vial. Using a pipettor, 5 mL of the thinned Dutch Boy paint was then transferred to another scintillation vial and combined with 5 mL of new residential white paint not containing any detectable Pb. After thorough mixing, 5 mL of this combination was again diluted with 5 mL of new paint in another vial and so forth for a total of 12 times. The resulting total of 14 paint samples, including the two end members, were applied with a brush to flat wooden paint mixing sticks and dried with a heat gun. The flat sticks were turned around, mixed randomly, and labeled with letters only on the back. They were then turned around, sprayed with the Lumetallix kit, and ranked independently by two observers according to the intensity of the green luminescence under UV light.

Two additional experiments were conducted to determine the sensitivity of XRF readings to the configuration of Pb-based paint layers. The first experiment was intended to document the influence of the backing material. A layer of paint containing 38,000 mg kg^{-1} Pb applied to cling film was placed on the XRF detector. Subsequently, an increasing number of wooden tongue depressors was added behind the paint layer to determine the XRF response for systematically increasing layers of backing material.

The second experiment assessed the role of paint thickness. For this purpose, an increasing number of paint layers on cling film were placed on top of the detector. The paint was applied to layers of cling film as uniformly as possible but without trying to measure the thickness of the layer.

Finally, four layers of paint from Abidjan were applied on top of each other on a wooden tongue depressor with an offset in coverage of each layer. These offsets made it possible to test the bottom layer alone, a combination of the bottom 2 layers, the bottom 3 layers, and all 4 layers with the Lumetallix kit and by XRF.

3. Results

The range of Pb concentrations measured in dry paint by digestion and ICP AES and in liquid paint measured by XRF track each other well across the entire <5 to 40,000 mg kg^{-1} range (Fig. 1). The Pb content of 9 paint samples was below the reported detection limit of 1000 mg kg^{-1} by ICP AES and the detection limit of 5 mg kg^{-1} by XRF. For visualization and regressions, entries below the detection limit of the two methods were replaced by one half of their respective values. The slope of a linear regression of Pb concentrations measured by XRF as function concentrations measured by ICP AES of 1.05±0.07 (2-sigma) and the intercept of -700±1100 mg kg^{-1} Pb are statistically indistinguishable from 1 and 0, respectively (r^2 = 0.98). Pb concentrations in liquid paint measured in the soil mode on the Niton XL3t instrument were essentially the same (Fig. S1a). Analysis of the same 23 samples as dry layers of paint on wood by XRF in the soil mode yields lower concentrations but also considerably more scatter in relation to ICP AES measurements (Fig. 1b, d), with a corresponding slope and intercept of 0.24±0.11 and 400±1700 (r^2 = 0.48), respectively.

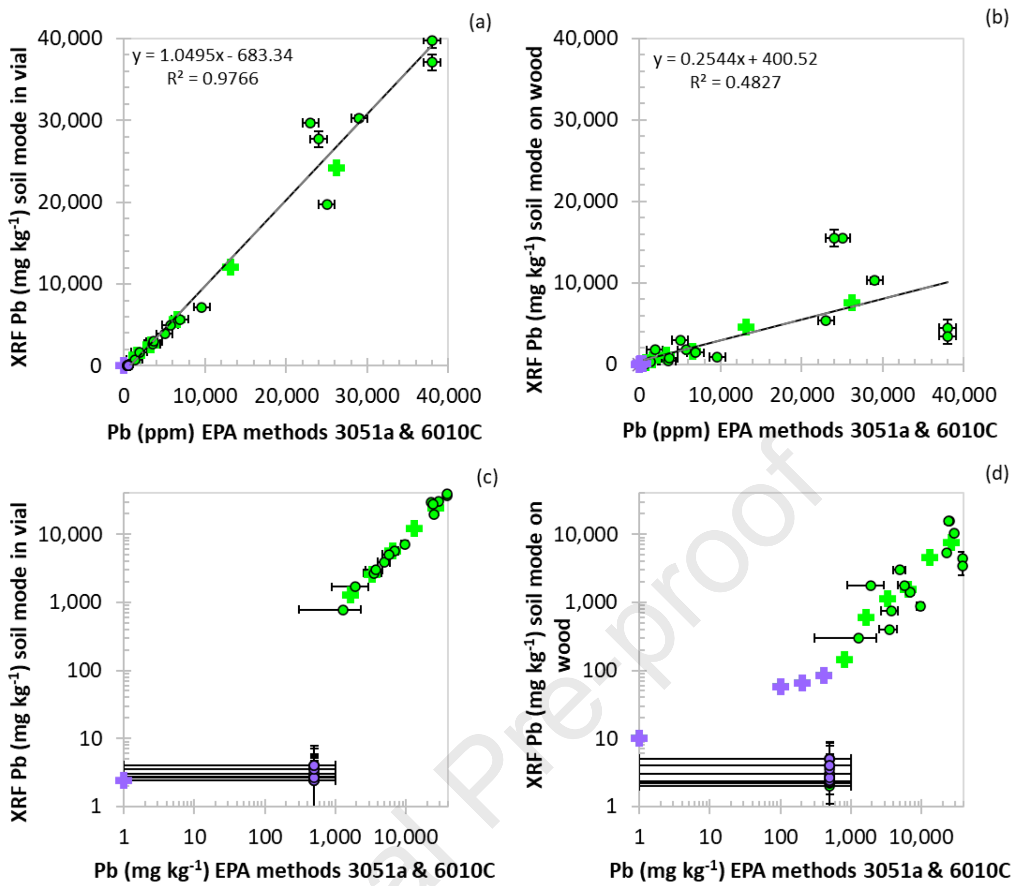

Figure 1. Comparison of Pb concentrations measured in dry paint by standard EPA methods (digestion and ICP AES) and by XRF in the soil mode in two different ways: (a, c) as liquid paint analyzed through plastic wrap in upside-down scintillation vials, and (b, d) as dry paint applied to wood. Circles indicate paint samples purchased in Abidjan; crosses show results from serial dilution of Dutch Boy White Lead. Symbol color indicates whether green fluorescence was observed when spraying the dry paint with the Lumetallix reagent. There are 3 additional purple crosses at the low end of Pb concentrations for measurements on wood compared to measurements in liquid paint because the samples were too small for the latter. The same data are displayed on a linear and a log scale. Also shown are 1-sigma error bars set at half the detection limit by ICP AES and calculated by the XRF instrument's software, respectively. Linear regressions in (a) and (b) are based on paint samples purchased in Abidjan only, not the dilutions.

Among the same set of paint samples analyzed by XRF and ICP AES, none of the 9 containing <5 mg kg^{-1} Pb by XRF analysis of liquid paint any showed green fluorescence under UV after applying the Lumetallix reagent to dry paint on wood (Fig. 1). By the same token, all 14 samples containing at least 780 mg kg^{-1} Pb according to XRF analysis of liquid paint responded to the Lumetallix kit. An additional 20 paint samples were analyzed only as a dry layer of paint on wood by XRF and with the kit. Among these, the sample with the highest concentration that did not respond to the kit contained 840 mg kg^{-1} Pb based on XRF analysis of dry paint (Fig. 2). The paint sample with the lowest Pb concentration that responded to the kit contained 480 mg kg^{-1} Pb based on XRF analysis of dry paint.

Figure 2. Photos under UV light of paint samples purchased in Abidjan, Ivory Coast, in (a) January 2022 applied to a 2-cm thick wooden plank and (b) February 2023 applied to 3-mm thick wooden tongue depressors. Also shown are Pb readings (mg kg^{-1}) with the handheld XRF in the soil mode applied directly to the paint layers.

According to ICP AES data, Dutch Boy Lead White contained 420,000±5,000 mg kg^{-1} Pb on a dry weight basis, which was again consistent with a reading of 430,000±11,000 mg kg^{-1} Pb by XRF in liquid form after dilution with linseed oil. According to XRF analysis of the other end-member of the dilution experiment, the recently manufactured white Valspar Signature paint contained <5 mg kg^{-1} Pb. Pb concentrations measured by XRF in liquid form for the various dilutions of Dutch Boy paint with the new paint were entirely consistent with the volumetric mixing ratios (r^2 = 0.998). With two exceptions at concentrations of 2,500 mg kg^{-1} and above, the independent rankings of green fluorescence intensity were internally consistent and followed the sequence of dilution. Both observers independently reported green fluorescence in the 9-fold dilution and no green fluorescence in the 10-fold dilution, corresponding to Pb concentrations of 840 and 420 mg kg^{-1} Pb, respectively (Fig. 3).

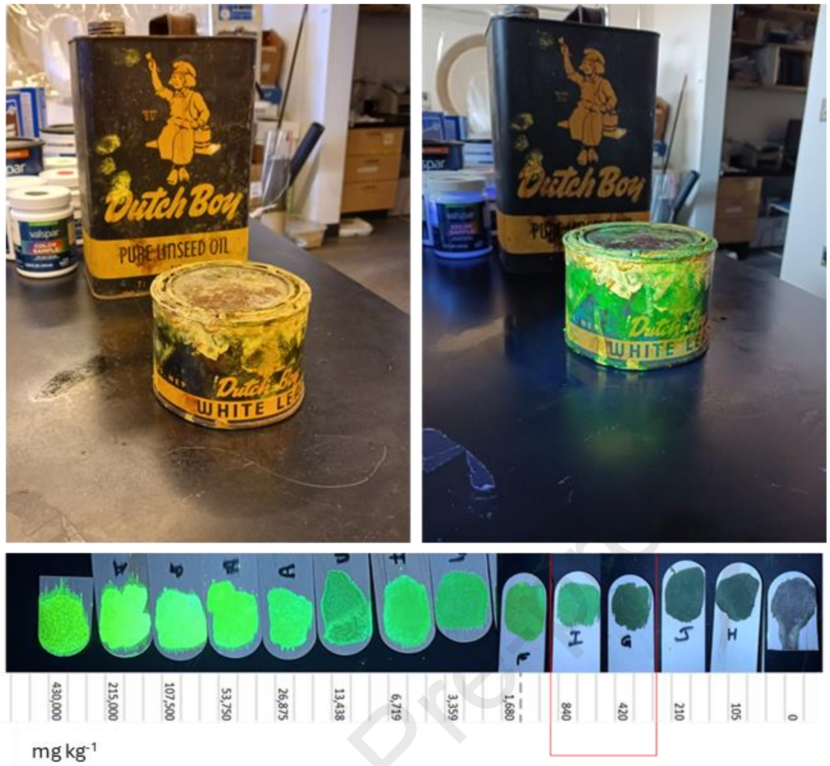

Figure 3. Photos of a vintage can of Dutch Boy White Lead paint and linseed oil used containing 43% Pb for the serial dilution experiment under (a) ambient light and (b) UV light after spraying the Lumetallix reagent. Photo of Dutch Boy paint diluted serially by a factor of two with new white paint containing <5 mg kg^{-1} Pb on a series of wooden tongue depressors under UV light.

The first of the paint configuration experiment shows that the concentrations of Pb of 64,500 mg kg^{-1} measured for a single layer of paint without any solid backing was more than twice the actual Pb concentration of 30,300 mg kg^{-1} measured by ICP AES and XRF in liquid form, and then dropped to 13,000 mg kg^{-1}, i.e. less than half that value when backed by a single overlying tongue depressor to eventually stabilize at 4,500 mg kg^{-1} when backed by 10 overlying tongue depressors (Fig. S2a). The second configuration experiment shows that after a first reading of 4,300 mg kg^{-1} each additional layer of paint increased the measured Pb concentration by an average of 3,400 mg kg^{-1}, with a slight curvature suggesting attenuation for each additional paint layer (Fig. S2b). Not only the thickness of the paint layer but also the thickness of the material backing the paint therefore affects Pb concentrations measured by XRF.

Concentrations of Pb indicated by simply placing chips of paint from US military bases on the XRF detector ranged from 6 to almost 500,000 mg kg^{-1}. All but one sample analyzed in this fashion containing more than 3,000 mg kg^{-1} Pb unambiguously responded to the Lumetallix reagent, with one exception containing 5,300 mg kg^{-1} (Fig. 4). Some of the fluorescence was patterned but still easy to identify. With one exception of faint fluorescence for a sample containing 210 mg kg^{-1} Pb in this mode of analysis, none of the samples containing less than 340 mg kg^{-1} Pb responded to the Lumetallix kit.

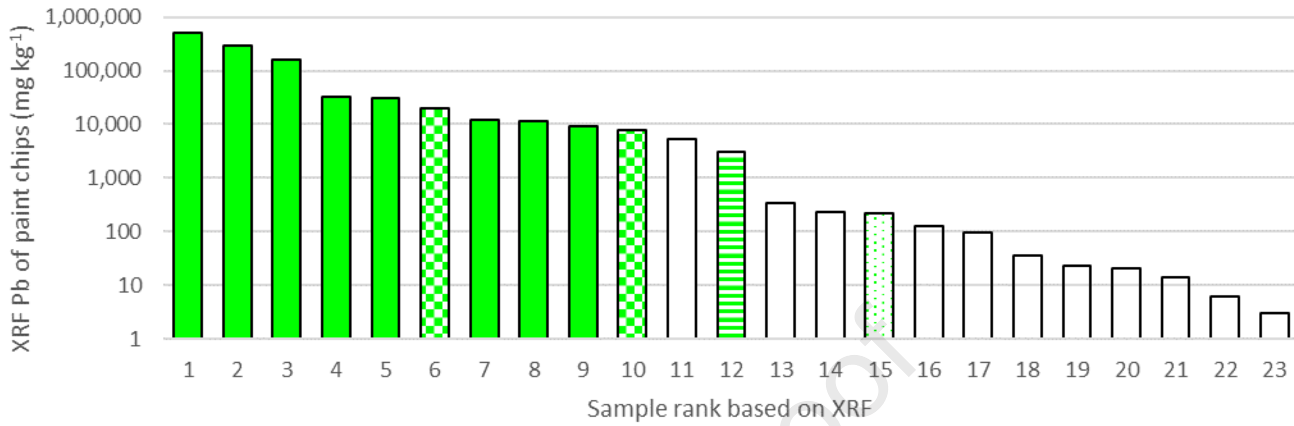

Figure 4. Green fluorescence recorded under UV light after spraying with the Lumetallix reagent a total of 23 samples of paint returned anonymously by families living in poorly maintained housing on US military bases (Schneyer and Januta, 2018). Uniform fluorescence vs. striations or a mottled pattern were also recorded as shown. Bias was minimized by recording fluorescence without referring to data previously collected by XRF and with the 3M LeadCheck kit (Filippelli et al., 2020).

In the case of the wooden tongue depressor manufactured with multiple layers of paint, Pb concentrations measured by ICP AES starting from the first layer applied were 40,000, 7,200 , 800, and <6 mg kg^{-1}, respectively. After applying the Lumetallix reagent, only the top layer without detectable Pb showed no green fluorescence whatsoever, while the fluorescence signal for the layer just below containing 800 mg kg^{-1} Pb was muted compared to the two layers containing more Pb (Fig. 5). Similar results were visualized after splitting the tongue depressor and applying the Lumetallix reagent to an exposed section of multiple layers (Fig. 5). Integrated Pb concentrations were also measured applying the XRF detector to the various combinations of layers in the soil mode. Concentrations varied from 5,300 mg kg^{-1} for the bottom (yellow) layer alone; 5,900 mg kg^{-1} for the combination of the bottom and 2nd (red) layer; 3,200 mg kg^{-1} with the addition of the 3rd (white) layers; and 2,600 mg kg^{-1} after covering the previous three layers with the last (brown) layer of paint containing <5 mg kg^{-1} Pb.

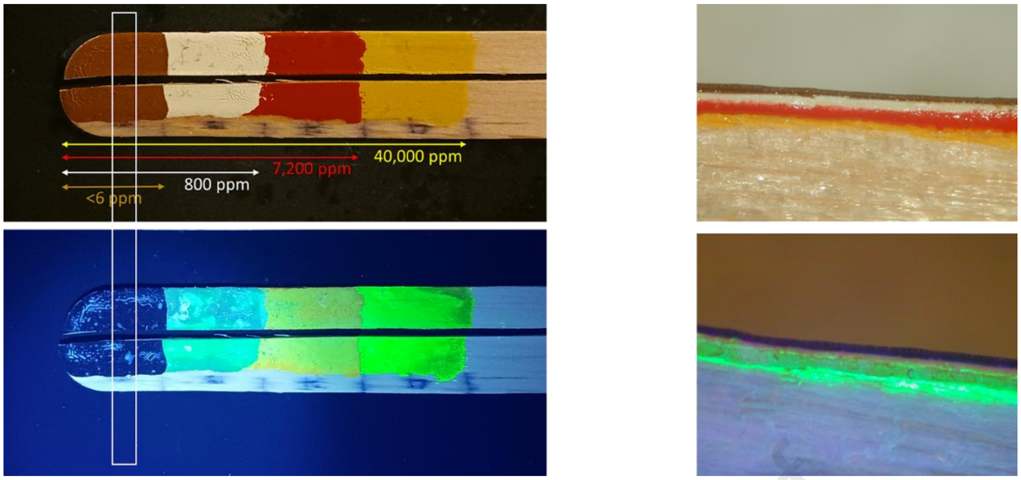

Figure 5. Photo of split wooden tongue depressor after applying 4 layers of paint from Ivory Coast spanning a wide range of Pb concentrations under (a) natural light and (b) UV light after spraying the Lumetallix reagent. Also shown are the 4 layers in cross-section under (c) natural and (d) UV light.

4. Discussion

In the so-called soil or environmental mode of different brands of handheld XRF's, elemental count rates are normalized to the Compton scatter and converted to concentrations with an internal calibration set by the manufacturer that relies on soil standards of known composition [25]. The process seems robust, even for a matrix other than soil, as both the InnovX and the Niton instrument report essentially the same Pb concentrations for a suite of liquid paint samples purchased in Abidjan (Fig. S1a). The data show that Pb concentrations for liquid paint measured by XRF in the soil mode are not only proportional but also closely match the absolute Pb concentrations in dry paint measured by acid digestion and ICP AES (Fig. 1). The Pb content of paint produced by manufacturers that still rely on Pb-based pigments, even in countries such as Côte d'Ivoire where current legislation sets a maximum Pb concentration of in paint of 90 mg kg^{-1} [26], could therefore readily be quantified in liquid form by XRF.

Analysis of liquid paint by XRF is effective across four orders of magnitude in concentrations whereas dilution of the paint digest would need to be modified for the standard ICP AES method to reach the necessary sensitivity at the lower end of Pb concentrations. In principle, this should be necessary in the case of analysis by ICP MS because of the instrument's wider dynamic range. Ashing followed by acid digestion led to results that are proportional to Pb concentrations measured by XRF but a factor of four lower (Fig. S1b). This lower response likely reflects an ashing temperature that was too high and caused considerable volatilization of Pb [27].

Comparison with the XRF data shows that the Lumetallix kit is well-suited to identify Pb-based paint, even if the intensity of green fluorescence is not consistently related to the Pb concentration (Fig. 2). A threshold of 500 mg kg^{-1} derived from the serial dilutions of Dutch Boy White Lead also optimizes classification of the other samples based on the Lumetallix kit. In the case of liquid paint from Abidjan, flawless categorization reflects in part the inclusion of only one sample with Pb concentrations in the 5-800 mg kg^{-1} concentration range (Fig. 1c). Sensitivity and specificity are defined, respectively, as ratio of the number of true positives to the sum of the number of true positives and false negatives and the ratio of the number of true negatives to the sum of the number of true negatives and false positives, respectively. On this basis, the overall sensitivity and specificity of the Lumetallix kit remain high at 95% (95% CI: 84-99%) and 94% (80-99%) respectively, when adding paint analyzed by XRF under suboptimal conditions, such as a dry layer of unknown thickness or as loose paint chips (Table 1). These additions include 14 samples with apparent Pb concentrations in the 5-800 mg kg^{-1} range and only 4 miss-classifications out of a total of 76 pairs of measurements.

For comparison with other Pb-based kits, sensitivity and specificity of the rhodizonate-based 3M LeadCheck kit calculated from the analysis of the same small set of 23 samples from US military bases were 100 and 77%, respectively relative to a 5,000 mg kg^{-1} threshold and 100 and 80% relative to a 500 mg kg^{-1} threshold after categorizing all intermediate visual readings previously reported positives [24]. A larger study conducted with synthetic Pb-paint samples conducted for the US EPA, however, concluded that the 3M kit did not perform as well. US EPA regulation is based on two definitions of Pb-based paint: a loading >1.0 milligram per square centimeter (mg/cm^2) or a concentration >0.5% (5,000 mg kg^{-1}) by weight. Assuming for simplicity a dry paint density of 2 g/cm^3, the two measures are equivalent assuming a paint layer containing 5,000 mg kg^{-1} Pb that is 1 mm thick. Relative to a threshold of 1 mg/cm^2, the sensitivity of the 3M kit recalculated from Table 6.3 in ref. [28] was 99% (n=343) but the specificity was only 25% (n=126). The sensitivity of the sulfide-based D-Lead kit recalculated from Table 6.3 in ref. [29] relative to the 1 mg/cm2 threshold was 99% (n=542) and 70% (n=399) for a technical operator. For both the 3M and the D-Lead kit, the specificity declined further for a non-technical operator. Relative to the lower threshold of 500 mg kg^{-1}, the sensitivity of the Lumetallix kit is therefore only slightly lower than the 3M and D-Lead kits at about 5,000 mg kg^{-1} while the specificity is much better for Lumetallix.

The available data do suggest that the composition or aging of certain paints might influence the Lumetallix response. Most striking is the partial inhibition of the signal for brown paint containing 15,500 mg kg^{-1} Pb (Fig. 1). This paint also contained a particularly high concentration of Fe of 2.2% but was otherwise unremarkable in terms of other frequently major constituents measured by XRF such Ti, Ca, or Zn. After completion of this study, the owner of a house built in the New York area in the 1920's asked us to test two chips of old paint. The chips contained 10,000 and 50,000 mg kg^{-1} Pb respectively based on XRF, but did not respond to the Lumetallix reagent at first. It took another day and additional spraying to generate a clear sign of green fluorescence in both. Here too the composition of the paint for other elements measured by XRF was not atypical. Potential matrix and kinetic effects therefore require further study, preferably in collaboration with an entity handling large numbers of samples in order to obtain a representative set of samples.

Other than perhaps some isolated matrix or kinetic effects, the Lumetallix kit appears ready for widespread distribution and use by the public at large. One issue is how Lumetallix results will compare to XRF testing, and which results are most relevant for environmental safety. The experiment with multiple layers of paint illustrates that XRF readings integrate the composition of multiple layers of paint, whereas the Lumetallix kit only responds to the surface layer. In New York City, for instance, mitigation of a Pb-based paint hazard is recommended only for an XRF reading >0.5 mg/cm2 and the presence of visibly damaged or peeling paint. A streamlined yet more effective inspection protocol could therefore entail applying the Lumetallix reagent to all possibly problematic areas followed by confirmatory XRF readings only where green fluorescence is visible under UV light.

In Abidjan, only various types and colors of solvent-based paints sold under the Industrap brand were Pb-based, albeit at highly variable concentrations. There are at least a half-dozen brands of solvent-based paint without Pb sold in Abidjan, including some at comparable prices. The Lumetallix kit was found to perform equally well when spraying liquid or dry solvent-based paint and could therefore be applied at the store before a purchase. Whereas water strongly inhibits the green fluorescence, water-based paint sold in Abidjan has not been documented to be Pb-based [12]. The implication is that the Lumetallix kit could be used by individuals to test paint before a purchase as a selection criterion.

5. Conclusion

Green fluorescence under UV light of Pb-perovskite produced by the Lumetallix reagent effectively identifies levels >500 mg kg^{-1} Pb in paint. This was demonstrated by comparing kit results with XRF readings for old and new paint from a variety of sources. Few if any interferences were encountered, which contributed to a sensitivity of 95% and a specificity of 94% based on the available set of 76 samples. This performance is superior to that of the rhodizonate-based 3M swabs, which in addition are no longer produced. Given the continued marketing of Pb-based paint in many African countries in particular, widespread use of the kit by the general public in the region could help reduce childhood Pb exposure. Pb-based paint was banned in Western Europe and North America decades ago but is still a legacy affecting children living in older, poorly maintained homes. Deployment of the Lumetallix kit at scale could help reach the World Health

Organization's objective of ending the use of Pb-based paint by pressuring elected officials to pass the legislation where needed and compelling paint manufacturers to change their product line.

Author Contributions

A.v.G. conceived the study, selected the paint samples to be tested, designed the experiments, conducted XRF measurements, and drafted the paper. E.K.A., P.S., and J.G. contributed to the design of the study, collected paint samples in Abidjan and conducted some of the XRF measurements. M.K. and M.N. were responsible for additional laboratory measurements. E.R. helped conduct the dilution experiment. L.H. and W.N. are the co-inventors of the kit and supplied prototypes for the experiments. All authors contributed to the interpretation of the results and edited the paper.

Notes

L.H. and W.L.N. are co-founders and co-owners of Lumetallix BV, which produces the kit. L.H. and W.L.N. played no role in the selection of paint samples used to compare kit results with XRF and laboratory analyses. E.R. was a distributor of the Lumetallix kit in the US via Amazon at the time of the initial submission. None of the remaining co-authors have a financial interest in Lumetallix or other competing interests.

Funding

Collection and analysis of samples in Ivory Coast was partly funded by grant AFD CCI 1907 01 L from the Fond d'Innovation au Développement (F. Gubert and M. Kouassi, Principal Investigators).

References

[1] Angrand, R. C.; Collins, G.; Landrigan, P. J.; & Thomas, V. M. (2022). Relation of blood lead levels and lead in gasoline: an updated systematic review. Environmental health 21(1), 138. https://doi.org/10.1186/s12940-022-00936-x

[2] Pirkle JL, Brody DJ, Gunter EW, Kramer RA, Paschal DC, Flegal KM, Matte TD. The decline in blood lead levels in the United States. The National Health and Nutrition Examination Surveys (NHANES). JAMA. 1994 Jul 27;272(4):284-91.

[3] Tsoi MF, Cheung CL, Cheung TT, Cheung BM. Continual Decrease in Blood Lead Level in Americans: United States National Health Nutrition and Examination Survey 1999-2014. Am J Med. 2016 Nov;129(11):1213-1218. doi: 10.1016/j.amjmed.2016.05.042.

[4] Lanphear BP, Hornung R, Khoury J, Yolton K, Baghurst P, Bellinger DC, Canfield RL, Dietrich KN, Bornschein R, Greene T, Rothenberg SJ, Needleman HL, Schnaas L, Wasserman G, Graziano J, Roberts R. Low-level environmental lead exposure and children's intellectual function: an international pooled analysis. Environ Health Perspect. 2005 Jul;113(7):894-9. doi: 10.1289/ehp.7688.

[5] Aizer, A. and Currie, J., 2019. Lead and juvenile delinquency: new evidence from linked birth, school, and juvenile detention records. Review of Economics and Statistics, 101(4), pp.575-587.

[6] Grosse, S.D., Matte, T.D., Schwartz, J. and Jackson, R.J., 2002. Economic gains resulting from Schneyerthe reduction in children's exposure to lead in the United States. Environmental health perspectives, 110(6), pp.563-569.

[7] Navas-Acien, A., Guallar, E., Silbergeld, E.K. and Rothenberg, S.J., 2007. Lead exposure and cardiovascular disease—a systematic review. Environmental Health Perspectives, 115(3), pp.472-482.

[8] Ericson, B., Hu, H., Nash, E., Ferraro, G., Sinitsky, J., & Taylor, M. P. (2021). Blood lead levels in low-income and middle-income countries: a systematic review. The Lancet. Planetary health, 5(3), e145–e153. https://www.thelancet.com/journals/lanplh/article/PIIS2542-5196(20)30278-3/fulltext

[9] Schneyer, Joshua, and M.B. Pell. "Legacy of Lead." November 14, 2017. Reuters Investigates. Available: https://www.reuters.com/investigates/special-report/usa-lead-newyork/

[10] Pieper, K. J., Martin, R., Tang, M., Walters, L., Parks, J., Roy, S., Devine, C., & Edwards, M. A. (2018). Evaluating water lead levels during the Flint water crisis. Environmental science & technology, 52(15), 8124–8132. https://doi.org/10.1021/acs.est.8b00791

[11] Dave, D. M., & Yang, M. (2022). Lead in drinking water and birth outcomes: A tale of two water treatment plants. Journal of health economics, 84, 102644. https://doi.org/10.1016/j.jhealeco.2022.102644

[12] IPEN. Lead in Solvent-Based Paints for Home Use in Côte d'Ivoire, International Pollutants Elimination Network, 2017. https://ipen.org/projects/eliminating-lead-paint/ipen-research

[13] UNEP (2023) 2022 Update on the Global Status of Legal Limits on Lead in Paint. United Nations Environment Program. https://www.unep.org/resources/report/2022-update-global-status-legal-limits-lead-paint

[14] WHO (2023). Exposure to lead: a major public health concern. Third edition. Department of Public Health, Environmental and Social Determinants of Health, World Health Organization. https://iris.who.int/bitstream/handle/10665/372293/9789240078130-eng.pdf?sequence=1

[15] HUD (2012) U.S. Department of Housing and Urban Development. "Guidelines for the Evaluation and Control of Lead-based Paint Hazards in Housing." Office of Healthy Homes and Lead Hazard Control. Second Edition. Washington, D.C.: HUD, 2012. https://www.hud.gov/program_offices/healthy_homes/lbp/hudguidelines

[16] Muller, Y., Favreau, P., & Kohler, M. (2014). Performance evaluation of currently used portable X ray fluorescence instruments for measuring the lead content of paint in field samples. Journal of Occupational and Environmental Hygiene, 11(8), 528–537. https://doi.org/10.1080/15459624.2014.880788

[17] EPA (2023).U.S. Environmental Protection Agency Recognized Lead Paint Test Kit Fact Sheet https://www.epa.gov/system/files/documents/2023-10/testkitfactsheet2023.pdf

[18] Stranks, S. D.; Snaith, H. J. Metal-halide perovskites for photovoltaic and light-emitting devices. Nature Nanotechnology 2015, 10, 391–402.

[19] Helmbrecht, L.; van der Weijden, A.; van Dongen, S.; van Campenhout, C.; Noorduin. W. L. Direct environmental lead detection by photoluminescent perovskite formation with nanogram sensitivity. Environmental Science and Technology 57, 49, 20494–20500, 2023. https://doi.org/10.1021/acs.est.3c06058

[20] NIST (2022). National Institute of Standards & Technology Certificate of Analysis. Standard Reference Material® 2711a Montana II Soil Moderately Elevated Trace Element Concentrations. https://tsapps.nist.gov/srmext/certificates/2711a.pdf

[21] EPA (2007). "Method 3051A (SW-846): Microwave Assisted Acid Digestion of Sediments, Sludges, and Oils," Revision 1. Washington, DC. https://www.epa.gov/sites/default/files/2015-12/documents/3051a.pdf

[22] EPA (2007) "Method 6010C (SW-846): Inductively Coupled Plasma-Atomic Emission Spectrometry," Revision 3. https://19january2017snapshot.epa.gov/sites/production/files/2015-07/documents/epa-6010c.pdf

[23] Schneyer, J.; Januta, A. Ambushed at home: Children poisoned by lead on U.S. Army bases as hazards go ignored, 2018. https://www.reuters.com/investigates/special-report/usa-military-housing/#:~:text=Reuters%20informed%20the%20Army%20it,devices%20to%20determine%20lead%20levels.

[24] Filippelli, G.; Anenberg, S.; Taylor, M.; van Geen, A.; Khreis, H. New approaches to identifying and reducing the global burden of disease from pollution. GeoHealth https://doi.org/10.1029/2018GH000167, 2020.

[25] Drake, B. L.; Taylor, B.; Hamilton, M. Chapter 4 - Quantitative Analysis. In Advances in Portable X-ray Fluorescence Spectrometry: Instrumentation, Application and Interpretation. Edited by B. L. Drake and B. L. MacDonald. The Royal Society of Chemistry, 2023.

[26] CODINORM (2018). Peintures et vernis - Spécification des peintures de finition pour pièces sèches. Décision d'homologation N°0001 / 2018 / CIN du 09 avril 2018. Centre d'Information sur les Normes et la réglementation (CINR), Ministère du Commerce, de l'Industrie et de Promotion des PME, République de Côte d'Ivoire. https://www.codinorm.ci/catalogue/catalogue_2022.pdf

[27] Fecher, P.; Ruhnke, G. Cross contamination of lead and cadmium during dry ashing of food samples. Anal Bioanal Chem 373, 787–791, 2002. https://doi.org/10.1007/s00216-002-1440-6

[28] Buehler, S.; Rhoda, D. 3M Leadcheck swabs qualitative spot test kit for lead in paint. Battelle, 2012. https://www.epa.gov/sites/default/files/documents/3M-leadcheck-report.pdf

[29] Buehler, S.; Rhoda, D.; Buxton, B.; Enriquez, J.; Hartzell, E. D-Lead paint test kit qualitative spot test kit for lead in paint. Battelle, 2010. https://www.epa.gov/sites/default/files/documents/D-Lead-results.pdf

Table 1. Performance of Lumetallix kit relative to XRF threshold of 500 mg kg^{-1}

XRF readings for liquid paint

	XRF>500	XRF≤500 mg kg^{-1}
Green fluorescence	14	0
No green fluorescence	0	9

XRF readings for dry paint on wood[1]

	XRF>500	XRF≤500 mg kg^{-1}
Green fluorescence	15	1
No green fluorescence	1	13

[1]after applying regression in Fig. 1b to obtain equivalent reading for liquid paint

XRF readings for paint chips

	XRF>500	XRF≤500 mg kg^{-1}
Green fluorescence	11	1
No green fluorescence	1	10

Supplemental Information

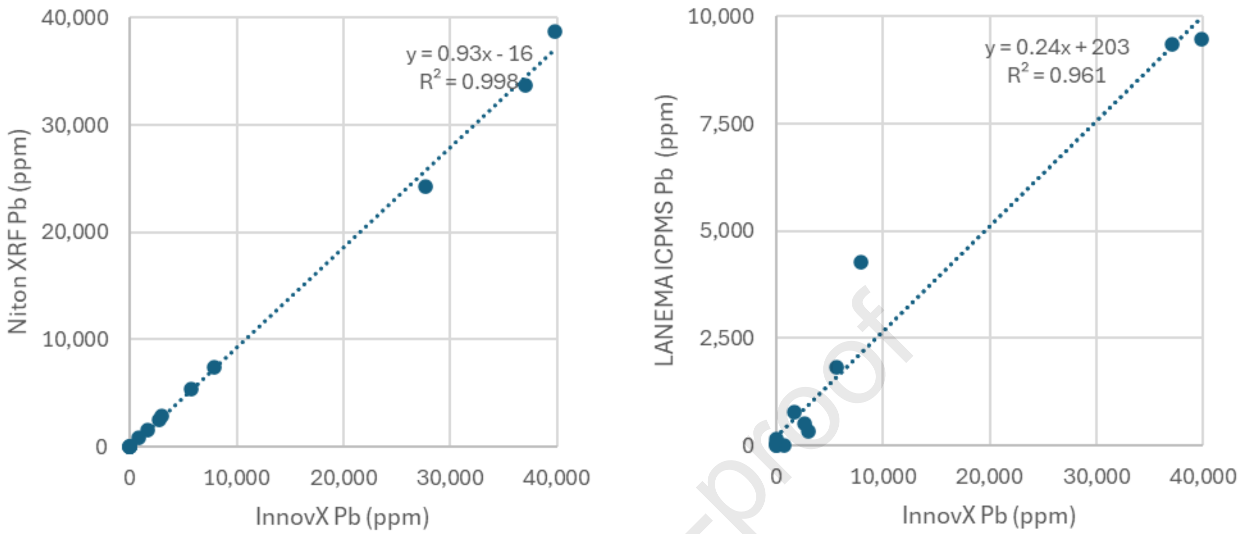

Figure S1. Comparison of Pb concentrations in paint measured by different methods and instruments: (a) Niton XL3t in the soil mode, (b) Ashing at 750°C and acid digestion followed by ICPMS analysis, both as a function of InnovX Delta Premium XRF in the soil mode.

Figure S2. Results form XRF analysis of (a) a single paint layer on cling film containing 38,000 mg kg^{-1} Pb placed on the detector on its own and subsequently backed by an increasing number of wooden tongue depressors and (b) up to 6 layers of the same paint on cling film backed by a constant number of wooden tongue depressors.

Location date ID	Brand	Color	CETLabs Pb (%)	Pb error	LANEMA Pb	InnovX Pb	Pb +/-	InnovX Cr	Cr +/-	InnovX Ca	Ca +/-	InnovX Ti	Ti +/-	novX Fe	Fe +/-	novX As	As +/-
Abidjan Feb '22 A	Industrap Delux	Yellow	2.9	0.10 %		30,263	391	3,973	63	173,777	2,310	433	25	<LOD	72	436	85
Abidjan Feb '22 B	Industrap Delux	White	0.50	0.10 %		3,885	45	<LOD	36	141,261	2,145	194,115	2,791	<LOD	34	<LOD	68
Abidjan Feb '22 C	Industrap Delux	Green	2.3	0.10 %		29,709	383	2,626	46	96,823	1,366	392	24	<LOD	66	<LOD	249
Abidjan Feb '22 I	Industrap Delux	Brown	2.5	0.10 %		19,713	238	2,826	56	302,524	4,525	19,323	330	19,833	282	<LOD	186
Abidjan Feb '22 J	Indutrap Delux	Yellow	0.57	0.10 %		5,015	49	15	2	1,826	53	1,103	24	<LOD	24	366	23
Abidjan Feb '22 K	Sipec Champion	Brown	ND	0.10 %		<LOD	7	<LOD	15	133,624	1,664	150	23	14,533	160	<LOD	6
Abidjan Feb '22 L	Maestria Ikarlac	White	ND	0.10 %		<LOD	8	<LOD	41	82,644	1,331	257,506	3,718	123	15	<LOD	7
Abidjan Feb '22 M	Maestria Ikarmat	White	ND	0.10 %		<LOD	8	<LOD	32	356,399	5,593	121,660	1,909	922	33	<LOD	7
Abidjan Feb '22 N	Maestria Latexor	White	ND	0.10 %		<LOD	7	<LOD	32	205,678	3,069	145,202	2,112	709	27	<LOD	6
Abidjan Feb '22 O	Maestria Latexor Vive	Yellow	ND	0.10 %		<LOD	6	<LOD	10	191,832	2,333	660	28	523	20	<LOD	5
Abidjan Sep '22 A	Seigneurie Pantinox	White	ND	0.10 %	154	<LOD	5	<LOD	30	<LOD	289	278,409	2,755	39	9	9	2
Abidjan Sep '22 B	Seigneurie Soudor	White	ND	0.10 %	1	<LOD	6	<LOD	24	322,169	3,462	147,663	1,574	199	12	7	2
Abidjan Sep '22 C	Industrap Delux	White matte	0.13	0.10 %	5	778	10	<LOD	18	400,279	4,390	76,706	858	138	11	<LOD	22
Abidjan Sep '22 D	Industrap Delux	Yellow glossy	3.8	0.10 %	9,356	37,077	362	4,910	56	249,100	2,439	531	21	102	21	<LOD	212
Abidjan Sep '22 E	Industrap Delux	White glossy	0.35	0.10 %	500	2,680	24	<LOD	23	241,291	2,537	155,373	1,601	48	9	<LOD	40
Abidjan Sep '22 F	Champion	White	ND	0.10 %	2	<LOD	5	<LOD	15	81,755	738	91,694	763	179	11	<LOD	4
Abidjan Sep '22 G	Industrap Delux	Enamel	0.69	0.10 %	1,826	5,699	45	250	9	381,968	3,878	1,647	42	15,420	135	<LOD	59
Abidjan Sep '22 H	Industrap Delux	White enamel	0.37	0.10 %	321	2,980	26	<LOD	23	189,230	1,947	163,856	1,631	243	13	<LOD	42
Abidjan Sep '22 I	Industrap Delux	Red enamel	0.96	0.10 %	4,270	7,914	59	714	13	332,210	3,036	168	12	130	12	<LOD	69
Abidjan Sep '22 J	Industrap Delux	Yellow enamel	3.8	0.10 %	9,484	39,844	399	5,286	62	303,685	3,074	62	11	164	23	<LOD	226
Abidjan Sep '22 K	Industrap Delux	Enamel	2.4	0.10 %		27,652	274	17	2	97,693	834	39	6	212	23	702	63
Abidjan Sep '22 L	Industrap Trapline		0.19	0.10 %	771	1,690	17	<LOD	12	463,865	4,365	37,211	375	85	10	<LOD	32
Abidjan Sep '22 M	Titan		ND	0.10 %	21	<LOD	5	<LOD	9	153,682	1,222	38,080	310	187	11	<LOD	4
Abidjan Sep '22 N	Perolac		ND	0.10 %	49	<LOD	6	79	11	134,397	1,440	9,263	126	64,276	460	<LOD	5
Abidjan Sep '22 O	Drocolor Topline		ND	0.10 %		<LOD	5	<LOD	14	405,230	3,898	49,583	498	155	11	<LOD	5

Highlights

- Fluorescence-based Pb detection kit tested on variety of liquid and dry paint samples
- High sensitivity and specificity indicated by comparison with two other methods
- Widespread use of kit could enhance efforts to reduce child exposure to Pb in paint

L.H. and W.L.N. are co-founders and co-owners of Lumetallix BV, which produces the kit. L.H. and W.L.N. played no role in the selection of paint samples used to compare kit results with XRF and laboratory analyses. E.R. was a distributor of the Lumetallix kit in the US via Amazon at the time of the initial submission. None of the remaining co-authors have a financial interest in Lumetallix or other competing interests.