The assessment of lead detection methods in Tamil Nadu India and Beyond

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Lead is a toxic chemical that widely affects the Indian population. Around one (1) in three (3) children, up to 800 million globally, have elevated blood lead levels, with 90% of the children with high lead blood levels living in low- and middle-income countries (Pure Earth, 2020). The best available data from Indian institutions and others suggest that India is the most lead-impacted country in the world, with staggering consequences to public health and economic development.

A major contributor is the informal or substandard recycling of lead-acid batteries. An estimated 60-80% of batteries in India are recycled under these conditions (Varshney et al., 2020). During this process, batteries are dismantled and the lead is smelted without proper environmental controls. This results in severe lead contamination of the surrounding area, including areas where children live and go to school.

When entering the body, lead mimics calcium in biochemical processes (Darwish et al., 2013). This process interferes with neurotransmitters, leading to a range of problems including but not limited to:

- Decrease of IQ
- Concentration and behavioral problems
- Cardiovascular damage
- Stunting and slowed development
- Premature death

In India, it is estimated that loss of IQ through lead-poisoning in children results in an annual loss of $236 billion, which is roughly 5% of India's GDP (Attina and Trasande, 2013).

Currently, together with conventional chemical analyses in the laboratory, the handheld X-Ray Fluorescence (XRF) analyzer is the most used technique to detect lead in various matrices. Although fast and reliable, the XRF is expensive and requires proper training, making it inaccessible to the local population and even government authorities. As such, there is a need for easy to use, fast, and affordable detection methods that can be used by individuals with limited training.

TAUW, Pure Earth, and Lumetallix, have formed a consortium to assess new, low-cost ways of detecting lead in different matrices. The project is funded by the TAUW Foundation, Pure Earth, and TAUW bv.

The project aims to make detecting lead more accessible to a wider group of people.

When residents can identify a source of lead pollution in a quick and affordable manner, the awareness of the issue and need for remediation of said source become more tangible. During the desktop study, we evaluated a total of 13 methods to determine their potential as low-cost options for identifying lead contamination in soil, spices, and cookware. Among these methods, we selected four for further testing in the laboratory: ferric ferrocyanide (Prussian Blue), sodium rhodizonate, RGB Image Recognition, and Lumetallix. Following the laboratory tests, two methods, sodium rhodizonate and Lumetallix, were considered potentially successful and were subsequently tested in a field setting. The methods and results of these tests are outlined in this White Paper.

Assessment of Lead Detection Methods

Two methods were chosen to undergo field trials in collaboration with partners in Tamil Nadu, India. The objective was to evaluate the effectiveness of these methods in accurately detecting lead contamination, as well as their practicality for use by community members and other stakeholders. The assessment process for the lead detection methods involved the following steps:

1. Conducting a literature review and laboratory testing to identify potential feasible lead detection methods
2. Selecting the most promising methods based on their feasibility; the selected methods are outlined in the "Lead Detection Methods" section, which provides background information on the methods and includes details about the handheld XRF analyzer.
3. Identifying sites contaminated with lead in Tamil Nadu, India, using the Toxic Site Identification Program (TSIP).
4. Conducting initial testing of the selected methods, namely the Lumetallix instant lead detection kit and sodium rhodizonate, in a field setup referred to as "Initial Field Trials".
5. Performing more comprehensive testing of the Lumetallix spray kit on additional lead-contaminated sites with varying characteristics and under different conditions during a subsequent period of Field Trials referred to as “Upgraded Field Trials.
6. Execution of testing of the Lumetallix instant lead detection kit additionally on different environmental settings, i.e., testing of the kit on contaminated cover layers within Amsterdam, the Netherlands.
7. Statistically analyzing the results obtained from the Field Trials, as described in the "Statistical Results" section.

By following this systematic approach, we aimed to assess the suitability of the selected lead detection methods, obtain reliable data on lead contaminated sites, and build capacity on the assessment of lead contaminated sites in Tamil Nadu, India.

Lead Detection Methods

A *handheld XRF* was used to determine lead concentrations in the soil samples. The handheld XRF is a fast and efficient way to measure metals in the field. The XRF sends high energy X-rays to the sample. This energy elevates electrons to a higher energy level, as a result a metal specific radiation is emitted. This signal is received by the handheld XRF and processed into an electrical signal, and eventually to a qualitative and quantitative analysis. The results are available in less than one minute. During the field trial, the handheld XRF analyzer Thermo FisherScientific Niton Xl3t was used.

The *sodium rhodizonate test*, first described in 1942, has been established as a reliable method for detecting lead, and other metals such as cadmium and mercury (Feigl and Sutern, 1942). Sodium rhodizonate is a coloring agent, resulting in different colours depending on the element. While sodium rhodizonate is commonly used as a color agent for detecting lead paint, the rhodizonate-based lead paint detection kit by 3M was found to be ineffective, with a 70% false positive rate for the tested samples (Batelle, 2012). Landes et al. (2019) conducted research on the detection of lead in soil using an acidic glycine solution with sodium rhodizonate (Landes et al., 2019). This test is derived from the US Environmental Protection Agency's method to estimate bio-accessible lead, and therefore it is not expected to exactly reflect the total amount of lead in soil. The study found that the test accurately classified all samples below 400 ppm and above 1200 ppm lead. For this purpose, the test is partially quantitative, as the color of the sodium rhodizonate solution darkens, allowing for a general scale based on the color change.

Lumetallix is an innovative technique for directly measuring lead, providing a visual indication of lead presence in the environment by causing it to illuminate a bright green under UV light when the reagent is sprayed or applied onto a surface.

Figure 1 Testing with Lumetallix in the field

The technology behind Lumetallix is based on semiconductor technology that has originally been developed for LEDs and solar cells. It works by reacting lead of any oxidation state into a so-called lead-halide perovskite semiconductor which fluoresces when exposed to UV irradiation.
In laboratory settings, the test has shown to react only with lead and to be up to 1.000 times more sensitive than rhodizonate (when testing lead acetate) (Helmbrecht et al., 2023). It has been extensively tested on paint where it shows a detection limit around 500 ppm (van Green et al., 2023). It has also been tested on many other solids such as pipes, plastics, ceramics and soil. The technique has shown in studies to react reliably with various lead compounds and does not give false positives with other metals, however the use for testing soil has not been studied in depth.

The method delivers instant results over a larger area as it is sprayed. Potential advantages of this could be that it helps analyze heterogenous substrates and that the visualization makes the results for the user intuitive while maintaining low costs.

The Toxic Site Identification Program

Pure Earth has an existing training and assessment protocol for site characterization through its Toxic Site Identification Program (TSIP). TSIP aims to locate, assess and document contaminated sites in low- and middle-income countries. The data is stored in a publicly available database, which represents the largest global collection of information on toxic sites. Project partner Vellore Institute of Technology (VIT) was trained in the TSIP methodology. By combining the search for feasible lead detection methods, the identification of contaminated sites, and capacity building within Tamil Nadu, the consortium's efforts were optimized.

The methods were tested in the TSIP over two periods: from April to September 2022 and from June to September 2023. Figure 2 shows a map of the 16 TSIP sites included in the field trials. In preparation of testing with the chosen lead detection methods, 34 potential lead contaminated sites across three districts in Tamil Nadu (Vellore, Ranipet, and Kanchipuram) were screened prior to the initial period to ensure that the site has locally at least lead contamination above 500 ppm. Sites for the second phase of sampling (upgraded field trial) were selected from previously identified sites. The selected sites exhibited lead contamination from battery recycling or processing activities, as well as other lead-related industries. An example of one of the visited sites is depicted in Figure 1.

Figure 2 Map with the locations used for testing the lead detection methods during the different field trials in Tamil Nadu, India

Methodology

We tested the different methods, sodium rhodizonate and Lumetallix respectively, within different settings (e.g., light conditions, moisture content) to determine the influences of external factors on the quality of the assessment, but as well to optimize the measurement protocols.

The *sodium rhodizonate test* was conducted on 45 samples of TSIP sites at Tamil Nadu Region, India and 21 samples from Zaandam Region, Netherlands according to the protocol described in Landes et al., (2019), see also Figure 3. Prior to following the testing protocol, the 44 TSIP samples were air-dried and sieved, the 21 Zaandam samples were oven-dried for 24 hours at 95 degrees and sieved, and a subset of 9 samples from the Zaandam samples were air-dried and sieved.

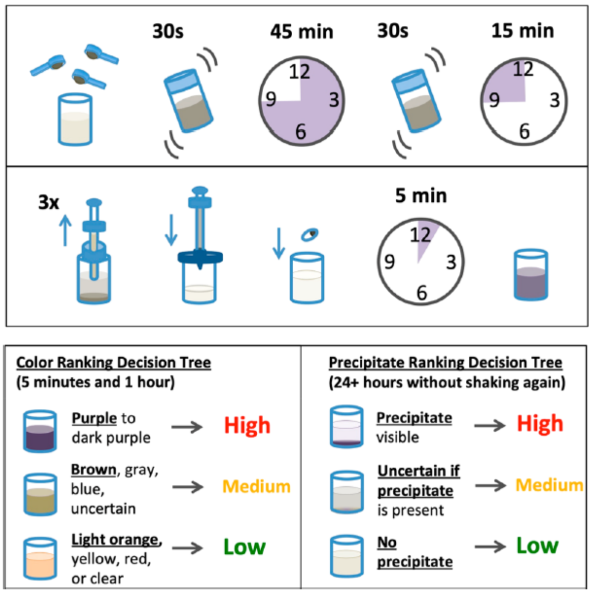

Figure 3 Schematic of the field procedure steps and a decision tree for the color ranking (Figure from Landes et al., 2019)

The general test procedures for the *Lumetallix test* involved the application or spraying of the reagent onto the soil surface or sieved and dried samples while directing UV light towards the sample. The subjective fluorescence was assessed, ranging from no luminescence to bright light. Figure 5 provides an overview of the various testing procedures conducted to evaluate different variables and improve the measurement procedure during both field and laboratory trials. In the initial field trials, the reagent was applied to the soil surface at 23 locations at TSIP sites, and 14 samples were tested in the laboratory. It was observed that, due to the bright sunlight, the results were often difficult to discern.

Based on these initial findings, the testing procedures were optimized, and the following three conditions were tested:

- Testing directly on the soil under ambient light, which can be very bright, especially at noon.
- Testing directly on the soil covered by a large cardboard box ('dark box') to shade the testing area while allowing observation and application of the test through openings in the box.
- Testing a dried and sieved sample in the laboratory under 'dark box' conditions.

Additionally, observations were recorded after one and two applications of the reagent. The rationale behind this was that lead may need to undergo a multistep reaction to form the luminescent halide perovskite, depending on how lead is bound to the soil. The light intensity of the environmental light was measured with a light meter (UNI-T UT383). To minimize subjectivity in reading, the readings were recorded by two examiners.

The Lumetallix test was also conducted on 10 samples collected from 8 different gardens in Amsterdam, The Netherlands, in November and December 2023. The city center of Amsterdam is known for its high local lead contamination, stemming from its long industrial history. Unlike the lead contamination in Tamil Nadu, which mainly consists of atmospheric deposited lead oxides, Amsterdam's lead contamination has diverse sources and compositions, resulting in a wider range of site conditions. Since light is less of an issue in winter in Amsterdam, the reagent was applied without a dark box, and a single application was conducted.

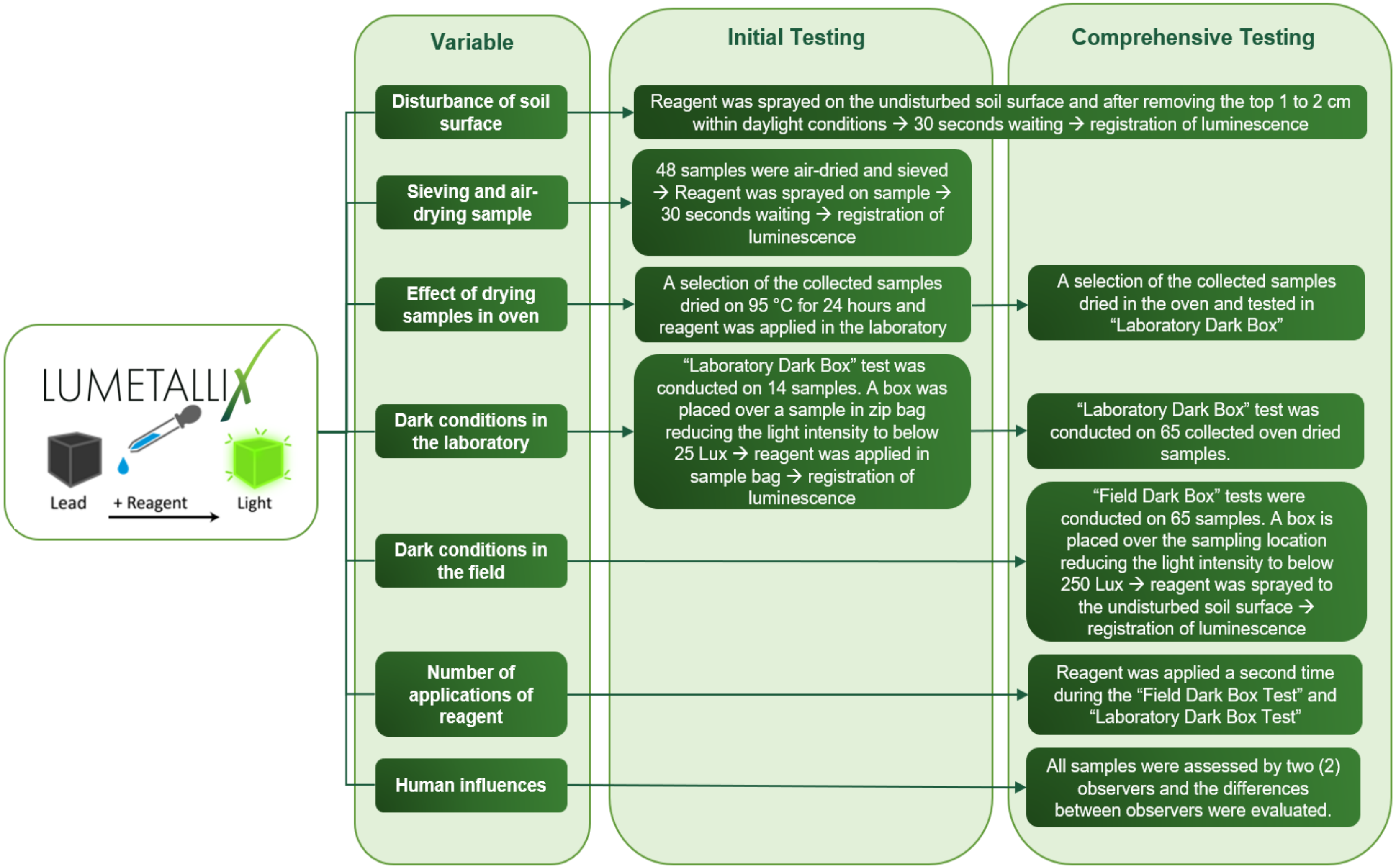

Figure 4 Overview of different testing conducted with the Lumetallix test kit to determine the influence of different variables and to improve measurement quality.

Statistical Results

To assess the suitability of these alternative methods, we generated graphical interpretations of the results and performed statistical analyses. We first examined the distribution of lead concentrations in the soil based on the XRF results.

Summary Statistics of XRF Results

Figure 5 presents a histogram of the average lead content of the dried and sieved samples used for the *sodium rhodizonate* testing in the initial field trials in Tamil Nadu. The average lead content is 2,300 ppm, with lead content, ranging from 20 ppm to 21,000 ppm. Unfortunately, the team was unable to collect a normally distributed sample set, as evidenced by the lack of samples in the mid-range, from approximately 1,000 ppm to 2,000 ppm.

The *Lumetallix* readings presented in this section of the report were obtained from soil surface testing conducted during the comprehensive field trials in Tamil Nadu. Figure 6 presents a histogram of the lead content measured on the soil surface. The average lead content is 5,272 ppm, with content ranging from 89 ppm to 812,000 ppm. Unfortunately, this data is also not normally distributed; as such, these readings provide insufficient data points to evaluate the sensitivity of the tests in the sub-1000 ppm range, neither do they provide enough information to determine an exact sensitivity threshold.

Results of Sodium Rhodizonate

Figure 7 shows the distribution of lead concentrations as recorded by the XRF against the colorimetric result from sodium rhodizonate. As shown in this figure, a yellow color was observed for samples with an average lead content of 270 ppm, with content ranging from 20 ppm to 810 ppm and an outlier of 21,000 ppm. This outlier could be attributed to a potential labelling error, sampling heterogeneity, or the presence of a refractory piece of Pb oxide. The grey, brown, and purple color was observed at samples with an average lead content of 2,400 ppm, ranging from 290 ppm to 12,000 ppm. The lead content of these colors cannot be clearly classified by color.

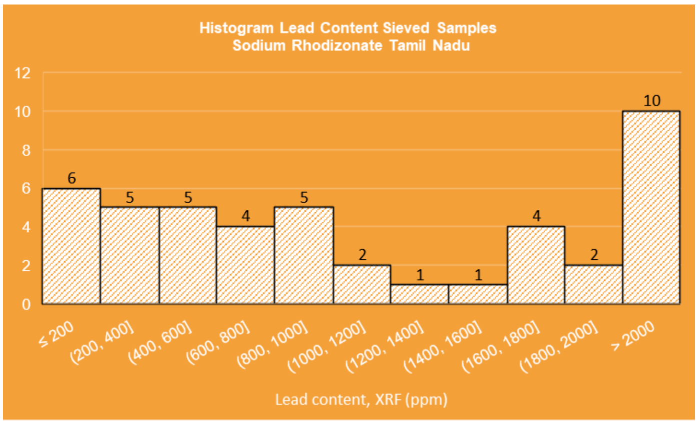

Figure 5 Histogram of lead content within the dried and sieved samples during the first period of field trials in Tamil Nadu. These samples were used for the initial testing of the sodium rhodizonate test kit.

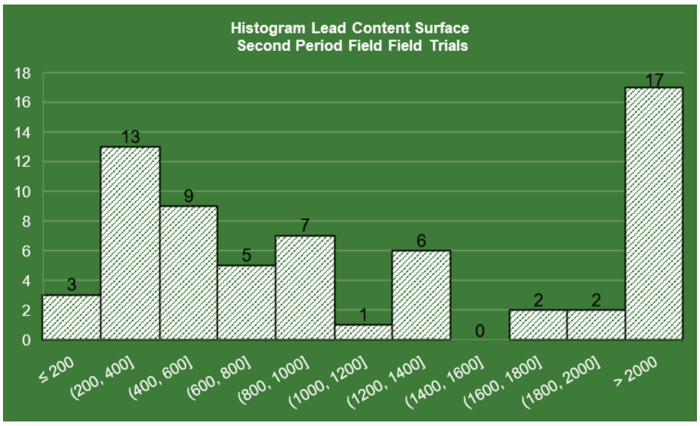

Figure 6 Histogram of lead content at the soil surface measured during the second period of field trials using the handheld XRF analyzer. These samples were used for the comprehensive testing of the Lumetallix test kit.

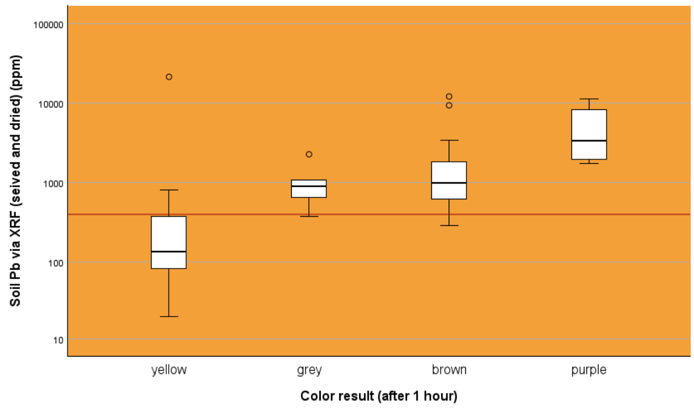

Figure 7 Results from sodium rhodizonate test, showing the recorded colour after 1 hr versus the XRF (sieved, dried, average of 3 readings). N=66. Several color categories observed during the reading were merged.

Table 1 presents a confusion matrix for the results of the sodium rhodizonate test kit, tested on two classes: yellow and coloration (e.g., grey-yellow, brown, purple). The overall accuracy, precision, and negative predictive value of the results are 88%, 94%, and 73%, respectively. When compared to a no-information rate of 50%, the test kit provides added value in situations where no information is available. The test kit successfully identified 94% of samples with lead content above 400 ppm. As shown in Figure 5, only a limited number of samples were evaluated at around 400 ppm.

Table 1 Confusion matrix of samples classified using the sodium rhodizonate test kit. Below a lead content of 400 ppm most samples (8 of 12) stay yellow (do not show coloration), above a lead content of 400 ppm most samples (30 of 32) do show coloration.

ACTUAL LEAD CONTENT	PREDICTED Yellow	Coloration
< 400 PPM	8	4
> 400 PPM	2	30

Results of Lumetallix

A comparative analysis was conducted to assess the observations when testing with Lumetallix under different conditions as outlined in the testing procedures above. As anticipated, a significant improvement in the ability to detect luminescence during bright daylight was observed by covering the test area with a cardboard box ('dark box'). Additionally, it was noted that re-applying the reagent resulted in enhanced data consistency. Overall, minimal variance was observed between the observations of the two examiners, except in cases of faint speckles of luminescence.

Unfortunately, the laboratory testing procedures during the trials were compromised. The samples were oven-dried instead of air-dried, which seems to affect the accessibility of lead in the Lumetallix testing based on the initial field trials.

Based on this preliminary assessment of the results, it was determined that the most practical approach for using Lumetallix is to conduct direct soil testing in the field by applying the reagent twice and shading the testing area with a simple cardboard box. Figure 8 shows the distribution of lead content as recorded by the XRF against the Lumetallix test kit using this most practical approach. As shown in this figure, no luminescence of lead was observed at samples with lead content ranging from 98 ppm to 3062 ppm. A green luminescence was observed at samples with a lead content ranging from 157 ppm to 80,000 ppm. If bright luminescence is observed, it typically indicates a lead concentration above 1,000 ppm.

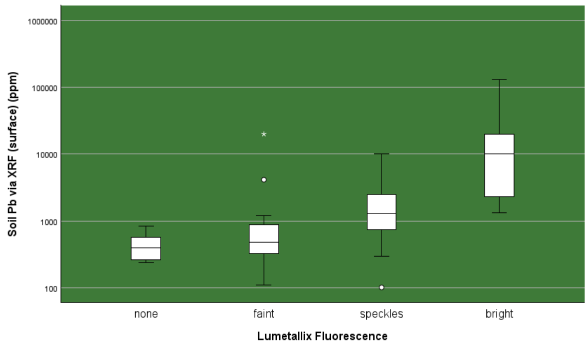

Figure 8 Lumetallix testing directly in the field on the soil with applying the reagent twice and shading the testing area with a cardboard box. The difference between different observers is marginal and we here plot observer one. The XRF reading was taken in situ on the soil surface. N=65.

Table 2 presents a confusion matrix for the results of the Lumetallix test kit, tested on two classes: none and green luminescence. The overall accuracy, precision, and negative predictive value of the results are 82%, 83%, and 73%, respectively. As mentioned in the summary statistics, a limited number of samples were analyzed with a lead content below 1000 ppm. This limitation may led to an overestimation of the accuracy in identifying lead-impacted soil (> 400 ppm) using the kit.

Table 2 Confusion matrix of samples classified using the Lumetallix test kit. Below 400 ppm most did not show luminescence (8 of 11), above 400 ppm most do show luminescence (45 of 54).

ACTUAL LEAD CONTENT	PREDICTED No Luminescence	Green Luminescence
< 400 PPM	8	3
> 400 PPM	9	45

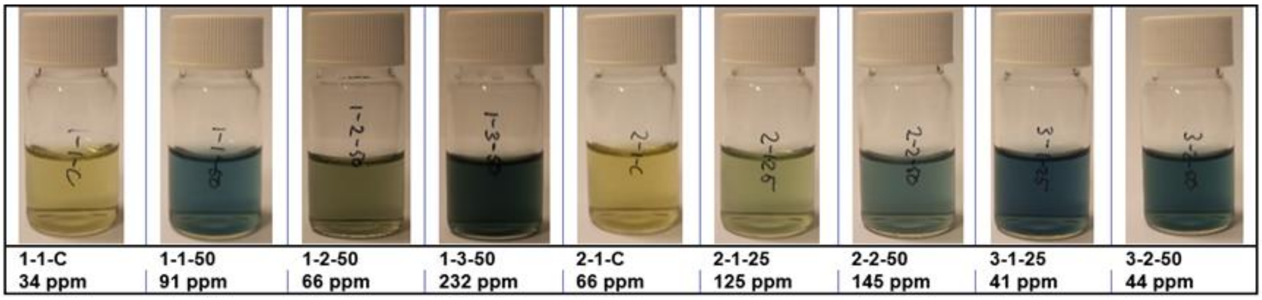

Figure 9 Results of sodium rhodizonate test kit on a sub-set of samples collected in the municipality of Zaanstad, the Netherlands

Lead Testing beyond Tamil Nadu

As detailed in the preceding sections, samples from the municipalities of Zaanstad and Amsterdam, the Netherlands, were collected and subjected to testing using the sodium rhodizonate and Lumetallix test kits.

The *sodium rhodizonate* test was initially performed on 21 oven-dried samples, and no lead was detected in any of the collected samples. However, considering the possibility that the drying process might affect the leachability of lead, a subset of the samples were also air-dried and analyzed using the test kit. The results, presented in Figure 9, do not show a clear relationship between lead concentration and the test results. This lack of correlation may be attributed to the varying solubility of lead compounds present in the samples when exposed to the acid solution.

In the 13 samples collected within Amsterdam, the average lead content was 844 ppm, with lead content ranging from 160 ppm to 1,400 ppm. When using the *Lumetallix* test kit in field conditions, no green luminescence was observed in these samples, except for one sample with a lead content of 700 ppm where faint speckles were observed. After air-drying the samples, none of them exhibited luminescence under lab conditions. This lack of detection may be attributed to the formation of lead-soil complexes, resulting in the entrapment of lead within the soil matrix.

Conclusions and Future Research

Based on our findings, it is evident that these methods should be viewed as complementary. The advantages and disadvantages of these approaches are summarized on the following page.

An important finding was the difference in performance of both sodium rhodizonate and LumetalliX between different soil types and lead pollution sources when comparing the Tamil Nadu samples to those from the Netherlands. The following discussion on performance relates primarily to lead pollution from the battery recycling industry, and soil types found in Tamil Nadu. Further validation would be needed to expand applications of these tools.

The sodium rhodizonate method was relatively time-intensive, involving soil processing and wait times. With the samples from Tamil Nadu, this method provides a classification of lead concentrations in soil by coloration, with an 88% accuracy in classifying lead content below or above 400 ppm. Sodium rhodizonate is a valuable tool with a gradual response for classifying lead content within this range, especially for the typical contamination found in the lead battery recycling industry. The test could be used for initial screening, followed by additional analysis using XRF or conventional laboratory analyses.

The Lumetallix test kit provides nearly instantaneous results but, in its current formulation, yields less definitive results on soil lead concentration, with an 82% accuracy in classifying lead content below or above 400 ppm for the samples from Tamil Nadu. Although the accuracy is comparable to that of the sodium rhodizonate, overlapping test results are more common with the Lumetallix test kit compared to the sodium rhodizonate test kit. For example, the

Parameters	XRF	Sodium Rhodizonate	Lumetallix
Ease of use	Requires basic training on operation and radiation safety	User friendly for the public; requires pre-assembled kit and some instruction	User friendly for the public; requires pre-assembled kit and some instruction
Cost	Very high (~30,000 USD)	~3 USD/test	80USD/Kit, < 1USD/Test
Duration	Approx. 30 seconds per reading	Approx. 60 minutes per reading	Approx. 1 minute per reading
Accuracy	Quantitative; narrow range of error, low detection limit	Semi-quantitative, provides categorical reading	Qualitative
Specificity	Has some interference from other elements, but likely not to the degree to reduce accuracy for lead	Can react with other elements (including cadmium and mercury), shows different color	Current research shows that it does not react with other elements
Sample area	Not applicable	20x20 cm averaged	5-50cm
Sample depth	6 mm penetration depth	Volume average/bulk sample	Surface
Level of confidence	Method has extensively used and reported within environmental soil testing	Published literature since 1942 with also scientific publications on its use for lead detection in soil.	Limited information on lead detection in soil despite validation on various lead sources in literature since 2023.
Notes	Measures total lead	Measures bioavailable lead	Measures lead on the surface
Scalability for community projects	Due to price and personnel constraints, large scale testing is limited. Suitable for targeted quantification follow-up.	Preparation and complicated procedure limit to medium scale projects. Indicative about the amount of lead present.	Large scale indicative testing possible. Suitable for mapping lead pollution.

average lead concentration not detected by the Lumetallix test kit was 363 ppm (n=11), with content ranging from 98 ppm to 3062 ppm under 'Dark Box' conditions. On the other hand, this method reveals the spatial distribution of lead on the surface and allows for testing of square meters within minutes. This makes the Lumetallix test kit a valuable screening tool for identifying pollution hotspots and initial mapping the spread of lead.

When developing lead poisoning prevention programs with community involvement, a combination of the three techniques—sodium rhodizonate, Lumetallix, and the handheld XRF analyzer or conventional laboratory analyses—would enhance the effectiveness of available resources. Both sodium rhodizonate and Lumetallix could be utilized by community members to pre-screen an area. The Lumetallix test would enable the identification of lead sources, as it allows for numerous indicative tests to be conducted in a short time, while the rhodizonate test can provide fewer tests but with a more definitive indication of soil lead levels above a threshold of concern. Based on the pre-screening, relevant authorities could then conduct more targeted and resource-efficient follow-up investigations.

The successful implementation of this approach relies on community members being aware of the issues and behavior of lead at these sites. Therefore, our goal to identify and address lead problems will be an ongoing endeavor. Furthermore, research and development on the technologies are ongoing at Columbia University for both the rhodizonate and Lumetallix reagents. For example, at Lumetallix, efforts are being made to enhance reactivity for more consistent results at low concentrations and to benchmark sensitivity on various soil samples.

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