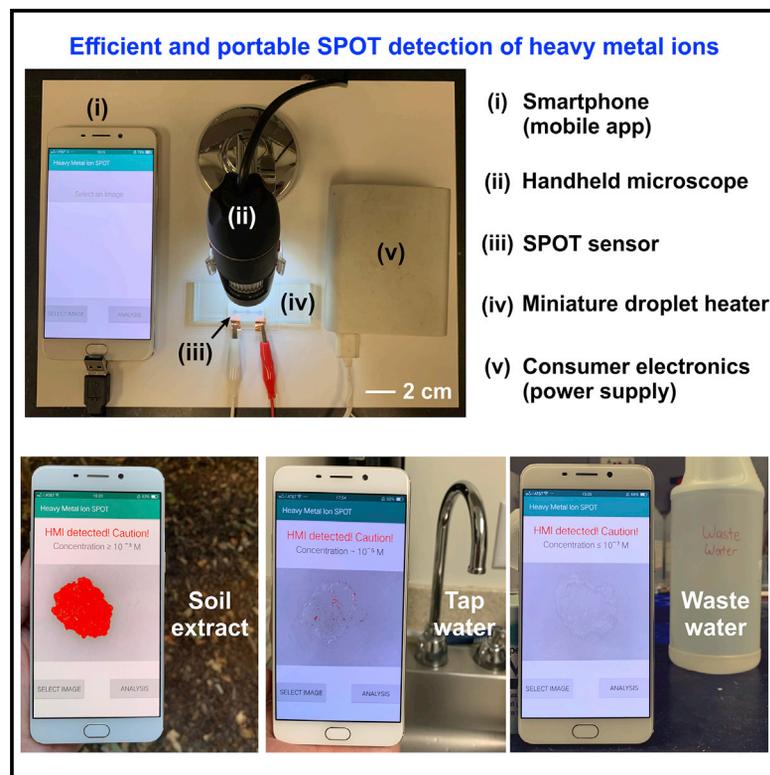


Sensitive, portable heavy-metal-ion detection by the sulfidation method on a superhydrophobic concentrator (SPOT)

Graphical abstract



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In brief

Access to clean water is a basic human right and necessary for the development of civilization. However, current reliance on centralized water monitoring retards the identification of potential water pollution crises, often only after irreversible health consequences are developed. Here, we develop an efficient, portable sensor to concurrently detect ultratrace levels of multiple heavy-metal-ion species, a major class of water pollutant linked to severe cytogenotoxicity. Notably, our sensor enables on-site detection of these toxins within 8 min and at \$0.02 per analysis.

Highlights

- We introduce an efficient, portable sensor to decentralize heavy-metal-ion testing
- The sensor quantifies five different heavy-metal ions down to the sub-nanomolar level
- A mobile app is developed for on-site detection in 8 min and at \$0.02/analysis
- Our easy-to-operate sensor helps to monitor water quality on a routine basis



Article

Sensitive, portable heavy-metal-ion detection by the sulfidation method on a superhydrophobic concentrator (SPOT)

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SCIENCE FOR SOCIETY Accessing safe drinking water is still a major global challenge because of rising water pollution. Among various water pollutants, heavy-metal ions (HMIs) with serious toxicities are the most prevalent because of rapid industrialization and urbanization. From the recent Flint water crisis, it is obvious that water testing should be decentralized and accessible to everyone to promote safe water quality as well as to identify potential contamination for prompt remediation. Here, we design an efficient, portable sensor to concurrently detect five HMIs at concentrations one million times lower than current permissible limits set by the World Health Organization and US Environmental Protection Agency. When combined with a smartphone application, our sensor is highly mobile and swiftly detects these pollutants within 8 min at 90% accuracy. With a cost of about \$0.02 per analysis, our design will expedite the decentralization of water monitoring for everyone to access clean water, a key Sustainable Development Goal established by the United Nations.

SUMMARY

One in three people worldwide does not have access to safe drinking water. Notably, heavy-metal ions (HMIs) are major water pollutants threatening human health because of their severe toxicity, even at trace levels. Efficient HMI detection thus plays a major defense against metal poisoning by enabling early pollution warning and efficient regulatory enforcement. However, it remains a formidable challenge to accurately detect these pollutants on site at ultratrace levels in a cost- or time-effective manner. Here, we introduce an efficient, portable sensor to concurrently quantify five different HMIs down to the sub-nanomolar level by sulfiding them on a superhydrophobic surface. Sulfidation serves as a colorimetric reaction while the superhydrophobic surface concentrates analytes for sensitive visual detection. Our superhydrophobic concentrator (SPOT) sensor can be made portable by being integrated with a smartphone application to quantify HMIs in <8 min and at \$0.02 per analysis. Decentralizing water monitoring by using our SPOT design is crucial to ensuring that clean water is accessible to everyone.

INTRODUCTION

Heavy-metal ions (HMIs) are environmental pollutants that readily react with biological matter to cause serious toxicological and carcinogenic effects on body systems and vital organs.^{1–3} These health threats are aggravated by the accumulation of non-biodegradable heavy metals in the ecosystem and

increasing anthropogenic pollution from industrialization and urbanization.² An example is the Flint water crisis,⁴ during which lead leached into the water distribution system as a result of the flow of corrosive river water in aging pipes. The contamination was detected only 10 months later, when the lead concentration was ~1,000-fold higher than the US Environmental Protection Agency (EPA)'s permissible limit. The delayed

identification and response to the crisis consequently endangered nearly 9,000 children and over 100,000 residents for a prolonged duration of 18 months. From this incident, the risk of heavy-metal poisoning is clear and is a prime example of how pollution problems are often uncovered only when health issues develop. This incident thus highlights a key lesson: it is absolutely critical to carry out easy-to-operate routine and frequent tests for HMI monitoring, especially in potable water. This would be particularly important for Global South countries given that they are facing larger heavy-metal pollution problems arising from rapid industrialization and urbanization. In the presence of these challenges, there is a clear need to make HMI testing decentralized, time efficient, and cost effective while maintaining high detection accuracy and sensitivity.

Ultrasensitive detection of HMIs is thus an important defense against heavy-metal poisoning because it enables early pollution warning and efficient regulatory enforcement. Ideally, an efficient analytical tool should detect HMIs at least down to their regulatory limits. For example, US EPA limits on common HMIs, such as lead (Pb), nickel (Ni), chromium (Cr), cobalt (Co), and copper (Cu), typically range from 10^{-8} to 10^{-5} M.¹ Standard analytical methods for detecting HMIs usually involve atomic absorption spectroscopy (AAS) and inductively coupled plasma (ICP)-mass spectrometry.^{5,6} Despite having detection limits at the nanomolar level, these methods are impeded by the need for sophisticated and expensive instrumentation, trained operators, and tedious pre-treatment requirements. Consequently, these testing facilities are usually centralized, are not suitable for routine or frequent tests, and lack portability for on-site detection. These drawbacks could potentially be the reasons behind the delayed identification of the Flint crisis. The need for frequent on-site testing is again emphasized in the more recent mining dam disaster in Brumadinho, Brazil. The rupture of a mining tailings dam at Brumadinho led to the discharge of 12 million m³ of mining tailings into the environment.⁷ This catastrophe consequently released bioavailable heavy metals (e.g., Fe, Pb, Hg, Cr, and Cu) into water supplies, rendering them unsafe for drinking because of the high genotoxicity. With limited access to testing facilities, a portable, simple-to-operate sensor is thus necessary for the long-term and frequent monitoring of the watershed to track the advance of a tailings plume, to provide information on water safety, and to make informed decisions for subsequent rectification.

Miniature portable sensors potentially address these limitations by offering a convenient, timely, and cost-effective approach to detecting HMIs directly at the point of concern for immediate decisions and counteractions to be taken.^{6,8,9} This advantage is especially important in remote areas with no access to testing facilities. Among various electrochemical and biological strategies,^{6,10–12} the optical strategy is particularly promising for field deployment because of its simplicity, fast response, and unique light responses that can be detected by the naked eye or consumer electronics (e.g., a smartphone).^{8,9,13,14} When coupled with ion-specific receptors, optical sensors routinely demonstrate detection limits at (sub)micromolar levels. For instance, a colorimetric sensor involving DNAzyme and gold nanoparticles has achieved selective Pb²⁺ detection down to 10^{-7} M.¹⁵ However, current optical sensors suffer from poor sensitivity and cannot meet the detection sensitivity required to enforce safe water

quality. The poor sensitivity is mainly attributed to the dilution of analytes over hydrophilic substrate- or solution-based sensors (Figure 1A).¹⁶ Moreover, the fabrication of colorimetric sensors is usually complex in that it involves expensive chromogenic or fluorogenic substrates and subsequent functionalization with ion-specific receptors.^{12–14} Because of the single-ion specificity of current optical sensors, it also remains a formidable challenge to collectively detect multiple heavy-metal species for high-throughput evaluation on general water safety.

Here, we introduce an efficient portable sensor to visually quantify five common HMIs (Pb²⁺, Ni²⁺, Cr³⁺, Cu²⁺, and Co²⁺) down to 10^{-10} M, thereby fulfilling the detection sensitivity required for enforcing safety regulations. We achieve this by reacting sample microdroplets with sulfide (S²⁻)-containing microdroplets on a superhydrophobic concentrator (Figures 1A and 1B). Our HMI sulfidation on a superhydrophobic concentrator (abbreviated as SPOT) combines two key concepts, namely a sulfidation-based colorimetric reaction and a superhydrophobic concentrator. On one hand, the sulfidation reaction chemically recognizes and arrests HMIs as insoluble, dark metal sulfides for visual detection. On the other hand, the superhydrophobic platform functions as an integrated analyte concentrator to deposit the generated dark metal sulfides into a small area upon drying of the sample microdroplet. This phenomenon promotes the formation of large, visible particle clusters for sensitive optical readout.

Using the SPOT sensor, we demonstrate the individual detection of five different HMIs down to the sub-nanomolar level and the collective quantification of these analytes in a single analysis. By integrating SPOT with a miniature droplet heater, handheld microscope, and automated smartphone analysis, we showcase a mobile, low-cost analytical ensemble to rapidly and accurately detect HMIs in actual or simulated household, environmental, and industrial samples. By achieving sub-nanomolar detection limits, collective analyte detection, fast response, portability, and low fabrication and operation cost, our work lays a strong foundation for the future design of ideal portable sensors that can be easily and inexpensively adopted by the general public for numerous applications, including routine water testing and as an early warning system for potential corrosion of urban infrastructure.

RESULTS AND DISCUSSION

Key concepts of SPOT detection

In SPOT detection, the sulfidation of HMIs ($M^{x+} + S^{2-} \rightarrow M_2S_x$) functions as a colorimetric reaction with generic selectivity and high reactivity toward these analytes (Figure 1A). We identified five HMIs (Pb²⁺, Ni²⁺, Cr³⁺, Cu²⁺, and Co²⁺) as our model analytes because they produce insoluble, dark metal sulfides (band gap < 1.77 eV; Figure 1B) suitable for visual detection.¹⁷ Mercury, cadmium, zinc, and arsenic are excluded from this study because their sulfides are colored or white. This chemo-recognition mechanism is selective for HMIs because non- or less-toxic group I/II cations produce hugely contrasting white or colorless metal sulfides. Notably, the high reactivity of heavy-metal sulfidation is driven by the low K_{sp} of the corresponding metal sulfides ($K_{sp,PbS} = 10^{-27}$ M, $K_{sp,NiS} = 10^{-19}$ M, $K_{sp,CuS} = 10^{-36}$ M, and $K_{sp,CoS} = 10^{-21}$ M),¹⁸ whereby S²⁻ ions spontaneously arrest

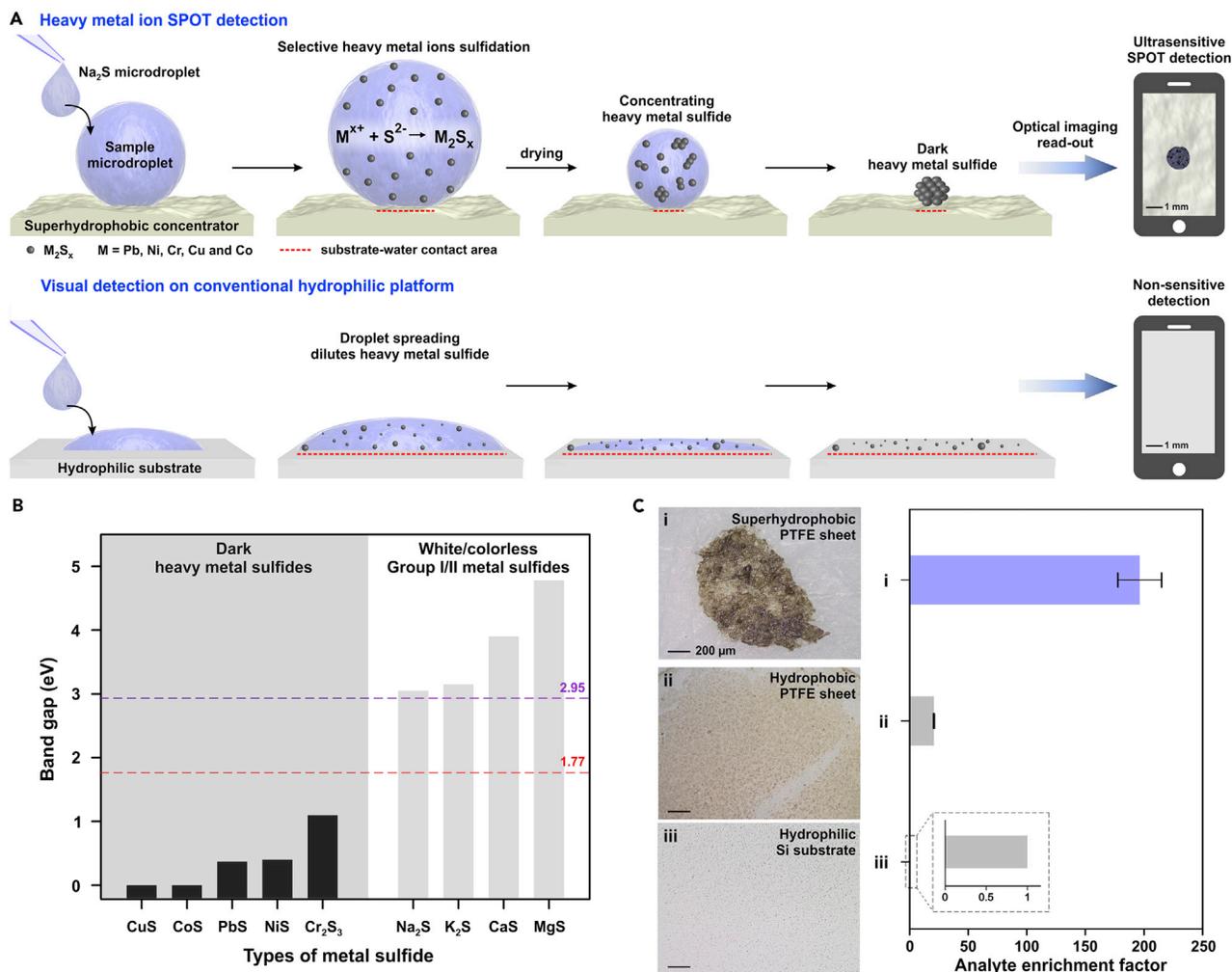


Figure 1. Key concepts of SPOT-based detection of HMIs

(A) Working principles of SPOT-based HMI detection and its superiority over a conventional hydrophilic detection platform. Red dotted lines denote substrate-water contact areas, which recede or remain pinned as the droplet dries on a superhydrophobic concentrator or hydrophilic platform, respectively.

(B) Band gaps of various metal sulfide species.

(C) Optical microscopic images (left) of dark heavy-metal sulfide when dried on a (i) PTFE-based superhydrophobic concentrator, (ii) pristine PTFE sheet, and (iii) hydrophilic Si substrate. Analyte enrichment factor (right) is the ratio of the dried spot area on a hydrophilic substrate to that on the respective platforms. The error bar denotes the standard deviation of data obtained from at least nine repeated trials.

these cations to generate insoluble heavy-metal sulfides.^{19,20} From the K_{sp} values, the sulfidation of HMIs should in principle generate a dark metal sulfide for detection even at $\leq 10^{-10}$ M. However, solution-based sulfidation of HMIs exhibits a detection limit of $\sim 10^{-4}$ M (Figure S1). This performance bottleneck is caused by the dilution of the generated dark metal sulfides over the entire three-dimensional solution volume, significantly reducing visual detection sensitivity. The sulfidation of HMIs alone is insufficient for their trace detection.

To overcome this limitation, we exploit a superhydrophobic platform (defined as contact angle $\geq 150^\circ$) as an integrated analyte concentrator (Figure 1A) to promote visual detection of HMIs by restricting the initial substrate-microdroplet contact to a small area. We use a polytetrafluoroethylene (PTFE) sheet as the starting material because it is hydrophobic (contact angle 102° ; Figures S2 and S3), is chemically inert, and

provides a white background to facilitate identification of dark metal sulfides.²¹ The PTFE sheet is mechanically roughened to achieve superhydrophobicity (contact angle = $152^\circ \pm 1^\circ$) with a contact angle hysteresis of $\sim 51^\circ$. This dewetting property enables sample droplets to adhere on the substrate for easy manipulation while allowing the substrate-water contact area to recede during droplet evaporation for additional analyte enrichment.^{22,23} Increasing surface particle density consequently promotes sensitive visual readout of dark particle clusters.

We evaluated our superhydrophobic platform's ability to concentrate insoluble heavy-metal sulfide by drying an aqueous reaction droplet containing Pb^{2+} ions (10^{-3} M) and sodium sulfide (Na_2S , 10^{-2} M) on its surface. Eye-visible dark solids denoting the formation of lead sulfide (PbS) were identified within the dried spot (area 0.70 ± 0.07 mm²) on the superhydrophobic

platform (Figures 1C and S4; characterization details in next paragraph). Conversely, a pristine PTFE sheet and hydrophilic Si substrate (contact angle $< 5^\circ$) generated larger spot areas of ~ 6.64 and ~ 138 mm² (Figure S5), respectively. The larger spot areas indicate the spreading and dilution of PbS particles across the control platforms, thereby leading to poor detection sensitivity as evident from the faint or nearly invisible sample spots. Comparing the dried spot areas, we note that the superhydrophobic platform clearly enriches analytes by >195 -fold relative to traditional hydrophilic sensors (Figure 1C). Such an analyte enrichment effect stems from the unfavorable substrate-water interactions that restrict their initial contact to a small area, followed by the shrinking of this contact area as the droplet dries to further concentrate analytes onto the substrate for sensitive visual detection.

SPOT detection and quantification of HMIs

We subsequently realized SPOT detection of HMIs by integrating the superhydrophobic concentrator with metal sulfidation chemistry. Typically, a 5 μ L sample droplet is first placed on the superhydrophobic concentrator, and a 5 μ L Na₂S solution (10^{-2} M, containing sodium carbonate) is then added into the initial droplet. We optimized the Na₂S concentration at 10^{-2} M to ensure that excess sulfide species were present in the reaction droplet to drive a complete metal sulfidation reaction for efficient SPOT detection (Figure S6). Sodium carbonate was included to (1) create an alkaline environment to minimize hydrogen sulfide (H₂S) evolution¹⁹ and (2) serve as a visual marker for tracking the dried sample's position without affecting SPOT detection (Figure S6). The droplets were dried under ambient conditions and characterized with an optical microscope. We began by detecting Pb²⁺ ions as a proof of concept because of their toxicity on the central nervous system and reproductive system.¹ At high Pb²⁺ concentration (10^{-3} M), an eye-visible dried spot containing large, dark particle clusters with a total area of 0.53 ± 0.08 mm² was formed on the superhydrophobic concentrator (Figures 2A and S7). The dark solid product is attributed to PbS via its characteristic X-ray photoelectron spectroscopy (XPS) peaks and 2-LO phonon Raman mode (Figures S8 and S9).^{24,25} Reducing the Pb²⁺ concentration decreased the dark area occupied by PbS (Figure 2B). The white solids observed at a Pb²⁺ concentration $< 10^{-3}$ M were a combination of sodium carbonate and sodium sulfate (Figure S10), whereby the latter was formed when unreacted sulfide was oxidized by air.²⁵ At the detection limit of 10^{-10} M (Figure 2C), we still observed dark PbS particles and ascertained their identity by using spatially resolved Raman measurement (Figure S9). We eliminated any false positives from neat Na₂S, NaCO₃, or analyte solutions because they did not produce dark solids when dried (Figures 2D and S11).

More importantly, the SPOT sensor quantifies Pb²⁺ ions down to the sub-nanomolar level through the positive correlation of the dark sulfide area with Pb²⁺ concentrations between 10^{-10} and 10^{-6} M (Figures 2E and S7). Dark sulfide areas recorded at various Pb²⁺ concentrations are highly reproducible with a relative standard deviation (%RSD) of $\sim 10\%$. Both the signal reproducibility and the dependency of the dark sulfide area on Pb²⁺ concentration again affirm the formation of PbS and exclude ambient contamination (e.g., dust), which should cause random error instead. We expect negligible interference from other com-

mon anions because only the sulfide salts generate a dark solid (Figure S12), and the low K_{sp} of metal sulfides readily drives anionic replacement.²⁰ Notably, SPOT's quantitative window spans 4 orders of magnitude and encompasses concentrations $\sim 1,000$ -fold lower than the World Health Organization (WHO)'s permissible limit (4.8×10^{-8} M).¹ Conversely, current optical sensors have inferior detection limits at the micromolar level and a narrow quantification range within 2 orders of magnitude.^{26,27} Moreover, SPOT detection requires a small sample volume of only 5 μ L, making it safer and more scalable than laboratory-bound techniques and other portable sensors with sample volumes typically ranging from milliliters to liters.^{5,12}

To demonstrate its versatility, we extended SPOT to detect a variety of common HMIs that also form dark metal sulfides with Na₂S, such as Ni²⁺, Cr³⁺, Cu²⁺, and Co²⁺ ions.^{17,28} We observed a similar formation of dark heavy-metal sulfides and achieved ultratrace detection down to 10^{-10} M for these four analytes (Figures 3A, S13, and S14). These detection limits are remarkably up to 10^6 -fold lower than the respective WHO and US EPA regulatory limits.¹ Interestingly, quantitative analyses demonstrate that the dark sulfide areas quantified at each analyte concentration closely agree among all five HMIs tested (% RSD $< 10\%$; Figures 3B and S15). This observation implies that SPOT sensing is dependent only on analyte concentration and not the type of analyte present, an important criterion for subsequent collective detection of multiple HMI species. Common non- or less-toxic cations do not interfere with SPOT detection of HMIs (Figure S16), even at a 10^6 -fold higher concentration. Compared with the high specificity of conventional sensors, our SPOT sensor excels as a universal platform to quantify different heavy-metal species for broad detection applications.

Collective detection of multiple HMI species

Building on our observation that the dark sulfide area depends only on analyte concentration, we further utilized SPOT to collectively quantify multiple HMI species present in the same sample droplet. For collective detections, we added up to five different types of HMIs (Pb²⁺, Ni²⁺, Cr³⁺, Cu²⁺, and Co²⁺) into a sample solution with a total concentration of 10^{-10} M. All collective SPOT detections gave consistent dark sulfide areas of ~ 297 μ m² (Figure 3C), which also matched the results from individual detection of the constituting HMIs (deviation $< 5\%$). Our SPOT design clearly demonstrates the collective detection of Pb²⁺, Ni²⁺, Cr³⁺, Cu²⁺, and Co²⁺ ions in a single analysis by producing dark metal sulfides. These toxic species can thus be quantified together into a unified term we coined "dark HMI concentration" for high-throughput and timely evaluation of general water safety, which is especially useful during an emergency or when a large number of samples are involved.

Accelerating SPOT detection at elevated temperature

In addition to designing a sensitive sensor, it is also crucial to achieve swift detection operation for practical in-field applications. For SPOT detection, the most time-consuming step is the drying of the reaction microdroplets on the superhydrophobic concentrator under ambient conditions (~ 4 h). To hasten SPOT detection, we dried reaction microdroplets on a hot plate at an optimized temperature of 75°C in < 6 min (Figure S17)

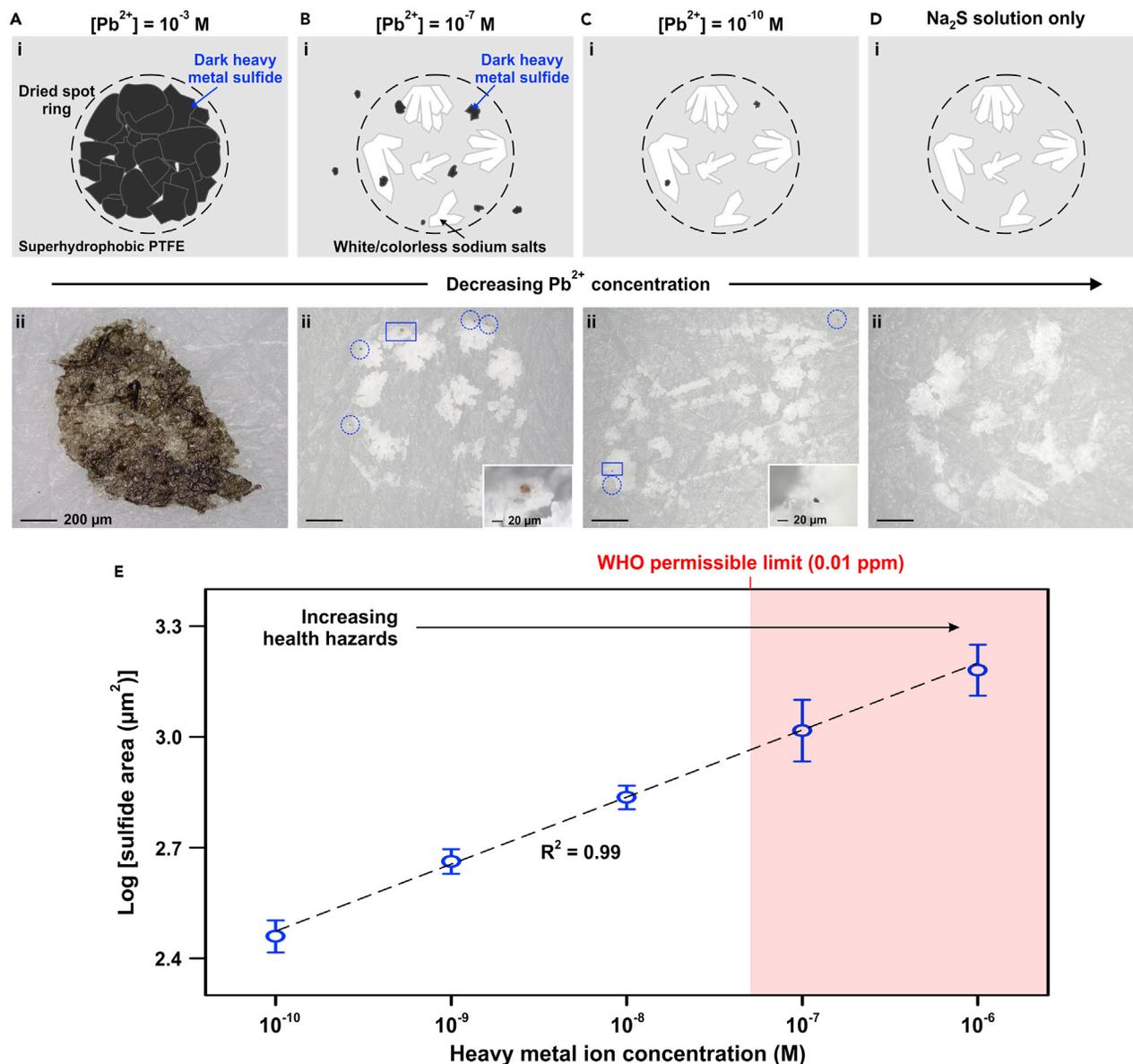


Figure 2. SPOT-based quantification of Pb^{2+} ions

(A–D) SPOT detection of Pb^{2+} ion at concentrations of (A) 10^{-3} , (B) 10^{-7} , and (C) 10^{-10} M and a (D) control experiment without Pb^{2+} ion. Also shown are (i) schemes and (ii) microscopic images of dried sample spots. Insets show magnified images of the respective regions in the blue boxes.

(E) Correlation of dark sulfide area with Pb^{2+} concentration. Error bars denote the standard deviation of data obtained from at least three repeated trials.

without affecting the analyte enrichment effect of the superhydrophobic concentrator (Figure S18). Although heating hygroscopic Na_2S leaves a liquid ring around the spot,²⁹ it has a negligible effect on SPOT-based quantification of HMIs (Figures S19 and S20). More importantly, SPOT detection at the elevated drying temperature achieves a similar detection limit of 10^{-10} M and a positive correlation between the dark sulfide area and the analyte concentration (Figure S21). We also noted a drastic surge in dark sulfide area when the Pb^{2+} concentration increased from 10^{-7} to 10^{-4} M, most likely because of enhanced sulfidation kinetics at higher temperature¹⁹ and reduced loss of Na_2S via H_2S evolution within the shorter duration of 6 min.²⁹ The enhanced PbS formation consequently enables naked-eye detection

down to 10^{-5} M and a wider quantification range between 10^{-10} and 10^{-3} M.

Portable SPOT ensemble for on-site HMI detection

Thus far, SPOT detections are laboratory bound because of the use of a stationary benchtop microscope and a hot plate. To realize timely and on-site detection, we designed a portable SPOT-based ensemble (Figure 4A) that can be compacted to the dimensions of a US letter-sized paper (22×28 cm) and comprises (1) a SPOT sensor, (2) a single-tube handheld microscope (11×3 cm), (3) a miniature droplet heater, and (4) a custom smartphone- or tablet-based mobile application (app) for image analysis and analyte quantification. When powered by a 5 V

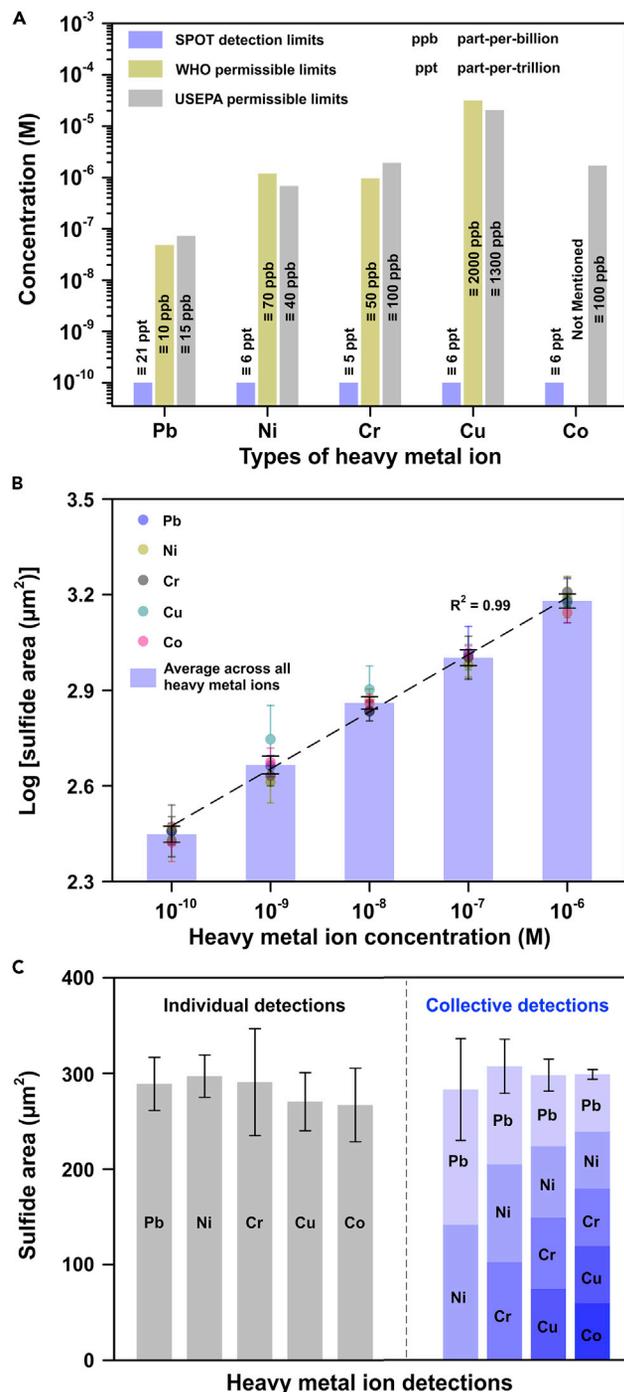


Figure 3. Universal and collective SPOT detection of five different HMIs

(A) Comparison of SPOT detection limits of various analytes with their respective WHO and US EPA permissible limits. (B) All HMIs tested exhibit similar correlations between the dark sulfide area and the analyte concentration. (C) Quantitative comparisons between individual and collective SPOT detections of HMIs. Error bars denote the standard deviation of data obtained from at least three repeated trials.

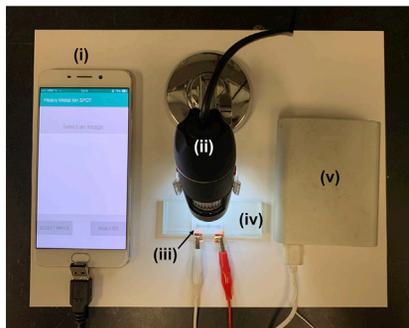
consumer electronic device such as a smartphone (Figures 4B, S22, and S23), our miniature joule heater rapidly heats the as-attached superhydrophobic concentrator to $\sim 75^{\circ}\text{C}$ in ≤ 110 s and remains stable throughout the detection. The dried spot is then imaged with the handheld microscope connected to a smartphone, where the mobile app automatically analyzes the image to identify the dark sulfide area and directly read out the analyte concentration in <30 s (Figures S24 and S25). Using this analytical ensemble, we quantify HMI concentrations between 10^{-7} and 10^{-3} M at $\sim 85\%$ accuracy (Figure S25). Dark sulfide areas apparently plateau as analyte concentration decreases below 10^{-7} M. The higher limit of quantification (10^{-7} M) for a handheld microscope is most likely due to limited optical or camera resolution to image particle clusters of <10 μm . Nevertheless, our portable SPOT ensemble achieves an ultratrace detection limit of 10^{-10} M, and the mobile app is clearly efficient in quantifying HMI concentrations.

More importantly, our portable SPOT ensemble reliably discerned HMI concentrations even during a blind test on unknown sample solutions. In this experiment, each of the five participants prepared five analyte solutions with concentrations (between 10^{-7} and 10^{-3} M) unknown to the operator. Output composite images (Figure S26) from our mobile app evidently demonstrate its ability to distinguish the dark sulfide area for all solutions tested. Datasets measured at all analyte concentrations were well separated and agreed with the actual spiked concentrations (Figure 4C) with $>85\%$ accuracy over 125 measurements (Figure S27), highlighting that our mobile app is robust and eliminates false positives by accurately differentiating between the dark sulfide, liquid ring, and PTFE sheet (Figure S26). Notably, our portable SPOT detection is completed rapidly in <8 min and is significantly faster than other portable sensors with analysis and incubation durations ranging from an hour to even a day.^{12,14}

Efficient SPOT detection in real and artificial samples

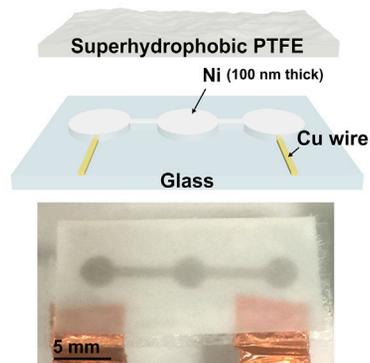
Another important attribute of an efficient sensor lies in its ability to accurately detect analytes in real-world samples, which typically comprise a complex pool of molecular and particulate interference. To demonstrate SPOT sensing in real-world applications, we spiked 10^{-3} , 10^{-5} , and 10^{-10} M Pb^{2+} ion into soil extract, tap water, and artificial Pb smelter wastewater to mimic Pb contamination in actual environmental, household, and industrial scenarios (Figure S28; refer to the experimental procedures),^{4,30} respectively. We filtered all samples before spiking them with Pb^{2+} ion to directly assess SPOT detection performance in real and artificial samples by eliminating potential analyte loss during sample pre-treatments. Using SPOT detection, we quantified spiked Pb^{2+} ions in all three real and artificial samples (Figures 4D and 4E) at $\sim 90\%$ accuracy, even at the trace 10^{-10} M level. Control sample microdroplets without spiked Pb^{2+} ion exhibited no or negligible dark areas (Figure S29), affirming that the observed dark solids were PbS and did not originate from the sample matrices. SPOT detection clearly allows accurate quantification of HMIs even in the presence of potential interference in soil (e.g., organic matter or minerals), tap water (e.g., phosphate-based corrosion inhibitors), and Pb smelter wastewater (e.g., $>10^8$ -fold more concentrated group I/II salts).^{4,5,31} The efficient SPOT detection in real samples stems

A Portable and on-site SPOT detection of heavy metal ion

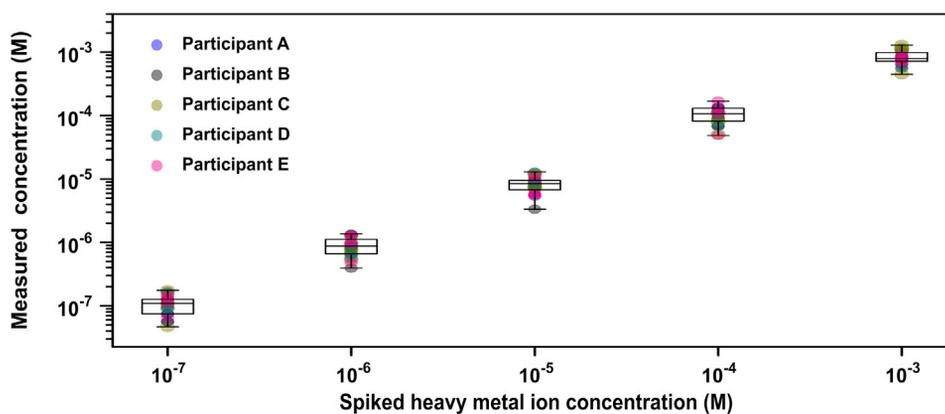


- (i) Smartphone/tablet/laptop (with mobile application)
- (ii) Handheld microscope
- (iii) SPOT sensor
- (iv) Miniature droplet heater
- (v) Consumer electronics (e.g. power bank)

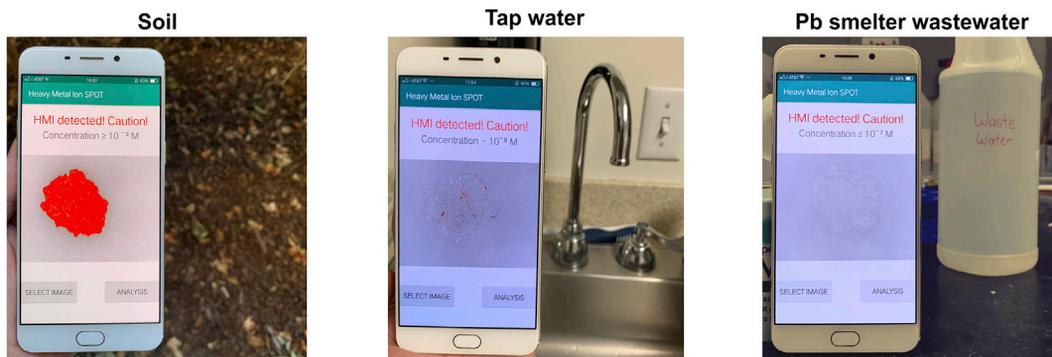
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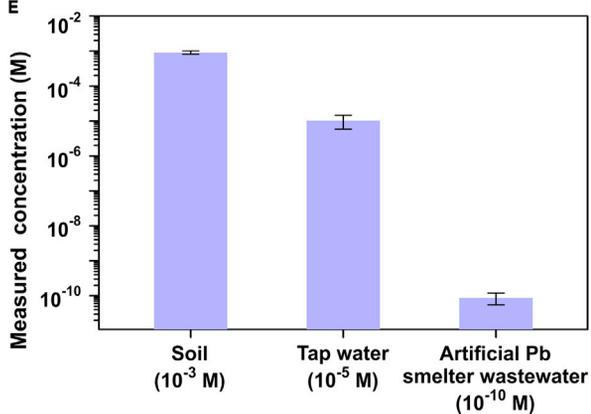
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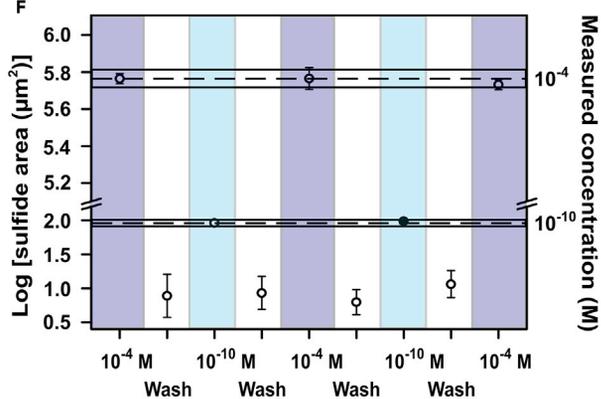
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(legend on next page)

from the high affinity of sulfide species for HMIs and the formation of dark solids as a unique concentration readout. Moreover, our SPOT sensor is also capable of (1) quantifying HMIs in acidic solutions, which are commonly used to dissolve metal compounds (Note S1); (2) accurately determining HMIs even in the presence of other metal ions (e.g., Fe^{3+} , Mn^{2+} , Zn^{2+} , and Cd^{2+} ; Note S2); and (3) minimizing potential interference from sample matrices when combined with widely employed analytical approaches such as the standard addition method (Note S3). Our SPOT sensor is also highly reusable simply by being cleaned with a pH 2 solution (Figures 4F and S30).

Conclusion

In conclusion, we introduce a SPOT-based sensor to efficiently detect HMIs by integrating the high reactivity and selectivity of HMI sulfidation with the analyte enrichment effect of a superhydrophobic concentrator. A potential limitation of our current SPOT design lies in its inability to detect other highly toxic HMI species, such as cadmium, arsenic, and mercuric ions, because their metal sulfides are colored and not dark. We are currently working on other complexation chemistry to generate insoluble, dark solids from the three mentioned HMI species. More importantly, our unique design achieves five key aspects of an ideal sensor, namely (1) high sensitivity, (2) the ability to indicate general water quality, (3) portability, (4) fast response, and (5) low fabrication and operational cost. Requiring a sample volume of just 5 μL , the SPOT sensor universally detects individual Pb^{2+} , Ni^{2+} , Cr^{3+} , Cu^{2+} , and Co^{2+} ions down to 10^{-10} M and collectively quantifies these analyte species to broadly assess water safety. We also showcase a mobile SPOT-based ensemble to swiftly (<8 min) and accurately (~90%) detect HMIs in real and artificial samples. Our portable SPOT detection requires an instrument capital of only \$20 and a cost per analysis of \$0.02 (Note S4), notably >5,000-fold cheaper than traditional AAS or ICP methods (instrumental cost = \$50,000–\$200,000; analysis cost ~ \$100). Among various portable optical sensors, SPOT detection is also more cost effective because it uses cheap Na_2S rather than costly fluorogenic or chromogenic substrates.^{13,14}

The SPOT sensor could potentially have numerous impacts on society. For instance, its ability to quantify HMIs (such as Pb^{2+}) at the sub-nanomolar level is crucial to driving permissible limits to a lower, safer concentration that is essential for providing safe drinking water. The multifunctional SPOT sensor also reduces the cost and hassle associated with the development and operation of a series of stand-alone, ion-specific sensors. Our low-cost, portable SPOT ensemble also holds enormous

potential to be used by everyone for diverse environmental, household, and industrial applications. Decentralizing pollutant and toxin monitoring is crucial to promptly identifying potential contaminations for immediate interventions. Our design is highly customizable to meet detection requirements for different practical situations (Figure S31) and can be potentially extended to other important sensing applications, especially when samples are scarce (e.g., bio-diagnosis or forensics) and/or highly toxic.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Yi Cui (yicui@stanford.edu).

Materials availability

This study did not generate new unique materials.

Data and code availability

The datasets and code generated during this study are available in Mendeley Data: <https://doi.org/10.17632/zthrtgr4nz.2>, but there are restrictions to the accessibility of the datasets and code because of patent-confidentiality restrictions, and so they will be made available upon request.

Chemicals

Sodium sulfide ($\geq 97\%$), lead(II) nitrate ($\geq 99\%$), Cr(III) nitrate nonahydrate (99%), Ni(II) nitrate hexahydrate (99.999%), Cu(II) nitrate trihydrate (99%), magnesium nitrate hexahydrate (>98%), potassium nitrate ($\geq 99.0\%$), zinc nitrate hexahydrate (98%), sodium sulfate ($\geq 99.0\%$), and potassium sulfate ($\geq 99.0\%$) were purchased from Sigma-Aldrich. Cadmium nitrate tetrahydrate (99.999%, Puratronic), sodium nitrate (>98%), calcium nitrate tetrahydrate (99%), and sodium carbonate (99.95%, ACS primary standard) were bought from Alfa Aesar. Co(II) nitrate hexahydrate (99%) was bought from ACROS Organics. Ferric nitrate nonahydrate (>98%, ACS reagent) was purchased from MP Biomedicals. All chemicals were used without further purification. Milli-Q water (>18.0 M Ω) was used for all experiments unless otherwise stated.

Fabrication of superhydrophobic concentrator

PTFE film (thickness ~0.34 mm, Hardware Factory Store) was selected as the starting material because of its chemical inertness and hydrophobic properties.²¹ PTFE was cut into 3 × 3 cm sheets, rinsed with Milli-Q water, and subsequently roughened with a commercial abrasive paper (grit P80; average particle diameter of ~200 μm). The as-roughened PTFE sheet was then rinsed with ample Milli-Q water and blown dry with a stream of N_2 gas. The superhydrophobic PTFE sheet was then characterized for its non-wetting properties and uniformity with a goniometer. Static contact-angle measurements were performed at 50 random sites on a superhydrophobic PTFE sheet to demonstrate its uniformity. At least 30 static contact-angle measurements were conducted for each batch of superhydrophobic PTFE sheet to demonstrate the high reproducibility of our fabrication method.

Figure 4. Portable SPOT-based ensemble for on-site HMI detection

(A) Photograph of portable SPOT-based analytical setup.

(B) Scheme and photograph of a superhydrophobic concentrator attached to a droplet heater.

(C) Application of portable SPOT ensemble to quantify HMIs in a blind test involving five participants. Each solution was measured five times, and error bars denote the standard deviation of the data obtained. The top and bottom limits denote the maximum and minimum concentrations measured, respectively. The bottom, middle, and top lines of the boxes represent the 25th, 50th, and 75th percentiles, respectively.

(D) SPOT detections of spiked Pb^{2+} ion in various real and artificial samples.

(E) Measured Pb^{2+} concentration quantitatively agrees with the spiked concentration for all three samples. Error bars denote the standard deviation of data obtained from at least three repeated trials.

(F) Reusability of portable SPOT ensemble. Dotted and solid lines denote the calibrated mean and its standard deviation, respectively, of dark sulfide area at the respective analyte concentrations. Remnant dark area detected during “wash” does not affect SPOT detection because it contributes <10% to the total dark sulfide area detected, even at $[\text{Pb}^{2+}] = 10^{-10}$ M.

Detection of HMIs by their sulfidation on a superhydrophobic concentrator (SPOT)

Solutions of various HMIs (Pb^{2+} , Ni^{2+} , Cr^{3+} , Cu^{2+} , and Co^{2+}) were prepared in Milli-Q water at a concentration of 10^{-2} M. The solutions were diluted to yield a series of concentrations ranging from 10^{-10} to 10^{-3} M. We prepared aqueous Na_2S solution (10^{-2} M) by dissolving the solid chemical in an \sim pH 9 aqueous Na_2CO_3 solution. The Na_2CO_3 solution served two purposes, mainly (1) to create an alkaline environment to reduce the loss of sulfide species through hydrogen sulfide (H_2S) evolution¹⁹ and (2) as a visual marker to track sample position without affecting the performance of SPOT detection.

In a typical detection, a 5 μL microdroplet containing HMIs was first placed on a superhydrophobic platform, and then 5 μL of Na_2S solution was added to the initial droplet. Reacting HMIs and Na_2S directly on the superhydrophobic concentrator ensures that all dark metal sulfides produced will be entirely deposited and adsorbed onto the superhydrophobic concentrator upon complete droplet drying, a key factor to drive efficient SPOT detection for trace HMI analysis. The resulting droplet was left to react and dry at ambient conditions or at pre-defined elevated temperature between 35°C and 105°C. The detection setup was covered during reaction and drying to minimize interference from the surrounding environment. The presence of dark sulfide spots was subsequently identified and captured by the naked eye, a camera, a handheld microscope, and/or a benchtop microscope. We analyzed the recorded images by using the freeware ImageJ and/or our custom mobile app to quantify HMI concentration in the sample through the apparent dark sulfide area observed. We performed a blank control in the absence of HMIs according to the same protocol by adding 5 μL of Na_2S solution to a 5 μL Milli-Q water droplet on a superhydrophobic concentrator. We performed all SPOT detections at least three times, unless otherwise stated, to ensure the reliability of the results and to eliminate the possibility of random errors caused by the surrounding environment (such as dust).

Collective detection of various HMIs

All solutions composed of various HMI combinations (including Pb^{2+} , Ni^{2+} , Cr^{3+} , Cu^{2+} , and Co^{2+} ions) were prepared at an effective concentration totaling 10^{-10} M. Collective detections were performed on sample droplets containing two, three, four, and five different types of HMIs. The reaction droplets were dried on the superhydrophobic concentrator under ambient conditions and later characterized with a benchtop microscope. We analyzed the recorded images by using ImageJ to quantify the total concentration of HMIs in the droplet. The quantitative result was termed “dark HMI concentration” because all five cations produced dark heavy-metal sulfides when reacted with Na_2S . This property formed the basis of collective HMI quantification.

Demonstration of the generic selectivity of SPOT detection toward HMIs

Solutions of group I/II cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) were prepared in Milli-Q water at a concentration of 10^{-3} M. 5 μL of Na_2S solution (10^{-2} M) was added to a 5 μL aqueous droplet of respective group I/II cations and dried under ambient conditions. The dried spot was characterized with a benchtop microscope and further analyzed with ImageJ. An aqueous solution containing divalent Pb^{2+} and Ca^{2+} cations with concentrations of 10^{-10} and 10^{-3} M, respectively, was used to demonstrate the negligible effect of group I/II cations on SPOT-based detection of HMIs.

Design and fabrication of miniature and localized droplet heater

The design scheme of the miniature droplet heater can be found in Figure S22. A patterned stainless steel mask was first obtained by laser cutting. The design was subsequently transferred onto a glass slide by thermal evaporation of 5 nm Cr and 100 nm Ni coatings over the stainless-steel mask. The Ni pattern was then electrically connected to Cu tapes (electrical contact points to external power sources) at both ends via wire bonding. The superhydrophobic PTFE-based concentrator was adhered to the miniature heater with double-sided tape. We measured the temperature of the superhydrophobic concentrator by attaching a thermocouple thermometer to its surface.

Smartphone mobile app for automated HMI quantification

We developed a custom Android app to automatically analyze microscopic images and quantify HMI concentration. We used the open-source integrated

development environment Android Studio (Google, Mountain View, CA) to develop the mobile app—Heavy Metal Ion SPOT—in the Android operating system, compatible with both smartphones and tablets. The app interface was designed to include (1) a text panel to instruct the user and to read out the HMI concentration; (2) an image panel to first display the selected image, which was subsequently replaced with a composite image after image processing; and (3) two action buttons for selecting the image from the device photo gallery and starting the analysis. The mobile app is available from the authors upon request.

In brief, the app prompts the user to first select an image from the gallery and then start the analysis. The image analysis is composed of a series of automated image-processing steps, including (1) the conversion of RGB pixels into gray scale, (2) mathematical operations on each pixel to better distinguish dark area from background and to shorten processing time, (3) binary conversion of the image with an automatic threshold, (4) counting of pixels to quantify the dark sulfide area, (5) translation of the pixel counts into HMI concentration with an embedded mathematical correlation between the dark sulfide area and the HMI concentration (described in Figure S25) in the algorithm, (6) creation of a composite image to highlight the dark sulfide area (in red) on the original image, and (7) display of both the composite image and the HMI concentration as an output of the analysis. Automatic thresholding is based on the following protocol. In brief, the averages of the pixels at and below or above the threshold are computed, and the composite average of these two is calculated. The threshold value increases by 1 repeatedly and stops only when the threshold is larger than the composite average (Equation 1). The quantitative results are calibrated with an image containing a dark area of known dimension. An analysis is typically completed in <30 s:

$$\text{threshold} = [(\text{average background} + \text{average objects})/2]. \quad (\text{Equation 1})$$

Quantification of HMI concentrations in a blind test

The blind test involved the testing of unlabeled aqueous Pb^{2+} solutions prepared by five participants with analyte concentrations ranging from 10^{-7} to 10^{-3} M. We prepared the reaction droplets by adding 5 μL of Na_2S solution to a 5 μL sample droplet on a superhydrophobic concentrator and dried them at an elevated PTFE surface temperature of 75°C. We then characterized the dried spots by using a handheld microscope and analyzed the images by using the mobile app to read out the HMI concentration. Each solution was measured five times.

Preparation and detection of HMIs in real and artificial samples

Three different real or artificial sample matrices were evaluated to exemplify the ability of SPOT detection to accurately quantify HMIs, even in the presence of a complex pool of potential molecule and particulate interference. The three sample matrices included (1) aqueous soil extract, (2) tap water, and (3) artificial Pb smelter wastewater, which were representative models for the demonstration of SPOT detection in environmental, household, and industrial applications, respectively. All samples were treated and filtered (described in the following paragraphs) before being spiked with aqueous Pb^{2+} solution. This experimental design is important for directly assessing the performance of SPOT detection in respective sample matrices by eliminating potential complications from sample pre-treatments such as analyte extraction.

For soil, 1 g of the sample (no prior treatment) was weighed into a 20 mL glass vial, and 10 mL of Milli-Q water was added. The mixture was mixed and allowed to stand for 10 min for extraction of aqueous-soluble soil components into the Milli-Q water. The aqueous soil extract was collected and passed through a syringe filter with a pore size of 0.45 μm for the removal of any solid residues. An aqueous Pb^{2+} solution (0.01 mL of 10^{-1} M) was then added into 0.99 mL of filtered soil extract to yield an effective spiked Pb^{2+} concentration of 10^{-3} M without significantly affecting the sample matrix. The solution concentration was equivalent to having an initial Pb concentration of 2,070 ppm (or 2,070 mg/kg) in the soil sample under the assumption that all Pb species were aqueous soluble and could be extracted into water. This sample preparation was designed to simulate soil contamination whereby Pb concentration exceeded the US EPA permissible limit of 1,200 ppm in soil (non-play area).³⁰

For tap water, 10 mL of household tap water was passed through a syringe filter with a pore size of 0.45 μm for the removal of any solid residues. An

aqueous Pb^{2+} solution (0.01 mL of 10^{-3} M) was then added into 0.99 mL of filtered tap water to yield an effective spiked Pb^{2+} concentration of 10^{-5} M (or ~ 2.07 ppm) without significantly affecting the sample matrix. This concentration was chosen to mimic the Pb contamination of the domestic water supply in the Flint water crisis,⁴ whereby the average and median Pb concentrations were reported to be 2.39 and 1.75 ppm, respectively.

For artificial Pb smelter wastewater, a solution containing various metal salts was prepared according to the literature,³¹ as summarized in Figure S28. The artificial matrix was then spiked with aqueous Pb^{2+} solution to an effective concentration of 10^{-10} M.

Analyte concentrations in the three sample matrices were subsequently measured according to the SPOT detection protocol with a drying temperature set at 75°C. The dried sample spots were characterized with a handheld microscope, and the resulting images were analyzed with the mobile app for quantification of HMI concentrations.

SPOT detection of HMIs in acidic sample solutions

In this experiment, sample solutions containing Pb^{2+} ions at 10^{-4} M were prepared. The pH of these sample solutions was varied between 1 and 4 by being adjusted with an aqueous hydrochloric acid solution. 5 μL of the sample solutions and 5 μL of Na_2S solution (10^{-2} M) were reacted on top of the superhydrophobic concentrator and dried at 75°C. All dried spots were imaged and characterized with an optical microscope.

SPOT detection of target HMIs in the presence of other metal ions

We chose Fe^{3+} , Mn^{2+} , Zn^{2+} , and Cd^{2+} ions as our model cationic interferences because they could be present in real water samples. For the individual detection of these cations, 5 μL of the sample solutions and 5 μL of Na_2S solution (10^{-2} M) were reacted on top of the superhydrophobic concentrator and dried at 75°C. For the detection of HMIs in the presence of these interfering cations, we prepared sample solutions by spiking Pb^{2+} ion at 10^{-10} M, as well as Fe^{3+} , Mn^{2+} , Zn^{2+} , or Cd^{2+} ions at the significantly higher concentration of 10^{-5} M. The same SPOT detection procedure was employed. All dried spots were imaged and characterized with an optical microscope.

Integrating SPOT detection by the standard addition method

A soil extract containing 10^{-5} M Pb^{2+} ions was prepared, and its aliquots were subsequently spiked with standard solutions containing known concentration of Pb^{2+} between 10^{-5} and 5×10^{-5} M. 5 μL of the spiked sample aliquots and 5 μL of Na_2S solution (10^{-2} M) were reacted on top of the superhydrophobic concentrator and dried at 75°C. The dried spots were imaged and characterized with an optical microscope.

Reusability of portable SPOT-based analytical system

SPOT detection was first performed on a 10^{-4} M aqueous Pb^{2+} solution. The dried sample spots were cleaned with an acidic pH 2 solution (prepared with hydrochloric acid). The superhydrophobic PTFE sheet was then reused for subsequent SPOT detection of 10^{-10} M aqueous Pb^{2+} solution. This detect-wash sequence was repeated with Pb^{2+} concentrations alternating between 10^{-4} and 10^{-10} M. All stages of the detect-wash sequences were characterized with a benchtop microscope and analyzed with ImageJ. The sample droplets were dried at a PTFE surface temperature of 75°C.

Material characterization

Static and dynamic contact angles were measured with a contact-angle goniometer (ramé-hart model 290). XPS characterization was performed with a PHI VersaProbe with a monochromatized $\text{Al}(K\alpha)$ source. Raman spectra were recorded with a Horiba Labram HR Evolution Raman system with an excitation wavelength of 532 nm. A 100 \times objective lens and 600 L/mm grating were used. Each Raman spectrum was acquired for 30 s and accumulated over five consecutive cycles. Images of the dried sample spots were captured on a benchtop light microscope through 5 \times and 20 \times objective lenses. All SPOT detections and quantifications were based on images recorded through the 5 \times objective lens. A cost-effective (\sim \\$20) and handheld optical microscope (Jiusion) was used for portable on-site detection of HMIs. This microscope can be powered by consumer electronic devices that support USB on-the-go output, such as smartphones and laptops. Equipped with a mini camera and eight LED light sources, the handheld microscope captured the

images of the dried sample spots and saved them directly into the display device (e.g., smartphone or laptop) in JPEG format with a resolution of 96 dpi and 24 bits RGB.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.oneear.2021.04.009>.

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AUTHOR CONTRIBUTIONS

H.K.L. and Y.C. conceived the initial idea. H.K.L. designed the SPOT sensor and planned the experiments. H.K.L., Y.Y., Y.P., A.Y., L.-Y.C., X.X., X.G., F.L., H.W., and B.L. performed experiments. H.K.L. and W.H. designed and wrote the Android-based mobile application. H.K.L., J.X., Y.P., T.W., J.W., and Y.C. analyzed the data. H.K.L. and Y.C. wrote the manuscript. All authors read and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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