Development of a 3d Paper-Based Device for the Qualitative Analysis of Lead in Waste Water

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Abstract

The widespread use of lead in the past, especially in plumbing, has resulted in the contamination of drinking water.Exposure to lead can cause severe damage to the central nervous system especially of children. The current methods for detecting lead are expensive and time consuming. This paper reports a portable, onsite and simple 3D paper-based device that can be used for the qualitative detection of lead in waste water. Proposed tool is a folding device composed of paper wells and hydrophobic regions which were created using polyurethane varnish. This portable tool is based on a rapid colorimetric reaction which occurs between lead(II) ions and rhodizonic acid. Water samples can be tested for the presence of lead by directly introducing 20.00 µl of sample on to the device. Development of the characteristic red color is used to determine the presence of lead in concentrations greater than 4 ppm in water.

Keywords: Lead, portable, 3D paper-based devices, portable onsite method.

1. Introduction

In recent years, there has been a growing interest in developing paper-based analytical devices for the onsite detection and analysis of chemicals. These paper-based devices are also known as point-of-care devices (POCs), and are currently being developed to be used in various fields such as food, water, environmental and biological fluid analysis (Yetisen, Akram, & Lowe, 2013). The main objective of developing POCs is to analyse samples without sophisticated equipment or basic laboratory facilities. In most developing countries, laboratory facilities and trained personnel are limited to carry out some essential laboratory experiments. Under these conditions, it is useful to have cheap and single use POCs that could be used for the onsite determination of various parameters. In 2004, the World Health Organization (WHO) established guidelines ("ASSURED") (Ballerini, Li, & Shen, 2012)for the production and use of POCs. According to these guidelines, these devices should be affordable, sensitive, specific, user-friendly, rapid and robust, and equipment-free.

Heavy metals have been extensively used in various industries since ancient times and have caused a great level of pollution due to their unregulated release to the environment. Most heavy metals are toxic to organisms, so some were used as pesticides and medicines to cure bacterial and fungal infections. However,heavy metals can be toxic to humans as well. In the vicinity of mines, factories and power plants the air, water, and soil is constantly contaminated with heavy metals. In such areas, it would be useful to have a cheap and easy method to monitor food and water quality. This research work is focused to develop a paper-based POC that can be used to detect lead in water samples.

2. Background/Literature Survey

Lead is a cumulative poison which accumulates mainly in soft tissue and bones. Lead may have adverse effects on the gastrointestinal tract, bone marrow, and nervous system. Paper is essentially a hydrophilic matrix of cellulose fibres extracted from raw materials such as wood, cotton, flax etc. For diagnostic applications it is desirable to use paper made from 100% cotton as they do not discolour or self-destruct over time (Yetisen, Akram, & Lowe, 2013).Many physical properties of paper have to be considered when choosing a medium for a paper-based device.

A few such properties are pore size, pore size distribution, porosity, capillary flow rate, the thickness of the paper and bed volume(Yetisen, Akram, & Lowe, 2013).A few techniques used to make paper channels on paper are photolithography, paper cutting, wax printing, wax screen printing and wax dipping(Yetisen, Akram, & Lowe, 2013). In this research the device was fabricated using polyurethane varnish instead of wax. Paper-based devices can be in 2D or 3D form. In 2D devices the sample flows laterally along the channel and gives a signal. In 3D devices the sample flows laterally as well as vertically through the device, enabling simultaneous detection of multiple analytes and reducing the amount of sample required to get the same result using a 2D device. These 3D devices are composed of two or more layers which are either glued or clamped together (Liana, Raguse, Gooding, & Chow, 2012).

Paper serves as a suitable platform to develop POCs because it is cheap, produced globally, lightweight, portable, and can be cut, folded or functionalised as per requirement (Ballerini, Li, & Shen, 2012). Also it can easily be destroyed by burning. However, the sensitivity of POCs is slightly compromised because the minimum detection limit should be perceivable by the human senses.Many spot tests can be used to detect lead, but the rhodizonate test has been one of the oldest tests. For a long time it has been used to detect gunshot residue at crime scenes. It is used to test lead on clothes, walls, and other surfaces.

3. Materials and Methodology

3.1 Chemicals

Analytical grade sodium rhodizonate (Fluka), HNO_3 (Technopharmchem, India),$Pb(NO)_3$(HiMedia Laboratories, India),HCl (Technopharmchem, India),and commercial grade vinegarwere used for the development of the device and further analysis. All chemicals were used as they were received, and sodium rhodizonate is referred as NaR from this point onwards.

3.2 Instruments

The lead concentrations of the water samples were measured using the atomic absorption spectrophotometer (GBC, 932 plus). The UV/visible spectrophotometer (JASCO, V-560) was used to measure the absorbance of the lead rhodizonate complex.

3.3Other Materials

The device was fabricated using Whatman No.1 filter papers. Vineger and polyurethane varnish were purchased from the local market. The hydrophobic regions of the device weremarked with polyurethane varnish using a paintbrush.

3.4.Preparation of Lead Nitrate Solutions

A series of lead solutions with concentrations of 20, 10, 8, 6, 4, 3, 2, and 1 ppm were prepared using a 100 ppm stock solution.

3.5. Assembling the Layers and Generating Test Zones

This device was developed using a $1.5\times5\ cm^2$ strip of Whatman No.1 filter paper. Two wells on the paper were created using varnish as shown in Figure 1. These two wells were created so that they aligned when the strip of paper was folded in half as shown in Figure 2. The detection well was designed with a radius of 1.5 mm, treated with $0.005\ cm^3$ of 0.16 M HNO_3 and heated over a heating mantle until dry. The reagent well designed with a radius of 3 mm was smeared with a crushed crystal of NaR using a toothpick. A second paper with a well (radius of 3 mm) was glued on to the reagent well to keep the rhodizonate crystals intact in the detection well (Figure 3).
Vinegar, 0.05 M HCl and 0.16 M HCl were initially chosen as colour-developing reagents to be used in the device. In order to determine the most suitable colour developer, $0.005\ cm^3$ of 0.2% NaR was added to the detection zone of the device followed by $0.010\ cm^3$ each the colour developing reagents, and the time taken forthe colour of NaRto completely disappearwas measured. Vinegar was chosen as the most suitable colour developing reagent since it produced the best result.

3.6. Qualitative Analysis

3.6.1.Application of Sample to the Detection Well

A volume of $0.020\ cm^3$ of the lead solution was introduced to the detection well, and the device was suspended over a heating mantle and heated at approximately 50 ˚C for 5-6 min. until it was completely dry.

Next, the device was folded so that the two wells lightly touched each other and 0.020 cm^3 of distilled water was added to the back of the reagent well to dissolve NaR crystals (Figure 2).As soon as the reagent well became completely wet with NaR, the device was unfolded and thecolour was allowed to develop for about 30 s. This prevents backflow of lead.Subsequently, vinegar (0.010 cm^3) was added and the device was left undisturbed for 2 min.,untilunreacted NaR became colourless and a pink to purple coloured ring was visible at the edge of the well.

3.6.2. Assessing the Performance of the Device

The performance of the device was assessed using a performance calibration curve. This was developed by replicating the test 10 times for each concentration in the series and observing the number of devices that showed a positive response. The minimum concentration that gave a 100% positive response was considered the minimum detection limit of the device.

4. Design and Results

The Reaction between rhodizonic acid and lead ions was used as the spot test. Rhodizonic acid makes colourful complexes with many heavy metals such as strontium, lead and barium, but at acidic pH values most metal complexes and NaR itself becomes colourless immediately.Lead rhodizonate loses its colour at a significantly slower rate, hence this reaction becomes specific for lead at pH values below 2.8 (Feigl & Suter, 1942).

The colour developer was used to remove all background noise. Background noise is mostly due to the orange NaR solution and some of it may be due to the presence of other metal-rhodizonate complexes.

5.Determining the Minimum Detection Limit

The minimum detection limit of the device was determined by applying the sample(a series of 20, 10, 8, 6, 4, 3, 2, and 1 ppm) to 10 devices for each concentration.A performance curve plotted using these results is shown in Figure 4. The device was also tested with 20, 100 and 1000 ppm lead solutionsmerely to observe the colour changes at high lead concentrations (Figure 5).Based on results, the minimum detection limit of this device is 4 ppm. However, the device detected concentrations of lead as low as 2 ppm with lesser accuracy. Suchtest results are shown in the Figure 5.

However, it is worth mentioning that most metal rhodizonate complexes are colourless in an acidic medium. Those that do produce a colour in an acidic medium such as Ag^+, Hg^+, Tl^+, Cd^{2+}, Ba^{2+}, and Sn^{4+}(Feigl & Suter, 1942)are yet to be tested to determine the minimum concentrations at which they interfere with the observations.

Water samples with debris or suspended particles need to be filtered prior to application of the sample to the device. Otherwise these particles may deposit near the edge of the well, masking the lead ring.Intensely coloured samples will also interfere with the results.This method may not be suitable to test acid-digested samples as they are usually very acidic. Lower pH values of such samples may remove the colour of NaR even before reacts with lead.

6. Conclusions

Much effort has been put to design this device according to WHO guidelines, but it still has few significant drawbacks. The device is simple to operate and it requires no technical expertise, analytical grade chemicals or sophisticated instruments. However a major drawback is that the device has to be suspended and heated for about 5-10 min. The readout from the device would be more reliable if varnish could be applied using a mould or a printer. This would also greatly increase the consistency of analysis. Hand drawn devices tend to have slightly varying surface areas in the detection zones and this would directly impact the final result as it affects the distribution of lead on the detection well.

The use of a heat and acid resistant medium instead of varnish would increase the variety of samples that could be tested using this device. The current version of the device cannot be used at very low pH values as it is prone to acid burns. It can only be heated with a radiation heat source to prevent burning of varnish and the paper.

In spite of all its shortcomings, this device can be used to identify aqueous samples containing 4 ppm lead or higher. The device is stable and can be stored in a cool dry place for a very long time. Solid NaR is infinitely stable in air. Although this device has a very basic design, with further research,it can be upgraded to be used as a reliable analytical tool.Thus, it has a greater potential to be used as a POC in future.

7. Tables and Figures

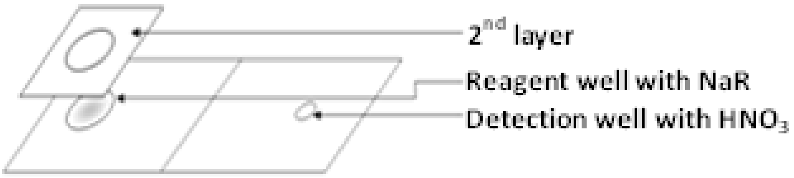

Figure 1: Schematic of the device before assembling the layers.

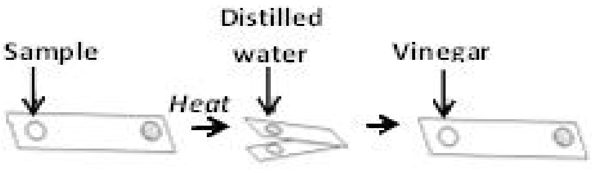

Figure 2: A diagram showing the process of sample application.

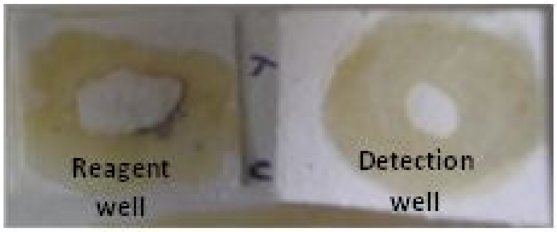

Figure 3: A lead detection device prior to use

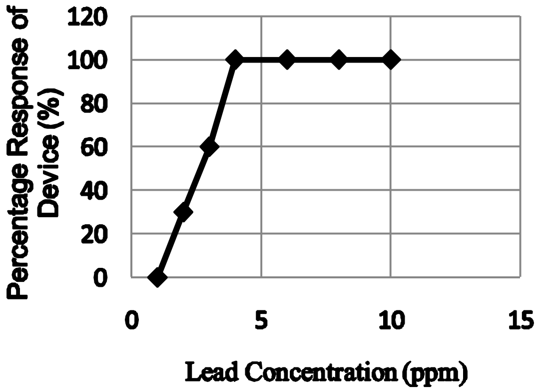

Figure 4: The performance curve for the determination of the minimum detection limit.

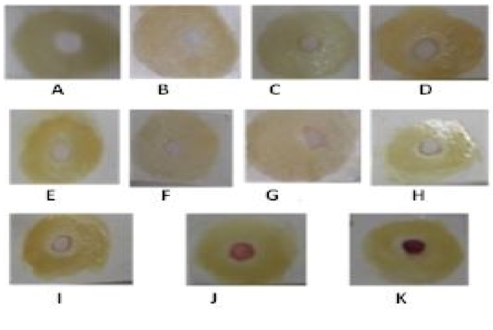

Figure 5: The response of the device for different concentrations of lead. (A) Distilled water control. (B) 1 ppm (C) 2 ppm (D) 3 ppm (E) 4 ppm (F) 6 ppm (G) 8 ppm (H) 10 ppm (I) 20 ppm (J) 100 ppm (K) 1000 ppm

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