

Materials in Colorimetric Detection of Water Pollutants



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Abstract Evolution in the sensor design and their potential usage in water quality monitoring has revealed the aptitude of material science in the environment protection practices. Consequently, the progress in scientific literature is rising to tail consistent and sophisticated sensory platforms. In this context, colorimetric sensors are categorised as benchmarked sensor models, owing to their cost effectiveness in sensor design, ease of analysis, on-site pollutant monitoring capability, circumvents the use of multifaceted instrumentation and most importantly, user-friendliness. This chapter is focussed on the potential use of colorimetric sensors for the water-pollutant sensing and discusses the promising prospects of sensor developments (from choice of material to read-out tools) to assist nascent researchers to review the principles, mechanistic and advancements in existing trends in colorimetric sensory probes.

1 Introduction: Colorimetric Sensors for Water Pollutants

Water is one of the most important elements essential for the survival of life on the planet and so the monitoring of its quality. In the present scenario, colorimetric sensors are being used for the detection of various analytes such as proteins, organic compound, peptides, nucleic acids, toxic gases, humidity sensors and water pollutants. Water pollutants are broadly classified into four categories i.e. pathogens, inorganic materials, organic materials and macroscopic pollutants. Of them,

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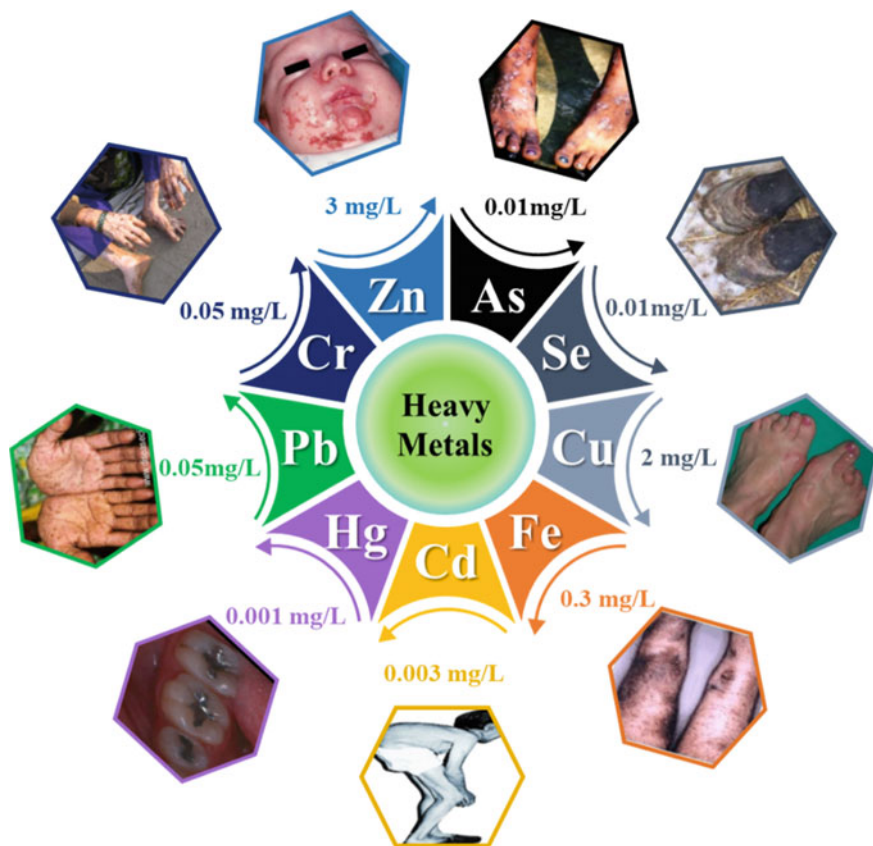


Fig. 1 Common heavy metals with their permissible WHO limits and the health effects caused due to their overdose

Inorganic materials like heavy metals in particular mercury, arsenic, lead, cadmium, and other metals having high de is wide spread concern of the society when present in high concentrations and can have lethal effects to ecosystem as well as human health as shown in Fig. 1. Their accumulation can be due to leaching from waste disposal, industrial wastes, burning of fossil fuels, mining and other human activities. Further, in worst case, their exposure may even lead to death of humans or animals. Due to these reasons development of water monitoring technologies is the prominent area of research these days. The colorimetric technique is one of the preferred methods for the onsite detection of water pollutants because of the usage simplicity and affordability i.e. in most cases observations can be made by naked eyes without need of any expensive instrumentation for analysis. It does not require any skilled manpower for the analysis and can be used by the general public. Despite these advantages, the colorimetric techniques lack in accuracy and may not be able to fulfil the criteria of low detection limits, as compared to other

spectroscopic and chromatographic techniques. These disadvantages is usually due to high background noise and in case of naked eye observation, color perception can vary person to person. In order to increase the accuracy and achieve the low limit of detection by colorimetric techniques, many research groups today combining these methods with digital imaging techniques.

This chapter intends to provide an overview of the design of colorimetric sensors which includes principle of colorimetry and various sensing mechanisms on which sensors are based Also, the recent developments in the materials utilized for the colorimetric sensing of the water pollutants. Nevertheless, a discussion on the commercially available colorimetric sensors.

2 Principles, and Sensing Mechanisms of Colorimetric Sensors

2.1 Principle of Colorimetric Sensors

In order to design the colorimetric sensors for the detection of analyte, there are two major principle factors which are considered i.e. the change in absorbance value at particular wavelength and second is the shift in maximum absorption wavelength. These two factors can be studied and confirmed with the help of UV/Vis spectroscopy and observed by naked eyes. The sensors based upon the first principle, appears to fade or darken when the analyte is introduced based upon its concentration and in second case, the change of color to the new color is observed. There are times, when color changes are not observed by naked eyes, even when these changes are observed with the help of UV/Vis spectroscopy. The rhodamine based copolymer poly(2, 3-dihydroxybutylene-alt-2,3-dihydroxybutylenedithioether) [P(DHB-a-DHBDT)] self-assembled onto 2-(5-bromopyridine-2-yl)-3',6'-bis(diethylamino)spiro-[isindoline-1,9'-xanthene]-3-thione shows the sensitivity towards the Hg(II) ions, in which color change from colourless to pink color observed by naked eyes as shown in Fig. 2. The said probe utilizes the second principle of colorimetry and its sensing mechanism is based upon the shifting of aromatic protons in the presence of metal ions [1].

Apart from these above-mentioned principles there are practical considerations which needs to be considered i.e. solubility of the sensor and matrix of the analyte, pH of the medium and behaviour of analyte in that pH, and medium does not have spectral overlap with the analyte to avoid interference while analysis.

Further, there are four major transduction methods or parameters which are considered or evaluated while designing colorimetric sensors i.e. aggregation observed while using metal nanoparticles, pH in case of organic dyes, in case of polymers conjugation geometry, and analyte induced reactions when dependent on irreversible chemical change. These transduction parameters cause the color changes upon the addition of the analyte to the matrix.

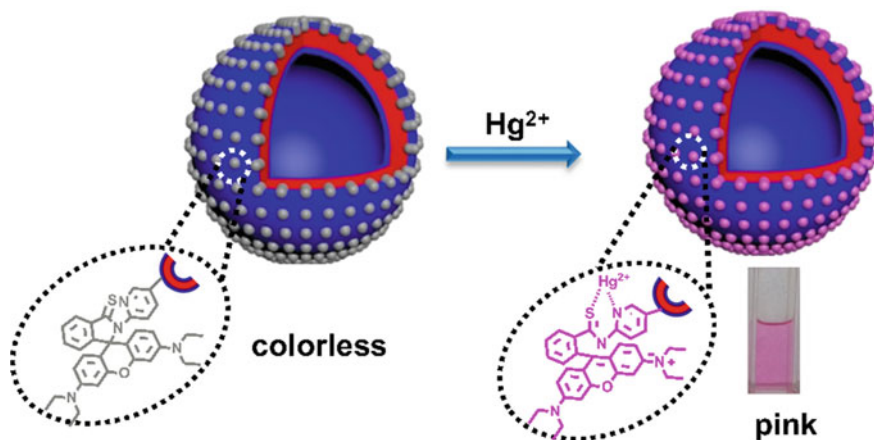


Fig. 2 Behaviour of Probe in the presence of Hg(II) (adapted from Ref. [1])

2.2 Sensing Mechanisms of Colorimetric Sensors

There are different sensing mechanisms based upon which colorimetric sensors can be designed i.e. Intramolecular Charge Transfer, Forster Resonance Energy Transfer, aggregation, pH, indicator formation,

2.2.1 Intramolecular Charge Transfer (ICT)

ICT refers to the charge transfer to the electron deficient acceptor from electron rich moiety within the same molecule. It generally occurs when the molecule is in the photoexcited state by absorbing the light of specific wavelength which facilitates the transfer of electron from one part of molecules to the another. This forms a π -bridge which connects the donor and acceptor groups. Utilizing this sensing mechanism, the receptor molecule aminonaphthoquinones is utilized to design the colorimetric detection of Cu(II) where pyridine N-atom and amine N-atom forms square planar complex with Cu(II) shown in inset of Fig. 3. This results in blue shift of ICT band and increase in d-d transitions upon the increase in concentration of Cu(II) ions. These results in change in color of receptor from yellow to blue instantaneously, which indicates the selectivity of Cu(II) towards the synthesized receptor as shown in Fig. 3 [2]. Similarly, hemicyanine is reported as colorimetric sensing agent for Hg(II) ions which changes its color from red to colourless, which is also confirmed by the changes in UV/Vis spectra [3].

The concept of ICT has been utilized in several for colorimetric sensing applications, but there are challenges which still exist to utilize its full potentials.

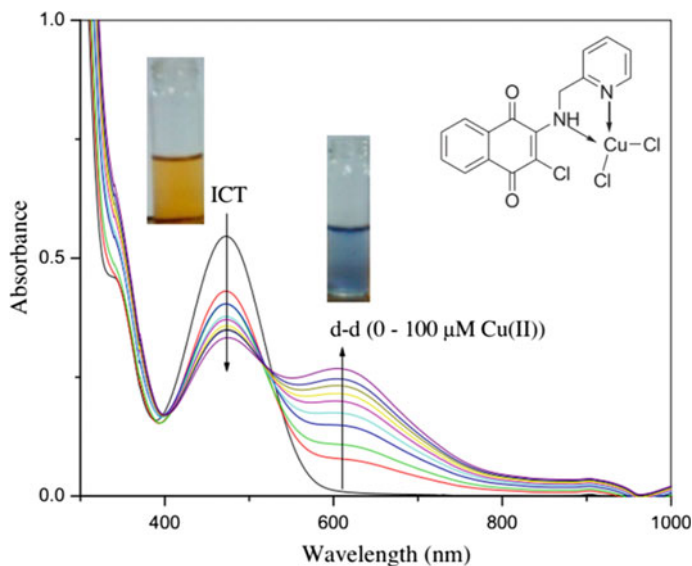


Fig. 3 Effect on receptor upon the addition of Cu(II) ions observed by UV/Vis Spectra and naked eye (inset: square planar complex formation upon the addition of Cu(II) (adapted from Ref. [2])

2.2.2 Forster Resonance Energy Transfer (FRET)

FRET occurs when there is transfer of energy from the donor fluorophore to acceptor fluorophore which are in close proximity between 1 and 10 nm in the absence of radiation through dipole-dipole interactions. For the FRET to occur, there should be a spectral overlap between the absorption of acceptor and emission of receptor and high quantum yield as shown with the help of example in Fig. 4a.

Recently Wanichacheva and his co-workers developed a FRET based Hg(II) sensor where helicene dyes used as energy donor fluorophores and exhibits high quantum yield and rhodamine 6G dyes as energy acceptor as it has absorption and emission wavelengths in the visible region, large molar extinction coefficient and high quantum yield as well [4]. Further, large Stokes shifts of donor minimizes interference and small Stokes shifts of the acceptor fluorophores which could leads to self-absorption. This small Stokes shift of the rhodamine 6G dyes also changes the ring structure of the amide, which produces a fluorescent enhancement and colorimetric change. The both donor and acceptor molecules connected to each other by hydrazine moiety and upon the addition of Hg(II) to the sensor, the color change from greenish yellow to orange is observed by the naked eyes and also confirmed by UV/Vis Spectroscopy as shown in Fig. 4b [4].

Further, rhodamine-6G in another work is appended with benzothiazole conjugated quinoline derivative and used as a ratiometric probe for the detection of Fe (III) using FRET mechanism. Here, color change to yellowish orange from

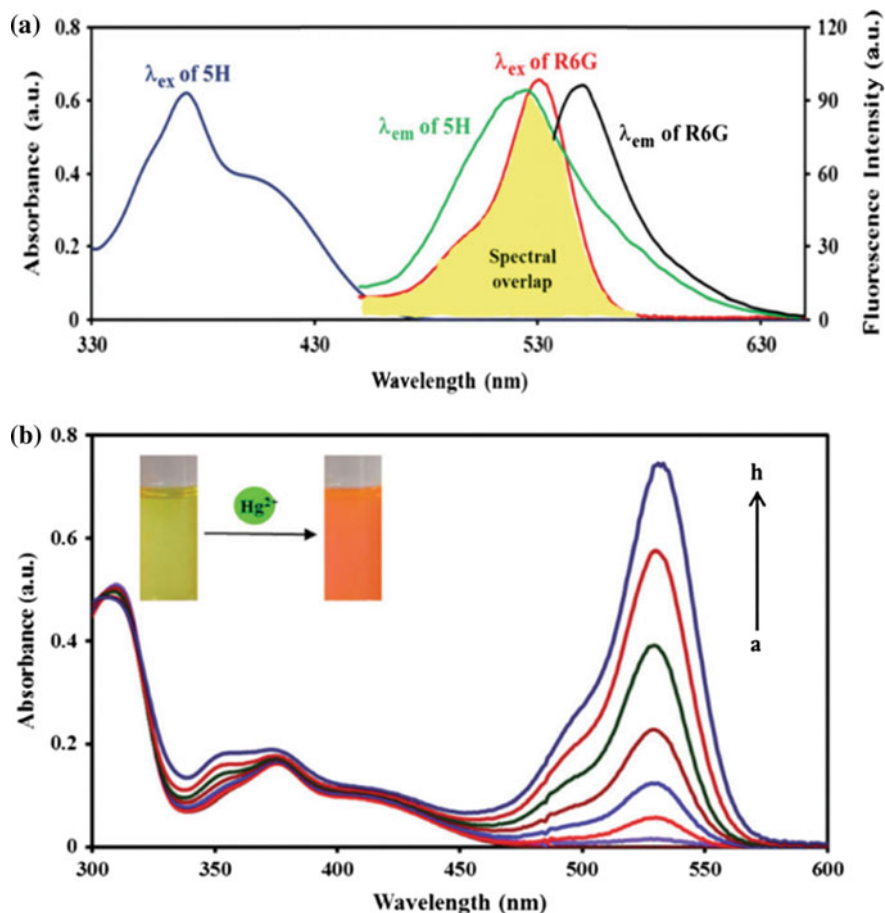


Fig. 4 **a** Overlap of emission and absorption of rhodamine 6G (R6G) and Helicene(5H). **b** Effect on UV/Vis spectra of sensor as function of Hg(II) concentration (a) 0 mM, (b) 10.0 mM, (c) 16.7 mM, (d) 23.3 mM, (e) 36.7 mM, (f) 50.0 mM, (g) 63.3 mM, (h) 83.3 mM (adapted from Ref. [4])

colourless is observed upon the addition of Fe(III) and their absorption spectra is also studied using UV/Vis spectroscopy for the different concentrations of the Fe(III) [5].

2.2.3 Aggregation Based Approaches

In colorimetric sensing, in most of the cases these approaches are utilized by the metal NPs such gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), and others like platinum nanoparticles (PtNPs) or their complex as they are having the characteristic property of localized surface plasmon resonance (LSPR). This

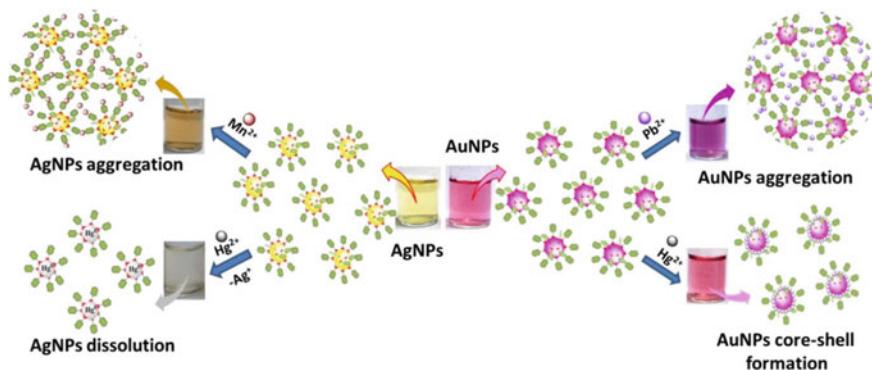


Fig. 5 Effect of aggregation on the color on nanoparticles (adapted from Ref. [6])

property exhibits its effect, when the frequency of conducting electrons matches with the incident electromagnetic radiations. LSPR effect is dependent upon the morphology i.e. shape, size, and interparticle distance, composition, and optical properties like refractive index of the nanoparticles. For example, when there is a decrease in interparticle distance, strong overlap between plasmon fields occurs which causes the red shift in LSPR and can result in change in intensity and observable color change that can be noticed by naked eyes. The aggregation-based approaches are usually simple in design in comparative to other mention approaches. In case of quantum dots, these approaches, when results in the increase of emission intensity then refer as aggregation induced emission and decrease in intensity refer as aggregation induced quenching.

Considering these approaches, Rajendiran and his co-workers synthesized the AuNPs and AgNPs stabilised by L-tyrosine for the detection of Pb(II), Hg(II) and Mn(II). When Hg(II) is added to the solution of as synthesized AgNPs, then color changes from yellow to colorless and changes to brown in case of Mn(II). Similarly, the color change is observed in case of AuNPs due to aggregation upon the addition of Pb(II) and Hg(II) as shown in Fig. 5. There is no color change is observed when other ions apart from these are added to the solution [6].

3 Advances in Materials Used as Colorimetric Sensors

In the recent years, various chromogenic materials have been reconnoitred for the colorimetric based quantification of heavy metal ions, especially in water matrix. Here, in this section, we have categorized the materials into three kinds based upon the molecular assembly and properties, i.e., organically tailored linkers, nanomaterials/quantum dots, and other polymeric, MOF etc. materials as tabularized in Table 1.

Table 1 Recent materials for colorimetric sensing of inorganic water pollutions

Material	Heavy metals	Analytical details	Water matrix
<i>Organic tailored linkers</i>			
P(DHB-a-DHBDT) grafted with PST probes [1]	Hg(II)	LOD: 10.6 ppb	River water; Distilled water
sulfo-rhodamine 101 with cuprizone [19]	Cu(II)	LOD: 0.1 ppb	Groundwater; Distilled water
HCFI [20]	Cu(II)	LOD: 1 ppm; LR: 0.1–10 ppm	Waste water
Heptamethine cyanine dye [9]	Ag(I)	LOD: 3 ppb	Lake water; Tap water; River water
MPA derivatized RS [8]	Hg(II)	LOD: 0.29 ppb	Waste water; Tap water; Drinking water
Nitro-functionalized Co(II) based MOF [11]	Hg(II), MnO_4^-	LOD: 800 ppb for Hg(II)	Distilled water
PyDPP [21]	Hg(II), Cu(II)	LOD: 5 ppb	Distilled water
Tpy-QL; Tpy-BZ [7]	Fe(II), Fe(III), Co(II) and Hg(II)	LOD: Hg(II), Co(II), Fe(II), and Fe(III) are calculated to be 6.51, 0.34, 0.49, and 1.01 ppb; Naked eye limit: 10, 25, 10, and 200 ppb for Fe(II), Fe(III), Co(II), and Hg(II)	Tap water; River water; Ground water
<i>Nanomaterials based platforms</i>			
HS-CH ₂ -6-GGGTGGGTGGGTGG aptamer modified oligonucleotide [22]	Pb(II); Hg(II)	LOD: 100 ppb for Pb(II); 500 ppb for Hg(II)	Lake water; Distilled water
BSA-AuNCs and L-Cys-AuNCs [17]	Hg(II)	LOD: 1.8 ppb	Distilled water
PEG functionalized AgNPs [15]	As(III)	LOD: 1 ppb	Distilled water
Glucose capped CuNPs [16]	Ag(I)	LOD: 10 ppm; LR: 10–60 ppm	River water
amino-carbon dots and AuNCs [23]	Cu(II); Pb(II)	LOD: 100 ppb for Pb(II); 9.5 ppb for Cu(II)	Distilled water
Nitrogen-doped graphene QDs [13]	Fe(III)	LOD = 132 ppb; LR = 88–132 ppm	Distilled water
captropril modified HgS/ZnS core/shell QDs [14]	Cr(III)	LOD: 51 ppb	Distilled water

(continued)

Table 1 (continued)

Material	Heavy metals	Analytical details	Water matrix
<i>Other chromogenic materials</i>			
ZIF-8/GO [24]	Ag(I)	LOD = 153 ppt	River water; Human serum
PAN fibre [25]	Hg(II), Cu (II)	Screening only	Distilled water
Curcumin based NFs [26]	Pb(II)	LOD: 207 ppm	Distilled water
PAR onto PAN fibre [27]	Hg(II)	LOD = 35 ppb	Distilled water

BSA bovine serum albumin, *Cys* cysteine, *GO* graphene oxide, *HCFI* 3-(5-hydroxy-4-carboxyphenylimino)-5-fluoro indol-2(H)one reagent, *LOD* limit of detection *LR* linear range, *MOF* metal-organic framework, *MPA* mercapto-propanoic acid, *NC* nanocluster, *NF* nanofiber, *NP* nanoparticle, *PAR* 4-(2-pyridylazo)-resorcinol, *PAN* polyacrylonitrile, *PEG* polyethylene glycol, *P(DHB-a-DHBDT)* poly(2, 3-dihydroxybutylene-alt-2,3-dihydroxybutylenedithioether), *PST* 2-(5-bromopyridine-2-yl)-3',6'-bis(diethylamino)-spiro[isoin-doline-1,9'-xanthene]-3-thione, *PyDPP* 2-(2-(2-methoxyethoxy)-ethyl)-3,6-di(pyridin-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione, *QD* quantum dots, *RS* rhodamine hydrazide, *Tpy-BZ* terpyridine benzo thiazolium iodide, *Tpy-QL* terpyridine quinolinium iodide, *ZIF* zeolite imidazolate frameworks

3.1 Organic Linkers

Organic Linkers refers to category of complexes which are organic ligands, for example, polyacrylonitrile (PAN) or coordinated to organic ligands like metal organic frameworks (MOFs). These organic ligands are defined as molecules that can bind to, and form a stable complex with, trace metals in the aquatic dissolved (typically <0.2 μm) phase. They have always been an attractive complexing agent in trace metals detection by virtue of the selective chelating ability of their heteroatoms such as oxygen, sulphur, nitrogen, etc. In general, the formed selective complex is either a chelate or a ring. They often used in conjugation with metallic nanoparticles and quantum dots. Further, previously discussed sensing mechanisms can be employed for the detection of desired analytes. Here, recently discovered or utilized organic linkers in the area of colorimetric sensing of inorganic water pollutants are discussed.

Recently Tian et al. recognises the potential of small organic molecules in field of colorimetric detection of multiple inorganic metals ions and utilized them for the detection of Hg(II), Co(II), Fe(II), and Fe(III) well below the prescribed WHO limits [7]. To achieve this, Terpyridine (Tpy), a heterocyclic compound having three nitrogen elements results in strong chelating effects and ability to shows color changes and change in absorption spectra on interacting with metal ions. To improve the hydrophobicity of Tpy molecule quinolinium iodide (QL) and

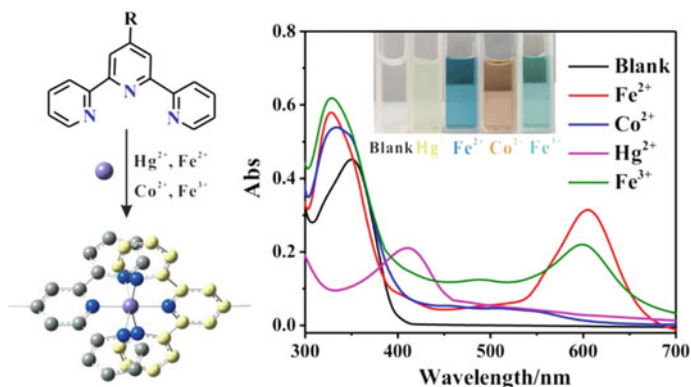


Fig. 6 Schematics of complex formed after interaction with metal ions and their effect on absorption spectra (inset: change in color w.r.t. metal ions) (adapted from Ref. [7])

benzothiazolium iodide (BZ) is introduced. The color changes from colourless to pale yellow in case of Hg(II), pink with Co(II), dark blue for Fe(III), and light blue for Fe(II), which can be observed by the naked eyes. Further, the change in absorption spectra is also studied as shown in Fig. 6 [7].

Likewise, organic dye is another class of organic molecule, which are emerging these days as new fluorophore because of their interesting properties i.e. absorption of visible light, presence of chromophore, resonating electrons, and conjugated system. These properties makes them a good candidate in the field of colorimetric sensing. Of them rhodamine 6G, is one of the most popular dye used while designing the colorimetric sensor. Recently it has been used for the detection of Hg(II) ions after its modification with mercaptopropionic acid (MPA) which provides thio functionality to the sensor so as to increase its sensitivity towards Hg(II). In the presence of Hg(II), color of sensor changes to pink from colourless [8]. Some examples of rhodamine 6G dye also discussed in Sect. 2. Apart from this, other dyes like heptamethine cyanine-based dye is used for the detection of the Ag(I) ions, where it changes its color to red from blue, which can easily notice by the naked eyes. Further, gradual change in UV/Spectra is observed upon increasing the concentration of Ag(I) ions [9]. Further boron-based dyes like boron-dipyrromethene are also gaining potential in this field. This particular dye is having thia-aza crown ether as metal ion receptor and is used for the uv-based colorimetric detection of Hg(II) ions, here color changes from colourless to green under the UV light [10].

Metal organic frameworks (MOFs) are another promising candidate used for the colorimetric detection. MOFs consists of coordination bonds between organic linkers and transition metal cations, offers many active sites for the detection of inorganic ions and have high surface area attributed to their high porosity. MOFs are having void spaces in between, which are utilized to capture the desired analyte and hence can have high selectivity. Recently, Sun et al. synthesized a nitro

functionalised Co(II) based MOF for the detection of Hg(II) and $\text{MnO}_4(-\text{I})$ ions. The MOFs contains a nitro-functionalised ligand (NPDC) which is synthesized by solvothermal method. The 3D structure of MOF consists of bipyridine linkers and NPDC ligand coordinated to Co(II). Upon the addition of ions to the MOF containing solution, change in intensity of color can easily be observed by naked eyes [11].

3.2 *Nanomaterials Based Platforms*

Nanomaterials such as quantum dots, and metallic nanoparticles offers large surface area and simplicity in sensor design which makes them suitable for the sensing applications. Quantum dots (QDs) are the zero-dimensional semiconductor nanocrystals with the size usually less than 12 nm. Due to this, they have substantial advantages in the field of sensing process as an outcome of their exceptional optical and electronic properties. These properties include high fluorescence quantum yield, broad absorption spectra, tuneable composition, high photostability, etc. Also, QDs can overcome issues including pH dependence, self-quenching at high concentrations, and photobleaching with the traditional fluorescent probes [12]. Upon realizing these advantages, Zhou et al., synthesized nitrogen doped graphene quantum dots for the colorimetric sensing of Fe(III). Here, these QDs prepared by hydrothermal treatment and ethylenediamine (EDA) is used as nitrogen source change in intensity of blue color w.r.t. change in concentration Fe(III) ions is observed by naked eyes under the UV light [13]. Further, Wang et al. developed a HgS/ZnS core/shell quantum dots for the visual sensing of Cr(III) ions [14].

Metallic nanoparticles are like gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), and copper nanoparticles (CuNPs) are another promising candidates which are used to described nanosized metals with dimensions (length, width or thickness) within the size range 1–100 nm. The main characteristics of these particles are large surface-area-to-volume ratio as compared to the bulk equivalents, large surface energies the transition between molecular and metallic states providing specific electronic structure (local density of states LDOS), plasmon excitation, quantum confinement, short-range ordering, increased number of kinks, a large number of low-coordination sites such as corners and edges, having a large number of "dangling bonds" and consequently specific and chemical properties and the ability to store excess electrons. Using these benefits, Biswas et al. reported the use of polyethylene glycol (PEG) functionalised AgNPs for the colorimetric detection of arsenic with the detection limit of 1 ppb [15]. PEG is a biocompatible polymer contains various hydroxyl groups which acts as the binding sites for the As (III) and AgNPs are having its characteristic property of Localized surface plasmon resonance which depends upon the dielectric constant of the surrounding environment. Here, red shift in localized surface plasmon resonance and color change from pale yellow to bluish color is observed upon the addition of arsenic(III). Further schematic representation of sensing of As(III) is shown in Fig. 7 [15].

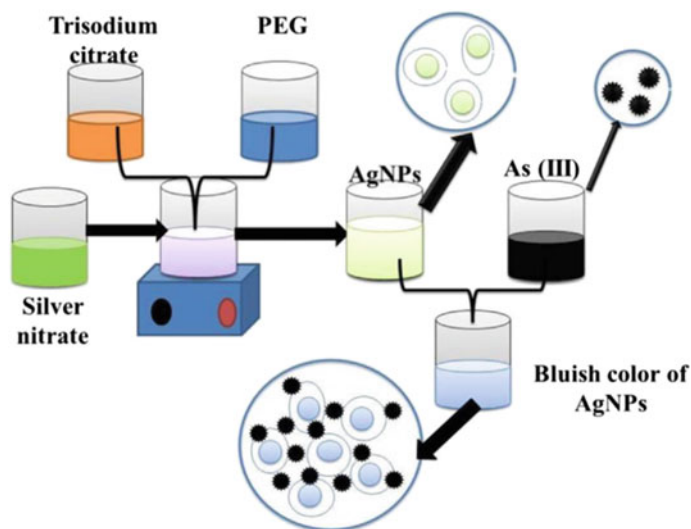


Fig. 7 Schematics of formation of AgNPs for the colorimetric detection of As(III) (adapted from Ref. [15])

Similarly, the use of glucose modified copper nanoparticles (Glc-CuNPs) having high fluorescence is reported for the visual detection of Ag(I). Upon the addition of Ag(I) ions to the sensor assay, aggregation of Glc-CuNPs occurs, which results decay of fluorescence and gradual change in intensity of color on increasing the concentration of Ag(I) is observed [16].

Further, Zhao et al. reported a ratiometric probe having blue colored L-cysteine-Au NCs as internal standard probe and red colored bovine serum albumin-Au nanocluster as detection probes for the sensing of Hg(II) ions. In presence of Hg(II) ions detection probe shows the fluorescence quenching but no effect on the fluorescent signals of internal standard probe i.e. AuNCs. This causes color variations from red to blue, and thereby enabling the visual detection of Hg(II) ions by naked eyes as shown in Fig. 8 [17].

3.3 Other Chromogenic Materials

Apart from organic linkers, metal nanoparticles, quantum dots, there are other materials deliberated here. Li F. et al. reported a two-fold metal-organic framework (MOF), [Co (NPDC) (bpee)]·DMF·2H₂O (1) (NPDC = 2-nitro phenylenedicarboxylate, bpee = 1,2-bis(4-bipyridyl) ethylene) nitro functionalized ligand (NPDC) and bipyridine type linkers (bpee) coordinated to Co(II). The complex consists of a 3D structure which exhibits high selectivity for the sensing of MnO₄⁻ and heavy metal ion Hg²⁺ in water by quenching or enhancing luminous intensity [11]. Similarly, Deng et al. reported a

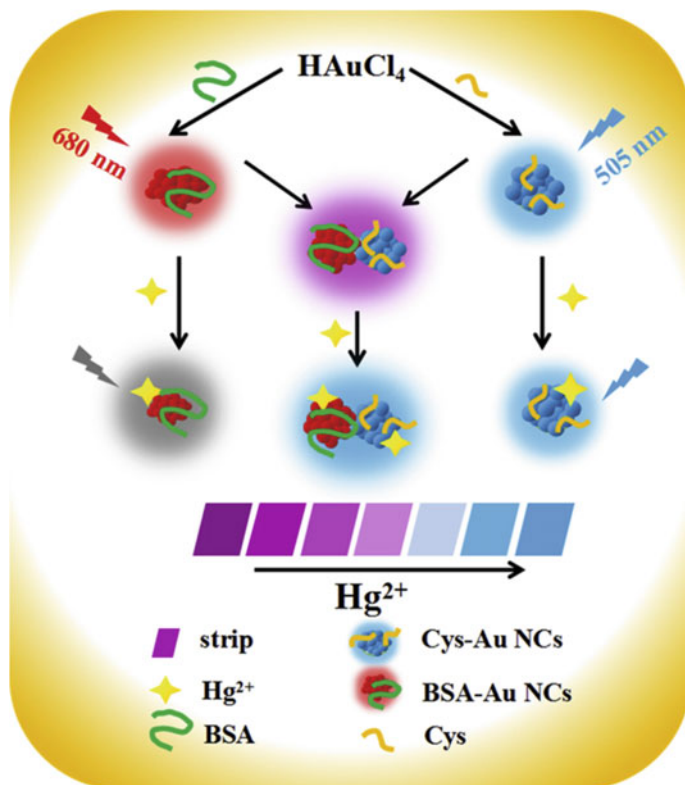


Fig. 8 Schematic for determination of Hg(II) ions (adapted from Ref. [17])

dual functionalized material by incorporating a chromophore, 4-(2-pyridylazo)-resorcinol (PAR), onto polyacrylonitrile (PAN) fiber for the detection and removal ability for heavy metal ions, including Hg²⁺, Cu²⁺, Pb²⁺ and Ni²⁺ [18].

4 Perspectives and Strategies in Colorimetric Sensor Development “Lab-to-Market”

4.1 Colorimetric Sensors on Solid Supports

The effectiveness of any colorimetric sensor is inclined not only by the choice of materials (e.g., chemo responsive dyes, organic ligands, metal nanoparticles quantum dots,) but also by the selection of substrate type and materials (e.g., geometry of flow path and immobilization technique) [28]. The vital characteristics of substrates include optical transparency (owing to high reflectivity), regular

structure, stability, and chemical compatibility. Mostly, opted substrates are based upon cellulose derivatives like cellulose paper, chromatography paper, printer paper, etc., polymeric membranes like polyvinylidene difluoride (PVDF), polypropylene (PP), and polyethylene terephthalate (PET). Like as, Zhou et al. reported a quenching paper based sensor using Fluorescent Nitrogen-Doped Graphene Quantum Dots for the detection of Fe(III) and fabricated a paper strip using inkjet printing technology by HP inkjet printer 2050 onto bond paper. The printed patterns were observed and photographed under 365 nm ultraviolet lamp, and the fluorescence intensity of the paper was scanned by fluorescence spectrometer [29].

4.2 Read-Out Signalling Approaches

The advancements in colorimetric sensing with the aid of ubiquitous consumer electronic products (like scanners, computers, mobile phones, etc.) as read-outs is a moderately new research arena. On the basis of reviewed literature, we have further analysed these consumer electronic products as read-out signalling approaches on the basis of commercial parameters such as market growth and user-friendliness as shown in Fig. 9.

Smartphones/mobiles (such as Apple, Samsung, OnePlus, and Nokia) have distinguished features of onboard processing potential similar to the hand-held reader. Furthermore, their worthy assets namely portability, user friendliness, and onboard image processing capability makes them a suitable candidate in this field. Like as, camera are also equipped with higher bandwidth data transfer methods to acquire images in a fraction of seconds. However, images acquired by the digital camera/camera can be affected by the improper focusing, alignment, lighting conditions, and many other factors. Furthermore, the high cost of digital cameras

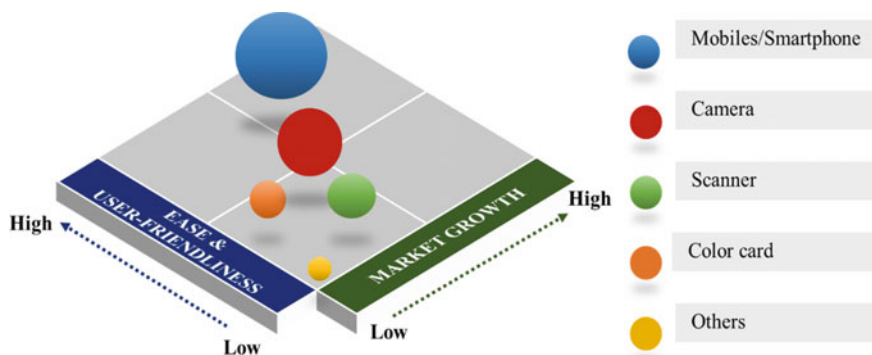


Fig. 9 Consumer electronic products as read-out signalling approaches: market potential and user-friendliness

and associated accessories for image capturing is a fall back for their frequent use in colorimetric sensors. Scanners has some benefits over digital cameras and smart-phones i.e. problems like focusing, blurry corners, movement, alignment, lighting, etc. which will affect the image quality and can cause variations in sensor data does not comes into existence while using scanners. But they suffer due to certain demerits like as lack of instant scanning of image, portability and extended scanning time for the acquisition of high-resolution image. Additionally, colour card are the physical colour reference for comparisons and measurements in colorimetric sensors. These are widely used in textile industry, food industry, photography etc. Although this approach is easy to implement and requires negligible instrumentation for the analysis but this method is largely affected by the intensity of light and error while color interpretation. Other devices like membrane strip reader which are type of microplate reader, fiber optic devices, etc. are also investigated in colorimetric imaging, but these devices suffer from user friendliness and portability, as they are not popular in comparison to the other available devices.

5 Case Study: Commercial Accomplishments of Existing Colorimetric Sensor Platforms for Water Pollutants

Knowingly, water pollution has turn out to be one of the utmost tenacious ecological glitch in the world today. Although a limited effort to commercialize the technology of colorimetric sensory platforms for the real-world water pollutant monitoring application have been known and now exists in global market. Some companies like *Thermo Fisher Scientific*, *Merck*, *Sigma-Aldrich*, *Hanna Instruments*, *Elabscience*, *Libelium*, *Cole Parmer*, *CHEMetrics*, *Appealing Products, Inc.*, *MicroWaterman*, *Appealing Products, Inc.*, *Industrial Test Systems*, *Vitality Plus Australia, Inc.*, *Industrial water systems*, have also fruitfully commercialized their kits for online water quality monitoring as portrayed in Fig. 10. In this section, case study on recent progress in existing colorimetric sensor platforms is described with an emphasis on the various water pollutants i.e. chemical, microbiological, and other ecological contaminants. Furthermore, we highlight the available commercial kits and deliberate their market-potential to water research. *Thermo Fisher Scientific* launched *Orion™ AQUAfast AQ4000* Colorimeter to measure water and wastewater pollutants with 65 pre-programmed methods, automatic selection of four wavelengths and timer [30]. The water quality parameters measured include dissolved ions like as cyanide, fluoride, nitrite, nitrate, chloride, iodide, bromide, sulphide, ammonia, zinc, phosphate and sulphate. The company provides auto-test ampoules reagent with *Orion™ AQUAfast AQ4000* colorimeter to abridge sample preparation and tests. The auto-test ampoules enclose a pre-measured quantity of liquid colorimetric reagent and effortlessly fill with the precise volume of sample to be tested for reagent mixing. Respectively, every

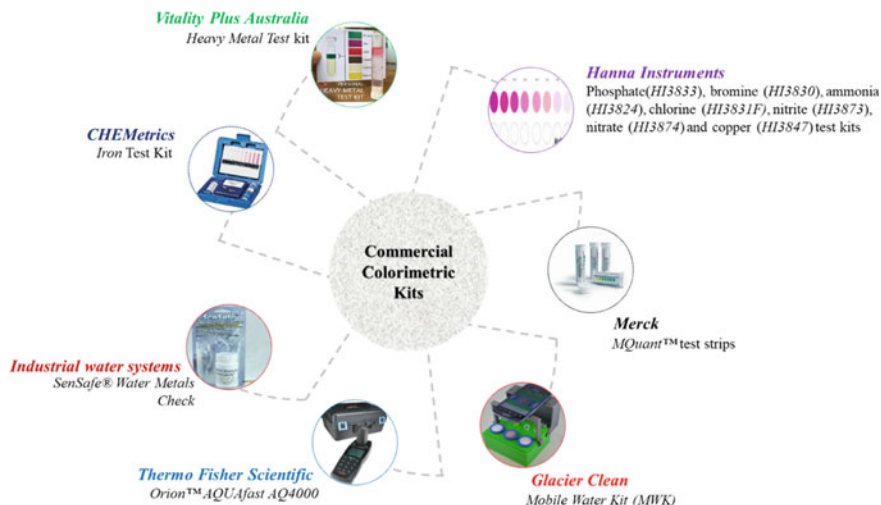


Fig. 10 Commercial colorimetric sensory platforms for the real-world water pollutant monitoring applications

ampoule contains an auto-ID barcode that is read by the *AQ4000* colorimeter and used to spontaneously recognize the test water pollutant parameter [30].

In addition, *Glacier Clean* launched *Mobile Water Kit (MWK)* to measure contamination of water resources with *Escherichia coli (E. coli)* bacteria [31]. It contains a plunger-tube assembly with an in-built filter. The plunger-tube assembly comprises of a hydrogel encapsulating the explicitly developed colorimetric substrates selective towards *E. coli* and can facilitate the colorimetric detection of bacteria and identification of their concentration. The presence of *E. coli* will craft a colour change on the substrate. Besides, the kit is handy and can be used at the point of source itself thereby eradicating the need for transport of the water samples. This test kit also allow the user to map the location data with the help of a custom built smart phone application (*m-Water*), which is then automatically uploaded to a central server [31].

Similarly, *MQuant™* test strips, from *Merck*, are pocket-sized laboratories for quick analysis and give the user a quick summary of substance concentrations present in the sample. By providing a means of pre-selection, they can contribute significantly to the lowering of the time and costs for laboratory analyses. The reaction zones are wetted by simple dipping into the solution being tested. After the given reaction time has elapsed (e.g., a maximum of two minutes), the colouring of the reaction zone is compared with the colour scale on the package to determine the concentration [32]. There is *MQuant® StripScan* app, by *Sigma-Aldrich*, to determine pH or concentrations of chemicals in aqueous solutions. This easy-to-use mobile analytical detection platform provides reliable quantification of water, food & beverage samples for customers from research, industry, environment and diagnostics. The *MQuant®* test strips are employed with contain all necessary

reagents, including those required for sample pre-treatment [33]. Additionally, *Merck's* colorimetric and titrimetric test kits are especially suited for the analysis of drinking water, ground water, clean water and mineral water as well as in water production. Each test kit pack contains all reagents necessary for the test with high-quality and brilliant colour cards decisively simplify the allocation of the samples to the stated values. In the titration tests the sample is titrated until the colour changes. The concentration of the tested parameter is determined by the number of drops consumed to the turning point or the scalar value read off from a pipette. For performing the colorimetric tests a colour reaction is produced by adding reagents to the sample solution. The special feature of these test kits range lies in the measurement of low concentrations down to the ppb range [34].

Likewise, *Hanna Instruments* launched colorimetric chemical (CC) test kits namely, phosphate test kit (*HI3833*), bromine test kit (*HI3830*), ammonia test kit (*HI3824*), chlorine test kit (*HI3831F*), nitrite test kit (*HI3873*), nitrate test kit (*HI3874*) and copper test kit (*HI3847*) [35]. The *HI3833* is a CC test kit that uses the ascorbic acid method to measure phosphate in water. The colour change determines the presence of phosphate. The *HI3830* is a CC test kit that determines the bromine concentration in samples within a 0 to 3 ppm bromine range. The *HI3830* is supplied with all of the necessary reagents and equipment to perform the analysis. The *HI3824* is a CC test kit that uses Nessler reagent to measure ammonia in fresh water within a 0.0 to 2.5 ppm range. The *HI3831F* determines the free chlorine concentration within a 0.0 to 2.5 ppm range by employing the DPD method. The *HI3873* uses the chromotropic acid method to measure nitrite within a 0.0 to 1.0 ppm range. The *HI3874* uses the cadmium reduction method to measure nitrate within a 0 to 50 ppm range. The *HI3847* uses the bichinchoninate method to measure copper within a 0–2.5 ppm range [35].

Similarly, *Elabscience* launched *Urea Colorimetric Assay Kit* to measure the concentration of main water-pollutant, urea, in water resources, serum, plasma and urine [36]. This kit uses the strong diacetyl oxime-urea chemistry. In the presence of urea, diacetyl oxime form red diazine compound. The gradient of red diazine colour is relational to the concentration of urea [36].

Also, *Heavy Metal Test kit*, from *Vitality Plus Australia*, is a home testing kit for checking heavy metals in both urine, saliva, and liquids. Easy to use it will detect the presence of ionic metals in the liquid solutions tested. This is an economical way to see what under the naked eye cannot see from water (bore water, tap water, and tank water), urine, and saliva. The testing kit can also be used to detect the presence of heavy metals (mercury, lead, cadmium, chromium and thallium) in other complicated media like paint, foods, makeup, skin care, etc. [37].

Likewise, *Libelium*, a reputed company of Spain, launched *Waspote Smart Water*, a smart water wireless sensor platform to abridge remote water quality monitoring [38]. Furnished with multiple sensors that measure the most relevant water quality parameters, *Waspote Smart Water* is the water quality-sensing platform to feature autonomous nodes that connect to the cloud for real-time water control. This platform is an ultra-low-power water-pollutant sensor designed for use in rugged environments to detect changes and potential risk to public health in real

time. It is suitable for potable water monitoring, chemical leakage detection in rivers, remote measurement of swimming pools and spas, and levels of seawater pollution. The water quality parameters measured include pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), conductivity (salinity), turbidity, temperature and dissolved ions (fluoride, calcium, nitrate, chloride, iodide, cupric, bromide, silver, fluoroborate, ammonia, lithium, magnesium, nitrite, perchlorate, potassium and sodium [38].

Likewise, *SenSafe*[®] *Water Metals Check*, from *Industrial water systems*, determines the presence of heavy metals (cadmium, cobalt, copper, iron, lead, mercury, nickel and zinc) present in water. This quick test uses a very sensitive non-specific indicator that detects many common heavy metals with detection limits to <10 ppb. This test is a screening tool and does not specify levels of each metal present [39].

Additionally, *Cole Parmer* launched *NECi Colorimetric Nitrate Water Test Kit*, for nitrate testing without the use of cadmium, a toxic heavy metal and known carcinogen. This kit uses the naturally occurring enzyme called nitrate reductase which safely measures nitrate within 0.5–10.0 ppm range by giving a colorimetric change in water samples [40].

Likewise, *TotalCARE Heavy Metal Screen Test*, from *MicroWaterman*, is a semi-quantitative, rapid, and user friendly test kit for the analysis of free zinc, copper, lead, mercury, cadmium, nickel, cobalt and manganese ions in the urine, saliva, water, etc. Any color change deviating from green to purple, pink, beige, red determines high heavy metal concentration (3–5 ppm) viewed directly below the surface level of the test tube represents the presence of heavy metal ions [41].

Furthermore, *CHEMetrics* launched *Iron Test Kit*, to measure the concentration of iron in water samples by using phenanthroline-colorimetric method. This kit uses 1,10-phenanthroline which securely measures iron within 1–10.0 ppm range by giving a colorimetric change in water samples. In the presence of iron, the reagent 1,10-phenanthroline forms an orange-coloured chelate [42].

An another kit namely, *Generic Heavy Metal Detector*, (GHM-01), from *Appealing Products, Inc.*, is developed to easily and rapidly detect common heavy metals (lead, thallium, mercury, cadmium, iron, nickel and zinc) in water and urine samples. The test kit consists of detection tube, testing paper and colour charts. A reference color chart is provided for interpreting the test results. The operating procedural steps include to simply add the detection tube to the vial, then add sample, shake for 30–40 s and allow the liquid to separate. Once the liquid gets separated into two phases, observe at the color formed on the top phase and compare it to the reference color chart [43].

The *eXact iDip*[®] *Smart Photometer System*[®], from *Industrial Test Systems, Inc.*, is the first patented and handheld photometer to provide 2-way communication with a Bluetooth[®] Smart (4.0) ready Apple or Android smartphone/tablet for the detection of cadmium, cobalt, copper, iron, lead, mercury, nickel, and zinc in water. The *eXact iDip*[®] photometer is waterproof (IP67) and has a permanent built-in

sample cell. This eliminates the separate cell and simplifies the test procedure, which improves accuracy. The multilingual *eXact iDip® app* system also allows for instantaneous software updates/upgrades, test customization, and mobile sharing of results with spreadsheet [44].

6 Summary

In summary, this chapter focussed on the potential use of colorimetric sensors for the water-pollutant sensing and discusses the promising prospects of sensor developments (from choice of material to read-out tools) to assist nascent researchers to review the principles, mechanistic and advancements in existing trends in colorimetric sensory probes. In this direction, smartphone-based colorimetric sensor platforms aim to empower easier and more resourceful water-pollutant testing in resource-limited locales, which accords with the important goal of field-deployable sensory systems. The adept features of smartphones namely, concept of miniaturization, ease-of-operation and portability recommend great prospective for their operative integration with sensory probes in the direction of facilitating a wide range of new mobile-based pollutant sensing applications.

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