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Heavy Metals (As, Cd & Pb) Toxicity & Detection of These Metals in Ground Water Sample: A Review on Different Techniques

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Abstract: *The main threats to living world are associated with the exposure to heavy metals like cadmium (Cd), lead (Pb), arsenic (As), zinc (Zn), manganese (Mn), copper (Cu), nickel (Ni), chromium (Cr) and mercury (Hg). Even though adverse effect due to heavy metals is known, still exposure continues the same in most of the developed and developing countries. Cadmium (Cd) found in low concentration in rocks, coal and petroleum, enters the groundwater and surface water through industrial discharge, metal painting and causes high blood pressure, liver and kidney damage and anaemia. Lead (Pb) enters environment from industry, mining and affects red blood cell chemistry, delays normal physical and mental development in babies and young children, increase in blood pressure in some adults. Exposure to the arsenic (As) is mainly through food and drinking water and causes the high risk of cancer of lung, skin, bladder and kidney, skin lesions such as hyperkeratosis and pigmentation changes. Therefore, this research review the general description of the occurrence of cadmium (Cd), lead(Pb) and arsenic (As) in environment, their toxicity and measure techniques for speciation analysis. The commercial Kit method, differential pulse anodic stripping voltammetry (DPASV), atomic absorption spectrometry (AAS) and X-ray fluorescence spectrometry are the most powerful methods for cadmium (Cd), lead (Pb) and arsenic (As) speciation in environmental and biological matrices. These methods provide strong reliability on understanding of cadmium (Cd), lead (Pb) and arsenic (As) metabolism and biological cycling.*

Keyword: *arsenic (As), cadmium (Cd), heavy metals, lead (Pb), metal toxicity.*

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1. Introduction

Heavy metals form a very heterogeneous group of elements widely varied in their properties and biological functions. Heavy metals are environmental pollutant due to their toxic effects on plants, animals and human being. Groundwater contamination with heavy metals is one of the most important environmental issues. They are toxic even at low concentrations [1-2]. Anthropogenic activities such as mining, smelting operation and agriculture have increased the levels of heavy metals such as cadmium (Cd), lead (Pb) and arsenic (As) in ground water up to dangerous levels. The largest availability of cadmium (Cd), lead (Pb) and arsenic (As) is in ground water and relatively smaller proportion in atmosphere as particulate or vapours. When several heavy metals are taken in excess, they become toxic as they exhibit adverse effect on human health. Heavy metal toxicity in animals varies with animal species, specific metal, concentration, chemical form and ground water composition, duration of exposure. Some of heavy metal such as cadmium (Cd), lead (Pb), arsenic (As) and mercury (Hg) are strongly poisonous to metal sensitive enzymes, resulting in growth inhibition and death of organisms. The heavy metals such as lead (Pb), mercury (Hg) and nickel (Ni) are non-essential trace elements. These are highly toxic elements as they are persistent, bio accumulative and do not readily breakdown in the environment or not easily metabolized. These metals accumulate in ecological food chain through uptake at primary producer level and then through consumption at consumer levels. Heavy metals may enter the human body via food, water, air and absorption through the skin in the developed agriculture, industrial and residential settings [3]. Heavy metals such as cadmium (Cd), lead (Pb), arsenic (As) poses a number of hazards to humans. Heavy metals are also potent carcinogens. Arsenic (As) causes poisoning due to drinking water contamination. Vapor form heavy metals such as Cd), lead (Pb), arsenic (As) combine with water in the atmosphere to form aerosols and cause health problems. Health risks of heavy metals are reduced growth and development, cancer, organ damage, nervous system damage and in extreme cases, death. Exposure to some heavy metals, such as mercury (Hg) and lead (Pb), may induce development of autoimmunity, in which a person's immune system attacks its own cells. There are several studies on the occurrence and monitoring of heavy metals in ground water and drinking water. The study on groundwater contamination with heavy metals lead (Pb), cadmium (Cd) and Aluminum (Al) in Nigeria exhibits that there is a significant risk for the population from drinking groundwater as these metals are detected in 98% of water samples analyzed in that study [4]. Studies on the heavy metal pollution of groundwater in India exhibits presence of heavy metals in samples [5,6]. The study on the assessment of heavy metals pollution in surface water in Ganga in West Bengal exhibits that the sequence of dominance of various heavy metals in the surface water of the river Ganga is Fe > Mn > Ni > Cr > Pb > Zn > Cu > Cd [7]. Heavy metal toxicity in plants depend on various factors such as plant species, specific metal, concentration, chemical form, soil composition and pH. The heavy metal such as Cd, Hg and As are highly poisonous to metal sensitive enzymes, resulting in growth inhibition and death of organisms. Heavy metals are also potent carcinogens. Mercury (Hg) causes minamata disease and arsenic (As) causes poisoning due to drinking water contamination. Several studies have reported concurrent administration of Pb, Cd, and As in male rats reduced weight gain as a consequence of decreased food utilization [8,9]. The increase in the weight of liver and kidney, the organs predominantly associated with biotransformation of xenobiotics, in exposed animals may be indicative of body's adaptive mechanism to combat systemic toxicity [10,11]. Both liver and kidney are the primary target organs, posing a risk of hepatic and nephrotic damage to a chronic exposure of mixture of heavy metals through drinking water. Mixture of lead (Pb), cadmium (Cd) and arsenic (As) induces anaemia type condition with decrease in RBC count and haemoglobin concentration [12, 13]. Study on oestrous cycle revealed that sub chronic treatment with the mixture of heavy metals cadmium (Cd), lead (Pb) and arsenic (As) causes irregularities in the reproductive cycle [14,15,16]. The study on implantation showed a significant pre implantation and post implantation loss in mixture of heavy metals cadmium (Cd), lead (Pb) and arsenic (As) treated animals with decrease in the number of live foetus [17]. This review attempts to guide crucial sources of information on toxicity of heavy metals, cadmium (Cd), lead (Pb) and arsenic (As) and most advance techniques for detection of theses heavy metals in the groundwater.

2. Heavy Metal

There is no widely agreed definition of a heavy metal. Different meanings may be connected to the term, depending on the context. In metallurgy, for example, a heavy metal may be defined on the basis of density whereas in physics the distinguishing criterion might be atomic number and in chemistry the distinguishing criterion might be chemical behaviour .Density criteria range from above 3.5 $g/cm^3$to above 7 g/cm^3. Atomic weight definitions can range from greater than sodium (atomic weight 22.98) [18]; (greater than 40 (excluding s- and f-block metals, hence starting with scandium) or more than 200, i.e. from mercury onwards.

3. Cadmium (Cd)

3.1.Description:- The name is derived from the Latin word "cadmia", the name for the mineral calmine. Cadmium (Cd) was discovered by Friedrich Stromeyer in 1817. It is a silvery metal with a bluish tinge upon it's surface. It is a transitional metal. The basic physical and chemical characteristics are given below:-

Table 1:-The basic physical and chemical characteristics of cadmium (Cd) [19].

Name	Cadmium
Symbol	Cd
Atomic number	48
Relative atomic mass (Ar)	112.44
Standard State	Solid
Colour	Silver bluish-grey
Classification	Semi-metallic
Group in periodic table	12
Period in periodic table	5
Block in periodic table	d-block
Electron shell structure	2,8,18,5
Electron configuration	$[Kr]4d^{10}5s^2$
Valence	2
Boiling point	767^0C
Melting point	321.069^0C at 28 atm
Vapour pressure	
Density/specific gravity	$8.75g/cm^3$

3.2. Sources of cadmium (Cd):- Cadmium (Cd) is released in the environment from different sources:

- Natural activities such as volcanic eruption, weathering and erosion and river transport.
- Human activities such as tobacco smoking, smelting and refining of nonferrous metals, mining, fossil fuel combustion, incineration of municipal waste, manufacture of phosphate fertilizers and recycling of cadmium-plated steel scrap and electric and electronic waste. Cigarette smoking is the most important source of human cadmium exposure.
- Remobilization of historic sources such as the contamination of watercourses by drainage water.
- Ingestion of contaminated food (e.g., crustaceans, organ meats, leafy vegetables, and rice), water (either from old Zn/Cd sealed water pipes or industrial pollution), drug and dietary supplements are sources of cadmium (Cd) [20].

3.3. Toxicity of cadmium (Cd):-

- Cadmium (Cd)-induced hepatotoxicity.
- Cadmium (Cd)-induced disturbance in calcium (Ca) metabolism [21].
- Cadmium (Cd)-induced cardio toxicity [22].
- Cadmium (Cd)-induced hematotoxicity [23].
- Cadmium (Cd)-induced immunotoxicity [24].
- Cadmium (Cd)-induced endocrine disruption [25] .
- Cadmium (Cd)-induced reproductive toxicity [26].
- Cadmium (Cd)-induced carcinogenicity [27].

4. Lead (Pb)

4.1.Description**:-** The word "Lead" (Pb) is of the Anglo-Saxon origin. It is a soft, malleable, ductile, bluish-white, dense, heavy post transitional – metal. Lead (Pb) exists as solid, liquid, gas and plasma. Lead (Pb) is a mixture of four stable isotopes, ^{208}Pb (51-53%), ^{206}Pb (23.5-27)%, ^{207}Pb (20.5-23)% and ^{204}Pb (1.35-1.5)%.The basic physical and chemical characteristics are given below:-

Table 2:- The basic physical and chemical characteristics of lead (Pb) [19].

Name	Lead
Symbol	Pb
Atomic number	82
Relative atomic mass (Ar)	207.2
Standard State	Solid
Colour	Bluish white -grey
Classification	Metallic
Group in periodic table	14 (IVA)
Period in periodic table	6
Block in periodic table	p-block
Electron shell structure	
Electron configuration	$[Xe]4f^{14}5d^{10}6s^{2}6p^{2}$
Valence	0,2,4
Boiling point	$1749^{0}C$
Melting point	$327.462^{0}C$
Vapour pressure	
Density/specific gravity	$11.3 g/cm^{3}$

4.2. Lead contamination in the world as well as in India:- According to the estimation of World Health Organisation (WHO) 120 million people are lead (Pb) poisoned i.e. have a blood lead level greater than 10 micrograms per decilitre (µg/dL) [28] around the world. Recent research indicates that the aim should be to get everyone below 5 µg/dl. In a survey in 1996, it was found that only the 7.3% Australian children of preschoolers became lead poisoned (and this is probably an underestimate). In a Chinese meta-analysis more than one third of the children in China were found to have blood lead levels greater than 10µg/dL. In an Indian survey of 2,031 children and adults in 5 cities, more than half of them had blood lead levels greater than 10 µg/dL [29]. In just one African city Johannesburg, which may be representative of all the cities in the 43 African countries still using leaded petrol – 78% of the children were lead (Pb) poisoned. According to the Henry Falk's Case Study of Lead Poisoning [30], the people living right next to backyard smelters, mines or shops where lead acid batteries are repaired, typically have a higher blood lead (Pb) level than 10µg/dL. The results of a study by Wang Sun-qin, Zhang Jin-liang in 2004 exhibited that blood lead (Pb) levels among Chinese children are very high and are considered to be one potential environmental risk factor for children's development [31]. According to WHO, in a survey of 'Quality Council of India,' over 26 cities in India 33% of over 370 samples were found to contain lead with 31% of them crossing above the maximum permissible limit of 10 ppb (parts per billion). Among of them 2% of the samples failed to meet even the lenient Indian norms of 50 ppb. Lead (Pb) is washed out as precipitate like rain, fog, snow and runoff. The lead (Pb) content in rain of three cities of Chattisgarh named Raipur, Bhilia and Korba were found to be 28-849 µg/l. Korba city was found to have the highest lead levels due to high amount of coal burnings. Similarly lead (Pb) content in runoff was found to be in the range of 131-3157µg/l (32).

Table 3:- Lead contamination in India {Source: LEAD Action News 10(1): 2010}

Lead (Pb) content in water: cities at risk			
Alarming	High	Medium	Low
Kolkata	Delhi	Chennai	Bangalore
Kochi	Coimbatore	Ludhiana	Ahmadabad
Mumbai	Madurai	Sutra	Hyderabad
	Bhubaneswar	Ghaziabad	Indoor
Pune		Jamshedpur	Bhopal
Nagpur			Chandigarh
Nasik			Luck now
Guwahati			Mangalore
			Mysore

4.3.Sources of lead (Pb):-

- Lead (Pb) is a naturally occurring heavy metal, found in air, water, foodstuff, soil and dust either from natural or anthropogenic sources. Lead can be found in batteries, petrol additives (no longer used in developed countries), rolled and extruded products, alloys and pigments. The most significant anthropogenic lead sources results basically from energy sector, production and processing of metals; mineral industry; chemical industry; waste and waste water management.
- Lead (Pb) -based paint is a common source of lead. Lead can contaminate household dust when lead-based paint is deteriorated or disturbed. Lead dust can collect in windowsills, troughs, floors, carpets, furniture, and ventilation filters. In oil painting yellow or white colour to be made with lead carbonate. Lead white oil colour was the main white of oil painters until superseded by compounds containing zinc or titanium in the mid-20th century.
- Occupational exposure is the main cause of lead poisoning. The workers can be exposed when working in facilitates that produce a variety of lead containing products such as battery recycling, ammunition, certain surgical equipment, developing dental x-ray films prior to digital x-rays (each film packet had a lead liner to prevent the radiation from going through), fetal monitors, plumbing, circuit boards, jet engines, and ceramic glazes, manufacture of rubber.
- Lead (Pb) may be found in food when food is grown in soil that is high in lead, airborne lead contaminates the crops, and animals eat lead in their diet.
- Residual lead in soil contributes to lead exposure in the urban areas. Lead content in soil may be arised by broken-down lead paint, residues from lead-containing gasoline, used engine oil, or pesticides used in the past, contaminated landfills, or from nearby industries such as foundries or smelters.
- Lead (Pb) from the atmosphere or soil can end up in groundwater and surface water. It is also potentially in drinking water, e.g. from plumbing and fixtures that are either made of lead or have lead solder.

4.4. Toxicity of lead (Pb):-

- Lead-induced neurotoxicity [33,34].
- Lead-induced hematotoxicity [35,36].
- Lead-induced nephrotoxicity [37,38].
- Lead-induced cardiotoxicity [39].
- Lead-induced reproductive toxicity [40,41].
- Lead-induced bone toxicity [42].

5. Arsenic (As)

5.1. Description:- The name "arsenic" is thought to come from "arsenikon",, the Greek name for the yellow pigment orpiment. Arsenic (As) was discovered approx 1250 by Albertus Magnus. It is a silver grey brittle, crystalline semi- metal or metalloid. It exists in three allotropic forms such as yellow, black and grey. It is odourless and tasteless. It is soluble in nitric acid, cold hydrochloric acid and sulphuric acid but insoluble in water and no oxidizing acids. Generally, arsenic (As) compounds are non-volatile except gaseous arsines and arsenic trioxide. The basic physical and chemical characteristics are given below:-

Table 4:-The basic physical and chemical characteristics of arsenic (As) [19].

Name	Arsenic
Symbol	As
Atomic number	33
Relative atomic mass (Ar)	74.92160 (2)
Standard State	Solid at 298K
Colour	Metallic grey
Classification	Semi-metallic
Group in periodic table	15
Period in periodic table	4
Block in periodic table	p-block
Electron shell structure	2,8,18,5
Electron configuration	$[Ar]3d^{10}4s^2 4p^3$
Valence	3,5
Boiling point	Sublimes at 612^0C
Melting point	817^0C at 28 atm
Vapour pressure	1 mmHg at 372^0C
Density/specific gravity	5.727 at 14^0C

5.2. Groundwater arsenic (As) contamination scenario in the world as well as India: **-** The global scenario arsenic (As) level beyond permissible limits in drinking water is the main cause of arsenic toxicity in the world. The arsenic (As) contamination in drinking water of Taiwan, China, Chile, Argentina, Mexico, India, Hungary Bangladesh, USA and Thailand are red alarming for the world. More than 20 Country along with India, is in the midst of a large scale thread cause by chronic mass toxicity through arsenic (As) contamination of ground water. However the largest mass of population in the world affected by chronic arsenic (As) toxicity due to drinking of arsenic contaminating groundwater belongs to Bangladesh, India and China. According to the investigations of Central Ground Water Board (CGWB) reveals that arsenic (As) contamination (>0.05 mg/L) is affecting the states of West Bengal, Bihar, Uttar Pradesh, Assam,Tripura and Chhattisgarh. The Bengal Delta Plain (BDP) covering Bangladesh and West Bengal in India is the most dangerous case of groundwater arsenic (As) contamination. Besides this, high arsenic (As) ground water has also been reported from Jharkhand and Manipur state.

5.3. Sources of arsenic (As):- Different natural and anthropogenic sources are deemed responsible for arsenic (As) contamination in groundwater. Arsenic (As) is a major constituent in more than 200 minerals [43]. The desorption and dissolution of naturally occurring arsenic (As) bearing minerals and alluvial sediments result in high arsenic (As) concentration in groundwater in deltas and alluvial plains even if the arsenic (As) concentration in the solid phase is not high [44,45]. In groundwater, arsenopyrite and pyrite contain arsenic (As) in excess concentration [46]. The main anthropogenic sources of arsenic (As) are burning of fossil fules, mining, use of arsenical fungicides, herbicides, insecticides and wood preservatives [47]. Most arsenic (As) is produced as a by-product of copper and lead refining.

5.4. The symptoms of arsenic (As) toxicity**:-** In the arsenic contaminated areas the children are often more affected than the adults. Most of the people from a poor socio-economic background suffering from arsenic skin lesions. The common features were noted (1983-2006) from the arsenic endemic areas of India: (i) Skin itching to sun rays, burning and watering of eyes, weight loss, loss of appetite, weakness, lethargy and easily fatigued limited the physical activities and working capacities, (ii) Chronic respiratory complaints were also common. Chronic cough with or without expectoration was evident in more than 50%, (iii) Gastrointestinal symptoms of anorexia, nausea, dyspepsia, altered taste, pain in abdomen, enlarged liver and spleen, and ascites (collection of fluid in abdomen), (iv) Moderate to severe anemia was evident in some cases, (v) Conjunctival congestion, Leg edema was less common. Various types of skin manifestations and other arsenic toxicity were observed from melanosis, keratosis, hyperkeratosis, dorsal keratosis, and non pitting edema to gangrene and 4 cancer. Overall prevalence of clinical neuropathy was noted in various studies in populations of 24- Pargana-North, 24- Pargana-South, Murshidabad, Nadia, and Bardhaman districts of West Bengal and in the states of Bihar, Uttar Pradesh, Jharkhand and Chhattisgarh.

5.5.Toxicity of arsenic (As):-

- Arsenic-induced cardiovascular dysfunction [48,49,50].
- Arsenic-induced diabetes mellitus [51].
- Arsenic-induced neurotoxicity [52,53,54].
- Arsenic-induced nephrotoxicity and hepatotoxicity [55].
- Arsenic-induced carcinogenicity [56].
- Arsenic-induced reproductivetoxicity [57,58,59,60,61,62].

Table 5:- Permissible limits of cadmium (Cd), lead (Pb) and arsenic (As) in drinking water according to United State Environment Protection Agency (USEPA), World Health Organization (WHO), Indian Standard Institution (ISI), Central Pollution Control Board (CPCB) and Indian Council of Medical Research (ICMR) are compared [63].

Sl.No.	Heavy metals	Symbol	USEPA	WHO	ISI	ICMR	CPCB
1.	Cadmium (mg/l)	Cd	0.005	0.005	0.01	0.01	No relaxation
2.	Lead (mg/l)	Pb	-	0.05	0.10	0.05	No relaxation
3.	Arsenic (mg/l)	As	0.05	0.05	0.05	0.05	No relaxation

6. Target Organs Of Cadmium (Cd), Lead(Pb) &Arsenic (As)

The degree of the toxicity of cadmium (Cd), lead (Pb) and arsenic (As) is not the same in all organs. Usually there are one or two organs which exhibit the major toxic effect. These organs are referred as target organs of toxicity of cadmium (Cd), lead (Pb) and arsenic (As). The central nervous system is the target organ of toxicity of cadmium (Cd), lead(Pb) and arsenic (As). The blood circulation system, liver, kidneys, lungs and skin follow in frequency of systemic effects. They attack muscle and bones. Both the male and female reproductive systems are susceptible to adverse and often debilitating impacts from cadmium (Cd), lead (Pb) and arsenic (As).The target organs for exhibiting toxicity of cadmium (Cd), lead (Pb) and arsenic (As) in animals include the liver, kidney, lungs, testes, prostate, heart, skeletal system, nervous system and immune system.

7. Heavy Metals & Their Routes Of Exposure

Traces of many heavy metals are required for proper functioning of the body. But, unfortunately, the incorporation of excess heavy metals in the body results in toxic effects. Therefore, exposure of the body to excess heavy metals and their incorporation must be avoided. Most of our foods and drinks that we consume contain small traces of heavy metals but in general, these traces are not harmful. However, once the heavy metals concentration exceeds optimum levels, different toxic effects occur in our body. There are over 30 heavy metals but approximately ten of them are important in terms of exposure and health effects. There are four routes by which the heavy metals can enter the body: inhalation, skin (or eye) absorption, ingestion, and injection.

Table 6:- Routes of exposure for common heavy metals.

* MRL = Minimal Risk Levels (Established by U.S. Centers for Disease Control - CDC)

Heavy metal	Symbol	Present in foods	Environmental exposure	Oral exposure limits
Arsenic	As	Drinking water & food	Contaminated groundwater, rat poison & soil.	MRL* = 0.005 mg/kg/day (Acute) MRL = 0.0003 mg/kg/day (Chronic
Cadmium	Cd	Water & food (Shellfish, Liver & Kidney)	Cigarette smoke, old paints & industries.	MRL = 0.0005 mg/kg/day (Acute) MRL = 0.0001 mg/kg/day (Chronic
Lead	Pb	Contaminated food & water	. Old pipes & pumps, lead-based paint & rat poison	EPA = 15 μg/L in Drinking Water

8. Toxicity Of Mixture Of Heavy Metals (As, Pb& Cd)

Chronic exposure to heavy metals causes many diseases such as liver disorders, cancer, neurological diseases and oesteoporpsis [64]. Exposure to low levels of cadmium (Cd) and lead (Pb) through food, water and air in industrial areas adversely affects the health of the general population. People are usually exposed to a combination of metals in their surrounding environment. The toxic effects of such mixtures, especially at low, chronic doses are recognised in few cases. The metals can contact with the human body and absorbed. During transport and distribution in the body, they bind with specific proteins. Such interaction of the metals with the human body can either increase or decrease the toxic action of single components [65]. Information on the effects of long-term combined exposure to environmental pollutants is minimum. Actually, all the studies about the toxicity of heavy metals are based on the acute or sub-chronic exposure cannot exhibit actual risk to the general population.

- Heavy metals mixture (As, Pb& Cd)-induced neuroyoxicity [66].
- Heavy metals mixture (As, Pb& Cd)-induced cognitive and motor development [67,68].
- Heavy metals mixture (As, Pb& Cd)-induced toxicity in behaviour [69].
- Heavy metals mixture (As, Pb& Cd)-induced birth defects [70].

9. Different Detection Techniques Of Heavy Metals (Cd, Pb & As) In Groundwater

9.1. Detection of cadmium (Cd), lead (Pb) and arsenic (As) in groundwater by commercial Kit method:- Arsenic (As), a common contaminant and toxicant of groundwater, affects human health adversely. According to the World Health Organization (WHO), the maximum recommended contamination level of arsenic (As) in drinking water is 10 μg/L. Differentt kits are widely used for detection of total arsenic (As) in water. The arsenic (As) in ground water is converted to arsine gas by a strong reducing agent. The arsine produced is then detected by paper strips via generation of color due to reaction with either mercuric bromide (KIT-1) or silver nitrate (KIT-2). These are previously immobilized on the detector strip. The mercuric bromide (KIT-1) gives a yellow color and the silver nitrate (KIT-2) produces grey. Both of these kits can detect arsenic (As) contamination within a range of 10 μg/L-250 μg/L. The detection time for both the kits is only 7 min. These two kits exhibited excellent performance compared to other kits available in the market with respect to detection time, ease of operation, cost. It can easily handle. The field trials with these kits give very satisfactory results [71].

9.2.Differential Pulse Anodic Stripping Voltammetry (DPASV):- Differential pulse anodic stripping Voltammetry (DPASV) is an established method for the analysis of trace metals such as lead (Pb) and cadmium (Cd) in contaminated samples. It is possible to analyze simultaneously very low levels of lead (Pb) and cadmium (Cd) by using ASV. It can detect levels in the range of part-per-million (ppm) or even part-per-billion (ppb). It has extremely low detection limits. It works in the presence high salt concentrations. This technique allows metal speciation and can differentiate between free and complexed metal ions. It is a successful, new, rapid, simple, selective and inexpensive qualitative and quantitative determination technique of heavy metals [72]. This technique is the two step measurement .In the first step the metal ions like lead (Pb) and cadmium (Cd), present in the test solution are get deposited on the mercury electrode surface (amalgamation) at deposition potential of -1150 mV. In the second step all the deposited ions are anodically stripped by scanning the potential range from -1150 to + 100mV.

9.3.Atomic Absorption Spectrometry (AAS):- Atomic absorption spectrometry (AAS) is an analytical technique. It measures the concentrations of elements. Atomic absorption is so sensitive that it can measure down to parts per billion of a gram (μg dm^{-3}) in a sample. The wavelengths of light specifically absorbed by an element in this technique. They correspond to the energies needed to promote electrons from one energy level to another, higher, energy level. Atomic absorption spectrometry (AAS) method is very suitable method for monitoring the levels of heavy metals such as cadmium (Cd), lead (Pb) and arsenic (As) in ground water. This technique provide accurate and rapid determination, but for the extremely low concentration of these pollutant, a direct apply of AAS is impossible without any previous concentration and separation of analytes from the sample. Today this problem can be solved by various highly modern expensive instrumentation for pre-concentration and separation of trace metals. However, many laboratories around the world, which cannot provide them, can yet apply the method as solvent–solvent extraction, solid-phase extraction, evaporation, co-precipitation, etc., which do not require expensive equipment. Some of these methods are rapid. On the other hand, others are slower. Some of them do not need expensive reagents; others do. So the development of accurate, rapid, and low-cost methods that help to monitor heavy metals in groundwater is very essential today. Among accurate, fast, and inexpensive procedures that can solve the separation of heavy metals from groundwater matrix immediately before their instrumental analysis is the colloid precipitate flotation method.[73] .

9.4.X-ray fluorescence spectrometry:- X-ray fluorescence spectrometry, a convenient method is described for monitoring cadmium (Cd), lead (Pb) and arsenic (As) at trace levels in ground water samples. These metals are preconcentrated on a chelating solid-phase extraction disk and then determined by X-ray fluorescence spectrometry. The method tolerates a wide pH range (pH 6-14). Th advantages of this technique are ease of operation, multi-element capability, non-destructiveness, high sensitivity, and relative cost efficiency. The solid-phase extraction step can be conducted in the field and then the disks can be mailed to a laboratory for the analysis. As a result the cost of transporting large volumes of water samples is eliminating. The overall cost for analysis of metals in ground water can be minimized by implementing the method [74].

Table7:- Overview of common laboratory methodologies used for detection of heavy metals, cadmium (Cd), lead (Pb) and arsenic (As).

Characteristics	Anodic Stripping Voltametry (Lead Only)	Atomic Absorption Spectroscopy	Inductively Coupled Mass Spectrometry
Principle of detection	Current required to strip plated electrode	Absorption of element-specific wavelength	Mass to charge ratio (*m/z*)
CLIA-waived	Yes	No	No
Approximate capital expense (x ~ $10,000)	<1x	3–6x	15–30x
Multi-analyte capability	No	Possible, but not common	Yes
Detection limit	3.3 µg/dL	-	Lowest
Dynamic range	65 µg/dL	-	Highest
Sample preparation	None	YES—dilution and chemical modifiers common	YES—dilution with nitric acid common

10. Conclusion

Heavy metals, cadmium (Cd) lead (Pb) and arsenic (As) contamination in ground water is a worldwide problem and has become a challenge for the world. The toxic effects of heavy metals, cadmium (Cd) lead (Pb) and arsenic (As) depend on their chemical state. The techniques used for the determination of cadmium (Cd), lead (Pb) and arsenic (As) in environmental samples should be more selective and sensitive. The most popular analytical techniques for the determination of cadmium (Cd), lead (Pb) and arsenic (As) have been described in this review. It is clearly indicated that there is a plethora of analytical techniques available for the detection of cadmium (Cd), lead (Pb) and arsenic (As) in groundwater sample. The commercial kit method, differential pulse anodic stripping voltammetry (DPASV), atomic absorption spectrometry (AAS) and x-ray fluorescence spectrometry are the most useful and widely accepted methods for speciation of cadmium (Cd), lead (Pb) and arsenic (As) in environmental samples. There are also different methods available for the speciation studies of these metals with their own advantages and limitations. However, more research efforts are needed for the development of inexpensive, rapid, sensitive and reproducible methodologies for cadmium (Cd), lead (Pb) and arsenic (As) capable of working in the range of drinking water limits.

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