

A Review on Nanomaterials as Solid Phase Extractants for Determination of Lead in Environmental Samples

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Abstract: Nanotechnology is an advanced technology that has gained much attention, due to their considerably small size and remarkable properties. Nanomaterials with their unique structural properties offer many advantages such as greater surface area, excellent adsorption capability and high selectivity. These exceptional properties make them preferable to be used as solid phase extractant for the removal of toxic metal ions, which have adverse effect on human health. Lead is one of the most toxic metal ions as even its trace concentration possesses risk to humans and other organisms. Since it is usually present in environmental samples in very low concentration, its direct determination is a challenging task. Many singular detection techniques have been used so far for this purpose, but these suffer from limitations such as high cost, more reagent consumption and low sampling rate. To overcome these challenges hyphenated analytical systems have been introduced. Flow injection is one of the simplest, fast, highly efficient techniques that can be coupled to different detection systems. Hyphenated flow injection detection system is an automated technique with high sampling frequency. This review discusses the recent studies done on removal of lead from various environmental samples using nanomaterials and determination by singular and hyphenated techniques.

Keywords: Flow-injection, Hyphenated, Lead, Nanomaterials, Solid phase extraction, Singular.

Date of Submission: 10-09-2018

Date of acceptance: 25-09-2018

I. Introduction

Nowadays, Nanotechnology has become popular due to their exceptional properties. Nano means decreasing the size of a particular material upto nanometer scale and when we do so, it is found that, the properties of that material changes tremendously. Nanoparticles with such small size possess many advantages such as large surface area and high adsorption capability. To further enhance the selectivity of nano adsorbent, it can be modified by a suitable chelating agent. These modified nanomaterials are highly useful in many fields including medicine, manufacturing, electronics and surface engineering. Now researchers are also focussing on using these nanomaterials in removal of toxic heavy metal ions present in various environmental samples. For these purpose nanomaterials such as carbon nanotubes (CNTs), silica (SiO₂), titania (TiO₂) and zinc-oxide (ZnO) are widely used [1]. The toxic metal ions including lead, cadmium, arsenic and mercury have adverse effect on human life. These toxic metal ions are significantly harmful as they get involved or interfere with various biological processes such as replacing essential metal ions and block the active site of enzymes. They directly or indirectly affect the life of various organisms by entering into food chain. These toxic metal ions get added in the environment because of their constant use in many industries for production of various goods such as dyes, paints etc., and get disposed unchecked in rivers and land. Among these toxic metals, Lead is considered to be highly poisonous, because it directly affects the human health. Its toxic effects include abdominal pain, headache, irritability, infertility and in severe conditions it damages kidney and central nervous system, may leads to coma or even death. Due to these toxic effects of lead, it is extremely important to develop a sensitive technique for its effective determination and removal [2].

Many singular techniques have been developed for the detection of lead including, flame atomic absorption spectroscopy (FAAS), electrothermal or graphite furnace atomic absorption spectroscopy (ETAAS or GFAAS), which are simple, rapid and cheap, used for detection of single element at a time. Others are inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectroscopy (ICP-MS) are highly efficient techniques, used for detection of more than one element at a time. All detection techniques mentioned above have many advantages and certain limitations but all these techniques suffer one common problem, that is, they cannot detect trace concentration of lead, and also cannot tolerate interferences due to matrix components. Thus, to solve this problem, various researchers have developed many analytical systems, one of which is introducing a preconcentration step before detection. In preconcentration step, the concentration of metal ion is extracted from large volumes to small volume and then it can be easily detected. The method in which preconcentration is done before detection is called batch method or offline

method. Preconcentration method is of different types including, solid phase extraction (SPE), liquid-liquid extraction (LLE), cloud point extraction (CPE), and co-precipitation.

Solid phase extraction (SPE) is one of the simplest preconcentration methods which have many advantages such as easy to perform, simple phase separation, reusable solid sorbent, and removal of interferences at initial stages. In this method a solid material is taken as adsorbent and to enhance its selectivity, it is modified or functionalized by an appropriate agent. The adsorbed metal ion on the surface of adsorbent is desorbed with the help of a suitable eluent [3]. Many adsorbents such as silica gel [4], alumina [5], Amberlite XAD [6], etc. have been used previously. Now Nanomaterials such as multiwalled carbon nanotubes (MWCNTs), Single walled carbon nanotubes (SWCNTs) are in high demand as they are used in small quantities and are also reusable [7].

The batch method or offline method shows good results in detection and removal of lead but have certain drawbacks such as they are much time consuming, use large volume of reagents, limit of detection is poor and require manual handling. To solve these problems, a technique is developed in which preconcentration step and detection technique is coupled. This technique is called Hyphenated flow injection preconcentration technique. In this technique, the eluate after preconcentration step is directly passed to a detection unit for analysis. The hyphenated flow injection and detection technique has many advantages as it requires less reagents and time. It also gives better recovery, has high sample throughput, and lower detection limit. Since it is an automated technique, it provides less manual errors and results are better than off-line systems[8].

The aim of this review is to discuss the use of various nanomaterials for effective preconcentration and determination of lead from various matrices and its determination by singular and hyphenated techniques in past 12 years.

II. Singular Analytical Techniques for Lead Determination

The direct determination of lead using a type of singular detection technique depends upon on the source of energy used in instrument. In atomic spectrometric technique flame or furnace is used for the atomization while in plasma analytical technique plasma energy is used for atomization.

2.1 Atomic Spectrometric Techniques

Atomic spectrometry is one of the most commonly used techniques for determination of concentration of metal ion present in a sample. Atomic absorption spectroscopy works on the principle that the free atom absorbs energy and get excited to higher energy level, the absorbed energy corresponds a particular wavelength which is detected by the detector. Atomic absorption spectrometry is widely applied for metal determination, and the most widely employed are Flame atomic absorption spectroscopy (FAAS) and Graphite furnace atomic absorption spectrometry(GFAAS). The difference between the two is the atomizer; in FAAS, a flame is used for atomization of the analyte while in GFAAS, a furnace made of graphite is used. These techniques are useful for single element detection with high precision.

2.1.1 Flame atomic absorption spectrometry (FAAS) is an analytical technique, in which analyte of interest is aspirated into the flame with the help of a nebulizer. In the flame, the free atom absorbs the suitable wavelength and get excited to higher energy level. The absorbed wavelength is detected by a detector. The technique has many advantages as it is simple, fast, and less expensive than other techniques. However, it suffers from a few limitations such as inferior detection limits, and interference from matrix components.

2.1.2 Graphite furnace atomic absorption spectrometry (GFAAS) is also called *Electrothermal Atomic Absorption spectrometry (ETAAS)*. In this technique, a furnace is used for atomization. The analyte to be determined in solid or in liquid phase is introduced in the graphite furnace where it is heated to remove excess solvent (in case of liquid sample) and other matrix component that can interfere in analysis. Then the remaining analyte was atomized. The advantage of graphite furnace over FAAS is that it can be used for solid samples as well. Its detection limit and sensitivity is better than FAAS and does not suffer from interfering matrix. The only drawback is that it takes longer time and is used for limited elements[9].

2.2 Plasma Spectrometric Techniques

In plasma spectrometric technique, plasma is produced using argon gas. When an electric current is passed through the chamber containing argon gas, the argon gas gets ionized and plasma is generated. The plasma has very high temperature and has tendency to atomize the element present in the sample completely. The high temperature of plasma removes the matrix interferences. The technique is of two type inductively coupled plasma optical emission spectrometry(ICP-OES) and inductively coupled plasma-mass spectrometry(ICP-MS).

2.2.1 *Inductively coupled plasma optical emission spectrometry (ICP-OES)* is an advanced technique used for detection of various metal ions. Here sample is injected in the plasma, the atom gets excited to higher energy level which when come back to ground state emit radiation. The emitted radiation is of a particular wavelength which is detected by the detector. The type of element present in the sample can be determined by the position of wavelength and the concentration by the intensity of radiation.

The technique is more beneficial than simple AAS as, it is used for detection of more than one element at a time, has low detection limit and faces minimum interferences.

2.2.2 *Inductively coupled plasma mass spectrometry (ICP-MS)* is a more advanced technique used for detection of metal ions in different water samples. Its working principle is same as that of ICP-OES. It is also a multi-element detection technique like ICP-OES but with more advantages, as it can be used for detection of isotopes also. However, it still has some limitations, the cost of instrument is very high, and its upper linear concentration range is also less [10].

III. Hyphenated Flow-Injection Analytical Technique

The hyphenated flow injection analytical technique is the combination of preconcentration step and detection unit. The flow injection preconcentration system consists of a micro/mini-column containing adsorbent and two peristaltic pumps—one for the sample injection and the other for eluent. Both the pumps work according to pre-defined programme, which allows simultaneous preconcentration and detection. All parameters such as eluent concentration, pH, and flow rate of both sample and eluent are optimized before analysis. The system not only saves time and energy, but also requires less volume of reagents. The results obtained through flow injection hyphenated techniques are reproducible and error free as minimum manual sample handling is required. Flow-injection preconcentration process can be coupled to any detection technique such as FAAS, ICP-OES, and ICP-MS to enhance their analytical performance [8].

IV. Discussions

4.1 *Nanomaterials as Solid Phase Extractant in Determination of Lead by Singular Analytical Technique*

Nanomaterials of various forms can be used as solid phase extractant in the determination of lead using various singular analytical techniques like FAAS, GFAAS, ICP-OES and ICP-MS. Since, nanomaterials have high tendency to adsorb various metals, they need to be modified to enhance their selectivity towards lead. The process of lead preconcentration is done manually and determination is done by using singular technique. In preconcentration, sample is passed through a column filled with suitable nanomaterial. Then an appropriate eluent is passed to elute the lead from the surface of nanomaterial. The eluate containing the desorbed lead is manually aspirated in the detection system where an analytical signal is generated. The result shows the exact concentration of lead present in the sample.

The process of preconcentration and determination using singular technique is explained by a schematic diagram given in Fig. 1.

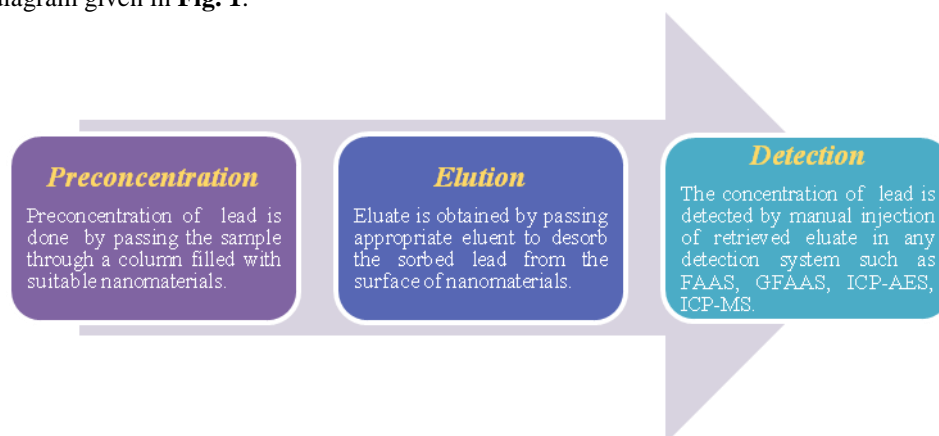


Fig. 1. Determination of Lead using Singular techniques

Analytical figures of merit

The efficiency of a preconcentration system is determined in terms of certain parameters known as analytical figures of merit. These parameters include preconcentration factor (PF), limit of detection (LOD), and relative standard deviation (% R.S.D.).

Preconcentration factor (PF) is defined as the ratio of concentration of the analyte in the final extract ready for its determination and in the initial solution. In off-line preconcentration systems it is calculated as the ratio of sample volume to final volume of eluate. In on-line systems, it is calculated as the ratio of the slopes of the calibration curves obtained with and without preconcentration.

Limit of detection (LOD) is defined as the lowest analytical signal obtained in the absence of the analyte, and is calculated as three times the standard deviation (3σ) of n replicate measurements of the blank sample.

Relative standard deviation (RSD) is a measure of the precision or agreement between replicate measurements.

4.1.1 Multiwalled carbon nanotubes as Solid Phase Extractant in determination of Lead by Singular analytical Technique

There are different types of nanomaterials used for this purpose, multiwalled carbon nanotubes are one of the best options as have large surface area, great adsorption capacity and can be easily modified by different functional groups or organic moieties. As in a recent study done by Z. J. Hu, et al. ethylenediamine grafted MWCNTs was used as an adsorbent for the preconcentration of lead. Atomic absorption spectroscopy (AAS) was used as detection technique. The preconcentration factor (PF) obtained was 60, limit of detection (LOD), $0.30 \mu\text{g L}^{-1}$ and relative standard deviation (RSD) was 2.6% [11]. E. Kazemi, and his co-workers also studied the extraction of lead and cadmium from various biological and environmental samples using MWCNTs modified with 2-mercaptobenzothiazole as adsorbent and FAAS for the detection. The samples analysed were drinking water, river water, sea water, well water and spring water. The PF determined was 150, LOD and RSD, were $0.21 \mu\text{g L}^{-1}$ and 1.8% respectively [13].

ETAAS was used as detection technique for the determination of lead and cadmium in urine samples by J. Á. Méndez, et al. In the study the dispersive solid-liquid extraction was done on multiwalled carbon nanotubes. The preconcentration factor, detection limit and relative standard deviation obtained were 5.4, $0.13 \mu\text{g L}^{-1}$ and 5.9% respectively (26). Similarly, M. Fayazi, et al. used GFAAS as detection technique for the determination of lead using MWCNTs modified with 2,3,5,6-tetra(2-pyridyl) pyrazine (TPPZ). The preconcentration factor obtained was 200, the detection limit was quite low as $0.0024 \mu\text{g L}^{-1}$ and relative standard deviation was 5.6 % [28].

Another technique used for lead preconcentration and determination includes ICP-OES where MWCNTs functionalised with thiosemicarbazide were used. Samples were collected from Huangpu river water and tap water samples. The PF value was found to be 60, RSD 1.6 % and limit of detection $0.18 \mu\text{g L}^{-1}$ [34]. MWCNTs loaded with 5-aminosalicylic acid were used for preconcentration of lead from aqueous solutions using ICP-OES technique. The water samples taken were mineral water, laboratory tap water, wastewater from electroplating industry and Red Sea water. Limit of detection was $0.25 \mu\text{g L}^{-1}$, RSD was 2.8% and PF value was 125 [35]. Out of various techniques used in the many studies ICP-MS was also used for determination and removal of lead ions from water samples. MWCNTs modified with pristine, oxidized, ethylenediamine, diethylenetriamine and triethylenetetramine were employed. The limit of detection was 0.04ng L^{-1} and RSD of 3% was obtained [37].

The oxidized MWCNTs were also used for the determination of lead as a recent study carried out by Saljooqi et al used o-MWCNTs as extractant and lead determination was done by ETAAS technique. The enhancement factor was 200, limit of detection $0.13 \mu\text{g L}^{-1}$ and RSD 6.3%. The samples used for analysis were red lipstick, pine leaves and well water sample [43].

The singular techniques for the determination of lead using multiwalled carbon nanotubes with different parameters are given in **Table 1**.

Table 1. Multiwalled carbon nanotubes as Solid Phase Extractant in Determination of Lead by Singular Analytical Technique

| S.No. | Solid Support | Chelating Agent | Technique | PF | DL ($\mu\text{g L}^{-1}$) | RSD (%) | Reference |
|-------|---------------|---|-----------|-----|-----------------------------|---------|-----------|
| 1 | MWCNTs | Ethylenediamine | AAS | 60 | 0.30 | 2.6 | 11 |
| 2 | MWCNTs | Polyhydroxyquinoline | FAAS | - | 0.41 | 2.98 | 12 |
| 3 | MWCNTs | 2-mercaptobenzothiazole | FAAS | 150 | 0.21 | 1.8 | 13 |
| 4 | MWCNTs | Dipyridylamine | FAAS | 182 | 0.7 | 5 | 14 |
| 5 | MWCNTs | Nano ZrO_2 | FAAS | 30 | 0.80 | 5 | 15 |
| 6 | MWCNTs | Poly(N-phenylethanolamine) | FAAS | 100 | 0.8 | 3.1 | 16 |
| 7 | MWCNTs | - | FAAS | 100 | 0.86 | 3 | 17 |
| 8 | MWCNTs | Dithizone | FAAS | 30 | 3.3 | 1.1 | 18 |
| 9 | MWCNTs | (E)-N1-(4-nitro-benzylidene)-N2-(2-((E)-4-nitrobenzylideneamino)ethyl) ethane-1,2-diamine | FAAS | 20 | 8.9 | 0.7-5.8 | 19 |
| 10 | MWCNTs | Pyridine | FAAS | - | 2 | 1.3 | 20 |
| 11 | MWCNTs | Poly(2-aminothiophenol) | FAAS | 304 | 1 | 3.2 | 21 |
| 12 | MWCNTs | Polypyrrole | FAAS | 200 | 1.1 | 5.9 | 22 |

| | | | | | | | |
|----|-----------------------|--|---------------|------------|----------------|------------|----|
| 13 | MWCNTs | Tris(2-aminoethyl)amine | FAAS | - | - | 0.11-0.17 | 23 |
| 14 | MWCNTs | Cyanuric acid | FAAS | 660 | 0.3 | 3.4, 3.5 | 24 |
| 15 | MWCNTs | Trimethoxysilylpropylamine (TMSPA) | FAAS | 17.9 | 2.89 | 3.21 | 25 |
| 16 | MWCNTs | - | ET-AAS | 5.4 | 0.13 | 5.9 | 26 |
| 17 | MWCNTs | - | GFAAS | 150 | 0.5 | <2.9 | 27 |
| 18 | MWCNTs | 2,3,5,6-tetra(2-pyridyl) pyrazine (TPPZ) | GFAAS | 200 | 0.0024 | 5.6 | 28 |
| 19 | MWCNTs | - | GFAAS | 150 | 0.5 | 2.9 | 29 |
| 20 | MWCNTs | - | HR-CS GFAAS | 15 | 0.03 | 4 | 30 |
| 21 | MWCNTs | 4-amino azobenzene | ICP-OES | 150 | 0.28 | 2.1 | 31 |
| 22 | MWCNTs | 2-aminobenzothiazole | ICP-OES | 100 | 0.27 | 1.6 | 32 |
| 23 | MWCNTs | Tris(2-aminoethyl)amine | ICP-OES | 60 | 0.32 | 3.5 | 33 |
| 24 | MWCNTs | Thiosemicarbazide | ICP-OES | 60 | 0.18 | 1.6 | 34 |
| 25 | MWCNTs | 5-aminosalicylic acid | ICP-OES | 125 | 0.25 | 2.8 | 35 |
| 26 | MWCNTs | Phenyl-iminodiacetic acid | ICP-OES | 100 | 0.18 | 2.5 | 36 |
| 27 | MWCNTs | ethylenediamine, diethylenetriamine and triethylenetetramine | ICP-MS | - | 0.00004 | 3 | 37 |
| 28 | o-MWCNTs | 1,8-diaminonaphthalene | FAAS | - | 0.7 | 4.7 | 38 |
| 29 | o-MWCNTs | D2EHPA | FAAS | 25 | 0.04 | 8.0 | 39 |
| 30 | o-MWCNTs | bis(2,2-bipyridyl) | FAAS | 160 | 0.06 | 2.4 | 40 |
| 31 | o-MWCNTs | 2-(2-hydroxy-5-nitrophenyl)-4,5-diphenyl imidazole | FAAS | 94 | 2.9 | 2.9 | 41 |
| 32 | o-MWCNTs | 1,10-phenanthroline | FAAS ETAAS | 200 100 | 0.26 0.0064 | 2.6 2.9 | 42 |
| 33 | o-MWCNTs | - | ETAAS | 200 | 0.13 | 6.3 | 43 |
| 34 | o-MWCNTs | - | ETAAS | | 0.08 | 3.4-8.2 | 44 |
| 35 | o-MWCNTs | - | ICP-AES | | 2.1 | 2 | 45 |
| 36 | MWCNTs(Silica Coated) | 1-(2-pyridylazo)-2-naphthol | FAAS | 15 | 1.76 | 3.3 | 46 |

4.1.2 Graphene based Nanomaterials as Solid Phase Extractant in Determination of Lead by Singular Analytical Technique

Graphene is also a very good adsorbent and was used as solid phase extractant for the determination of various metal ions, it also can be easily modified. As, A. Islam, and his co-workers modified graphene oxide with polystyrene for the preconcentration of lead and determined it with the help of FAAS. The parameters like PF, LOD and RSD obtained were, 400, 2.3 $\mu\text{g L}^{-1}$ and 5% respectively [47].

Similarly, M.Shojai, et, al. used graphene oxide covalently linked with porphyrin as solid phase extractant for the preconcentration of lead and used FAAS for determination. The PF, LOD and RSD obtained were quite good as, 200, 0.049 $\mu\text{g L}^{-1}$ and 2% [48]

The determination of lead was also carried out using ETAAS, with graphene-silica hybrid as adsorbent. The samples on which the developed method was applied were river water, human urine and saliva. The enrichment factor 18, limit of detection 0.089 $\mu\text{g L}^{-1}$ and RSD 3.1-3.8% were determined [50].

The singular techniques for determination of lead using graphene based nanomaterials with different analytical parameters are given in **Table 2**.

Table 2. Graphene based Nanomaterials as Solid Phase Extractant in Determination of Lead by Singular Analytical Technique

| S.No. | Solid Support | Chelating Agent | Technique | PF | DL ($\mu\text{g L}^{-1}$) | RSD (%) | Reference |
|-------|---|---|-----------|-----|-----------------------------|---------|-----------|
| 1 | Graphene oxide | Chloromethylated polystyrene via ethylenediamine spacer | FAAS | 400 | 2.3 | 5 | 47 |
| 2 | Graphene oxide | Covalently linked porphyrin | FAAS | 200 | 0.049 | 2 | 48 |
| 3 | Graphene oxide | Molybdenum disulfide | FAAS | 90 | 0.71 | 2.2 | 49 |
| 4 | Graphene-Silica hybrid | - | ETAAS | 18 | 0.089 | 3.1-3.8 | 50 |
| 5 | Graphene and the zeolite clinoptilolite nanoadsorbent | - | ETAAS | 20 | 0.07 | 3.4 | 51 |

4.1.3 Magnetic Nanomaterials as Solid Phase Extractant in Determination of Lead by Singular Analytical Technique

Magnetic nanoparticles gained much attention as apart from their high surface area, great adsorption capacity and selectivity it is also very easy to separate them with the help of external magnet. Recently, N. Baghban, (2017) used magnetic nanoparticles modified with molybdenum disulphide (MoS₂) as an adsorbent for the preconcentration of lead (II) and copper(II) ions using FAAS for detection. The PF, LOD and RSD found were 50, 3.3 µg L⁻¹ and 4.9% respectively [52]. Similarly, M. A.Karimi, et al₂ synthesized alumina coated magnetic nanoparticles and modified it with dithizone/sodium dodecyl sulfate for the determination of lead in various environmental samples. The samples used were opium, heroin, lipstick, plants and water. Both FAAS and GFAAS techniques were used for detection and it was found that both showed good results. The parameters like PF, LOD and RSD obtained using FAAS were, 280, 0.28 µg L⁻¹ and 4.6%, while that obtained using GFAAS were, 300, 0.002 µg L⁻¹ and 3.1 % respectively [55].

Magnetic nanoparticles were also combined with other nanomaterials to make nanocomposite which gave better results as a study done by G. D.Tarigh, and his co-workers where the magnetic nanoparticles were combined with multiwalled carbon nanotubes. The nanocomposite was used for preconcentration and determination of lead and manganese in various matrices using FAAS. The PF, LOD and RSD obtained were, 390, 1 µg L⁻¹ and 4.3 % respectively [57].

Recently, magnetic graphene oxide nanocomposite modified with polyimide was prepared by A. Mehdinia, (2017) and used for the preconcentration of lead ions in fish and mollusc tissues. FAAS was used for detection. Various parameters obtained like PF, LOD and relative standard deviation were, 141, 0.25 µg L⁻¹ and 7.3 % respectively [61].

Similarly, the other solid phase extractants for determination of lead using magnetic nanomaterials with different analytical parameters are given in **Table 3**.

Table 3. Magnetic Nanomaterials as Solid Phase Extractant in Determination of Lead by Singular Analytical Technique

| S.No. | Solid Support | Chelating Agent | Technique | PF | DL (µg L ⁻¹) | RSD (%) | Reference |
|-------|--|--|-----------|------|--------------------------|---------|-----------|
| 1 | Magnetic nanoparticles | Molybdenum disulfide (MoS ₂) | FAAS | 50 | 3.3 | 4.9 | 52 |
| 2 | Magnetic nanoparticles | poly(2-amino thiophenol) | FAAS | 50 | 2.1 | 2.4 | 53 |
| 3 | Magnetic nanoparticles | - | FAAS | 200 | 1.61 | 1.45 | 54 |
| 4 | Magnetic nanoparticles coated with alumina | dithizone/ sodium dodecyl sulfate | FAAS | 280 | 0.28 | 4.6 | 55 |
| | | | GFAAS | 300 | 0.002 | 3.1 | |
| 5 | Magnetic nanoparticles coated with carbon | polyacrylamide | ICP-MS | 37.5 | 0.11 | 7.4 | 56 |
| 6 | MWCNTs-Fe ₃ O ₄ | - | FAAS | 390 | 1 | 4.3 | 57 |
| 7 | Magnetized MWCNTs-Fe ₃ O ₄ | - | ICP-AES | - | 0.6 | 1.23 | 58 |
| 8 | Magnetic graphene oxide | 8-Hydroxyquinoline | FAAS | 130 | 0.27 | 3.9 | 59 |
| 9 | Magnetic graphitic carbon nitride nanoparticles | Ethylenediamine | FAAS | - | 0.6 | 3.6 | 60 |
| 10 | Magnetic graphene oxide-Fe ₃ O ₄ nanocomposite | Polyimide | FAAS | 141 | 0.25 | 7.3 | 61 |
| 11 | Magnetite-TiO ₂ nanoparticles | Polypyrrole | FAAS | 185 | 0.21 | 3.9 | 62 |
| 12 | Magnetic ion-imprinted polymer nanospheres | 3-aminopropyltriethoxysilane | FAAS | 150 | 0.01 | 2.41 | 63 |

4.1.4 Other Nanomaterials as Solid Phase Extractant in Determination of Lead by Singular Analytical Technique

Other nanomaterials like modified silica nanoparticles, nano-alumina, nano titania etc. were also used for the determination of lead in various environmental samples. Shemirani et al, synthesized calcium ferrite

nanoparticles modified with APTES and were used in lead preconcentration using FAAS. The optimised parameters included preconcentration factor of 133, limit of detection $0.78 \mu\text{g L}^{-1}$ and RSD of 2.5%. The samples used for determination were well water, tuna fish, tomato paste, milk and parsley [64]. Similarly, A. Afkhami, and co-workers used nano-alumina modified with 2, 4-dinitrophenylhydrazine for the preconcentration and determination of lead and chromium using FAAS as detection technique. The various parameters like PF, LOD and RSD were, 267, $0.43 \mu\text{g L}^{-1}$ and 1.4 % [65].

The polymeric nanoparticles were also used by some researchers as recently, M. G. Kakavandi, (2017) used ion-imprinted polymer nanoparticles modified with 2-vinylpyridine for the preconcentration and determination of lead ions in various food and water samples. FAAS was used as detection technique and the Detection limit obtained was $0.7 \mu\text{g L}^{-1}$ and relative standard deviation was less than 4% [66]. Similarly, the other solid phase extractants for determination of lead using graphene based nanomaterials with different analytical parameters are given in **Table 4**.

Table 4. Other Nanomaterials as Solid Phase Extractant in Determination of Lead by Singular Analytical Technique

| S.No. | Solid Support | Chelating Agent | Technique | PF | DL ($\mu\text{g L}^{-1}$) | RSD (%) | Reference |
|-------|--|---|-----------|------|-----------------------------|---------|-----------|
| 1 | APTES modified calcium ferrite nanoparticles | Phthalic anhydride | FAAS | 133 | 0.78 | 2.5 | 64 |
| 2 | Nano-alumina | 2,4-dinitrophenylhydrazine | FAAS | 267 | 0.43 | 1.4 | 65 |
| 3 | Ion-Imprinted polymer nanoparticles | 2-vinylpyridine | FAAS | - | 0.7 | <4 | 66 |
| 4 | Lead ion imprinted polymer nanoparticles | - | FAAS | 92.9 | 0.9 | 3.4 | 67 |
| 5 | Titania/Silica Nanoparticles | Amine | FAAS | 200 | 0.12 | 3.1 | 68 |
| 6 | Zinc oxide nanoparticles | Anhydrous 5% N-[2-aminoethyl]-3-aminopropyltrimethoxysilane | FAAS | 5 | - | 1.73-13 | 69 |

PF-Preconcentration factor, DL- Limit of Detection, RSD- Relative Standard Deviation

4.2 Nanomaterials as solid phase extractant in determination of lead by Hyphenated flow-injection analytical system

In hyphenated flow-injection analytical system, preconcentration step is coupled with detection system. Sample containing lead is loaded on the mini/micro-column filled with nanomaterial, which then gets eluted by a suitable eluent. The eluate thus obtained reaches directly to the detection system. The detector analyses the sample of lead and generates the required results. The analysis is done by a pre-defined computer programme operated in a time based mode provided with operational steps optimized for lead retention. The working of the on-line preconcentration system is a two-step process involving loading and elution. A schematic representation of the flow injection analysis system coupled to FAAS is given in **Fig. 2** [70].

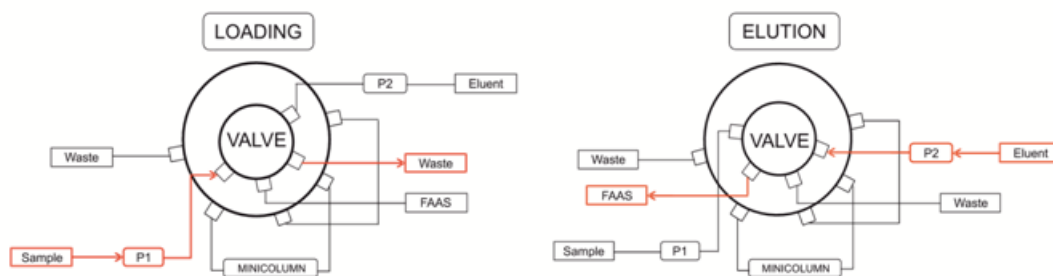


Fig. 2. Determination of Lead using Hyphenated flow injection-FAAS system

The flow-injection preconcentration system hyphenated to detection unit makes the detection process faster, using lesser reagents as mini/micro-column is used, minimum manual work is done, and therefore the chances of contamination are also reduced.

The flow injection system can be hyphenated to different detection systems. In a recent study, the preconcentration and determination of lead in different samples was done using the FI-FAAS technique. MWCNTs functionalized with 2,2'-(1E,1E')-(4-Methyl-1,2-phenylene)bis(azene-1-yl-1-ylidene)bis(Methane-1-yl-ylidene)diphenol was used as the solid phase extractant for lead preconcentration. The real samples on which the determination method was applied were tap water, river water, dark hair samples, corn samples and standard alloys. Various parameters were optimized for maximizing lead preconcentration. The preconcentration factor, limit of detection, and RSD values were reported to be 21.5, 1.80 $\mu\text{g L}^{-1}$ and 1.8%, respectively [71]. The FI-FAAS method was also used by C.R.T. Tarley et al for the solid phase extraction and determination of lead using 3-mercaptopropyltrimethoxysilane immobilized on MWCNTs. The limit of detection, enhancement factor and RSD values were found as 1.7 $\mu\text{g L}^{-1}$, 31.5 and 1.97 – 4.20 %, respectively. The real samples on which the developed method was applied were mineral water, tap water and effluents released from car battery plants [72].

J Wang et al. used Flow Injection technique coupled with Inductively Coupled Plasma Mass Spectroscopy (FI- ICP-MS) for lead determination in water samples using Iminodiacetic acid functionalised MWCNTs as a solid support. The analytical parameters studied were limit of detection, 0.007 $\mu\text{g L}^{-1}$, enhancement factor, 91 and RSD 1%. The real samples used for determination were fish, shrimp and scallop [73].

In another study reported by Hong Wu and co-workers, the flow injection was hyphenated hydride generation-atomic fluorescence spectrometric (HG-AFS) technique. The developed method was used for detection of lead in natural water samples such as sea water, river water, lake water and rain water. The RSD value, limit of detection and PF values were 4.4%, 0.0028 $\mu\text{g L}^{-1}$ and 26, respectively [76].

The coupling of flow-injection preconcentration to different detection techniques enhances the detection limit, automates the preconcentration process, and increases the sampling frequency. The on-line lead preconcentration and determination literature has shown that flow-injection techniques have not been well exploited. The analytical technique which was mostly found to be hyphenated to FI was FAAS. A single FI-HG-AFS and FI-ICP hyphenated analytical technique was carried out in the last decade, and they reported the better detection limit amongst other systems.

The Hyphenated flow-injection techniques for determination of lead with different analytical parameters are given in **Table 5**.

Table 5. Nanomaterials as solid phase extractant in determination of lead by Hyphenated flow-injection analytical system

| S.No. | Solid Support | Chelating Agent | Technique | PF | DL ($\mu\text{g L}^{-1}$) | RSD (%) | Reference |
|-------|---------------------------------|--|-----------|------|-----------------------------|-------------|-----------|
| 1 | MWCNT | 2,2'-(1E,1E')-(4-Methyl 1,2-phenylene) bis(azene-1-yl-1-ylidene) bis (Methane-1-yl-ylidene) diphenol | FI-FAAS | 21.5 | 1.80 | 1.8 | 71 |
| 2 | MWCNT | 3-mercaptopropyltrimethoxysilane | FI-FAAS | 31.5 | 1.7 | 1.97 - 4.20 | 72 |
| 3 | MWCNTs | Iminodiacetic acid | FI-ICP-MS | 91.0 | 0.007 | 1.0 | 73 |
| 4 | o-MWCNT | - | FI-FAAS | 44.2 | 2.6 | 7.7 | 74 |
| 5 | o-MWCNT | - | FI-FAAS | 15.4 | 1.00 | 4.6 | 75 |
| 6 | o-MWCNT | - | FI HG-AFS | 26.0 | 0.0028 | 4.4 | 76 |
| 7 | Silica-grafted graphene oxide | - | FI-FAAS | 15.0 | 0.91 | 3.8 | 77 |
| 8 | Graphene oxide-silica composite | - | FI-ICP-MS | 10.0 | 0.028 | 4.6 | 78 |

PF-Preconcentration factor, DL- Limit of Detection, RSD- Relative Standard Deviation

V. Conclusion

Commercial workhouses such as chemical factories, mining industries, etc. continue to pollute the environment by failing to implement hazardous waste disposal protocols. Due to this negligence, metallic wastes such as lead-rich effluents from various industrial sources find their way into the environment and exert toxic biological effects. Prolonged exposure to lead can cause life-threatening disorders and even death. Thus, monitoring and removing lead from environmental samples is of utmost importance. Although various

analytical techniques have been used for the determination of lead in real samples, however, they lack sensitivity and selectivity due to interference by the matrix components. Therefore, preconcentration steps such as solid phase extraction (SPE) are required to simultaneously remove interferences and enrich the lead ions into a different phase with smaller volume. SPE is advantageous as it provides higher enrichment factors, the SPE adsorbents can be reused numerous times, and ease of coupling with detection techniques. The most popular SPE adsorbents today are nanomaterials, as they possess exceptionally high surface areas. They also provide ease of surface modification with chelating agents, which serves to improve their selectivity towards lead preconcentration.

The aim of this review was to discuss the various singular and hyphenated SPE preconcentration systems making use of nanomaterials in lead determination from a variety of samples. The performance of singular and hyphenated preconcentration systems was compared based on their figures of merit obtained in lead preconcentration, and it was found that the hyphenated methods reported better parameters for preconcentration. This could be attributed to the several advantages offered by the hyphenated flow injection methods, such as improved detection limits, efficient removal of interferences, rapid analysis, reduction in reagent volumes, excellent precision, fully automated system with minimum risk of contamination and errors. From the literature survey, it was found that in spite of the excellent performance characteristics of hyphenated flow-injection preconcentration systems in lead determination, their application has been scarce. On the other hand, extensive research has been carried out on singular preconcentration systems. It was also found that multi-walled carbon nanotubes (MWCNTs) were the most popular choice for SPE, which can be attributed to its easy availability, chemical stability, and ease of modification with functional groups of choice.

Acknowledgments

The authors are thankful for the financial support from University of Delhi for the Innovation project- KMC 302.

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IOSR Journal of Applied Chemistry (IOSR-JAC) is UGC approved Journal with Sl. No. 4031, Journal no. 44190.

Reena Saxena*, " A Review on Nanomaterials as Solid Phase Extractants for Determination of Lead in Environmental Samples" IOSR Journal of Applied Chemistry (IOSR-JAC) 11.9 (2018): 27-38.