Chapter 1

General Introduction

And

Literature Review
Analytical chemistry is the study of the separation, identification, and quantification of the chemical components of natural and artificial materials [1]. This branch of science has played critical roles in the understanding of basic science to a variety of practical applications, such as biomedical applications, environmental monitoring, quality control of industrial manufacturing, forensic science and so on. It has been important since the early days of chemistry, providing methods for determining which elements and chemicals are present in the world around us. During this period significant analytical contributions to chemistry include the development of systematic elemental analysis by Justus von Liebig and systematized organic analysis based on the specific reactions of functional groups.

Analytical methods can be separated into classical and instrumental [2]. Classical methods (also known as wet chemistry methods) use separations such as precipitation, extraction, and distillation and qualitative analysis by color, odor, or melting point. Quantitative analysis is achieved by measurement of weight or volume. Instrumental methods use an apparatus to measure physical quantities of the analyte such as light absorption, fluorescence, or conductivity. The separation of materials is accomplished using chromatography or electrophoresis methods.

The first instrumental analysis was flame emissive spectrometry developed by Robert Bunsen and Gustav Kirchhoff who discovered rubidium (Rb) and caesium (Cs) in 1860 [3]. Most of the major developments in analytical chemistry take place after 1900. During this period instrumental analysis becomes progressively dominant in the field. In particular many of the basic spectroscopic and spectrometric techniques were discovered in the early 20th century and refined in the late 20th century. Also, analytical chemistry has been an indispensable area in the development of nanotechnology. Surface characterization instruments, electron microscopes and scanning probe microscopes enables scientists to visualize atomic structures with chemical characterizations.
1(a).1 Material Science

Material science is an interdisciplinary field involving the properties of matter and its applications to various areas of science and engineering. The material of choice of a given era is often its defining point; the Stone Age, Bronze Age, and Steel Age are examples of this. This is one of the oldest forms of engineering and applied science, deriving from the manufacture of ceramics. This science investigates the relationship between the structure of materials at atomic or molecular scales and their macroscopic properties. With significant media attention focused on nanoscience and nanotechnology in recent years, material science has been propelled to the forefront at many universities.

Material science encompasses various classes of materials, each of which may constitute a separate field.

1. Ionic crystals
2. Covalent crystals
3. Metals
4. Intermetallics
5. Semiconductors
6. Polymers
7. Composite materials
8. Vitreous materials

1(a).2 Composite material

Society has always wanted and continued to seek materials that are strong, tough, and light. In this quest, it was discovered that the macroscopic combinations of two or more different materials resulting in a new material with improved properties could be described as “composite” [4]. The term “composite materials” may, perhaps, be simply defined on the classical definition of a composite material as given in Longman’s dictionary “something combining the typical or essential characteristics of individuals making up a group”.

The concept of composites is very old as it dates back to the times of Israelis, 800 B.C. and also Egyptian pharaohs in third millennium B.C. who used straw in bricks manufacturing as reinforcement. Naturally occurring composites are bone, bamboo, feathers, natural fibers, and wood. Bone is an organic-inorganic composite of protein (collagen) and minerals (calcium apatite) and bamboo is cellulose reinforced by silica. These combinations make a hard material with high impact strength. The cellulose cell structure of wood and fiber is bound together with lignin, a natural polymeric substance. The first man made composites based upon polymers
appeared in about 5000 B.C. in the Middle East where pitch was used as a binder for reeds in boat-building. In 1950s, composites entered the automobile industry when they were used in cars because of desirable properties such as strength and durability. With time the research conducted on studying more properties and improving the manufacturing process of composite material has increased. Thus composite materials are those which are formed by combination of two or more materials (reinforcing elements, fillers, and composite matrix binder), differ in form or composition on a macroscale. Composite materials consist of two separate components, the matrix and the filler.

Composites can be classified into roughly three or four types according to the filler types:

- Particulate- eg. Cement is a metal matrix with ceramic filler.
- Short fiber- eg. Fiber glass filler for boat panel.
- Long fiber- eg. Carbon fiber, aramid fiber.
- Laminate – eg. Formica countertop

1(a).3 Nanocomposites

Nanocomposites are composites in which at least one of the phases shows dimensions in the nanometre range (1nm = 10^{-9}m) [5]. The definition of nanocomposite material has broadened significantly to encompass a large variety of systems such as one-dimensional, two-dimensional, three-dimensional and amorphous materials, made of distinctly dissimilar components and mixed at the nanometer scale. They are reported to be the materials of 21st century in the view of possessing design uniqueness and property combinations that are not found in conventional composites. The general understanding of these properties is yet to be reached [6], even though the first inference on them was reported as early as 1992 [7].

It has been reported that changes in particle properties can be observed when the particle size is less than a particular level, called 'the critical size'[8]. Additionally, as dimensions reach the nanometre level, interactions at phase interfaces become largely improved, and this is important to enhance materials properties. Further, discovery of carbon nanotubes (CNTs) in 1991[9] and their subsequent use to fabricate composites exhibiting some of the unique CNT related mechanical, thermal and electrical properties [10-12] added a new and interesting dimension to this area. Nowadays,
nanocomposites offer new technology and business opportunities for all sectors of industry, in addition to being environmentally friendly.

Nanocomposite materials can be classified, according to their matrix materials, in three different categories as shown in Table 1(a).

i. Ceramic Matrix Nanocomposites (CMNC): The potential of ceramic matrix nanocomposites (CMNC), mainly the Al₂O₃/SiC system, was revealed by the pioneering work of Niihara [13].

ii. Metal Matrix Nanocomposites (MMNC): They show an extraordinary potential for application in many areas, such as aerospace, automotive industries and development of structural materials [14].

iii. Polymer Matrix Nanocomposites (PMNC): Polymers have been filled with several inorganic compounds, either synthetic or natural, in order to increase heat and impact resistance, flame retardancy and mechanical strength.

<table>
<thead>
<tr>
<th>Class</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td>Fe-Cr/Al₂O₃, Ni/Al₂O₃, Co/Cr, Fe/MgO, Al/CNT, Mg/CNT</td>
</tr>
<tr>
<td>Ceramic</td>
<td>Al₂O₃/SiO₂, SiO₂/Ni, Al₂O₃/TiO₂, Al₂O₃/SiC, Al₂O₃/CNT</td>
</tr>
<tr>
<td>Polymer</td>
<td>Thermoplastic/thermoset polymer/layered silicates, polyester/TiO₂, polymer/CNT, polymer/layered double hydroxides</td>
</tr>
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Table 1(a) Different types of nanocomposite

1(a).3.1 Conducting Polymer Nanocomposites and their Classification

Nano-ordered composite materials consisting of organic polymers and inorganic materials have been attracting attention for the purpose of the creation of high-performance or high-functional polymeric materials. Especially, the word of “polymer hybrid” claims the blends of organic and inorganic components at nano-level dispersion. Significant effort is focused on the ability to obtain control of the nanoscale structures via innovative synthetic approaches. The properties of nanocomposite materials depend not only on the properties of their individual parents, but also on their morphology and interfacial characteristics. Structure-property correlations in polymer nanocomposites have been extensively dealt with in a recent
book [15], which describes the mechanical properties of polymers based on nanostructure and morphology.

Many methods, mostly chemical and electrochemical methods, have been described for the preparation of conducting polymer nanocomposites, including layered materials and those containing CNTs [16-25]. The most important ones are:

a) Intercalation of the polymer or pre-polymer from solution
b) In-situ intercalative polymerization
c) Melt intercalation
d) Direct mixture of polymer and particulates
e) Template synthesis
f) In-situ polymerization
g) Sol-gel process.

It is possible to synthesize a uniform polymer hybrid using “in-situ polymerization method” of polymerizing organic monomers as well as forming an inorganic matrix by a sol-gel reaction. The merit of this method is that, compared to the organic polymer, the monomer has superior solubility and dispersibility, and hence it is easy to obtain a more uniform hybrid. The sol-gel reaction makes possible to incorporate the organic polymer segments in the network matrix of inorganic materials. The interaction between the organic polymer and the inorganic matrix in a polymer hybrid can be done by using:

i. Hydrogen Bonding
ii. π-π interaction
iii. Ionic interaction

The inorganic components can be three-dimensional framework systems, such as zeolites; two-dimensional layered materials, such as clays, metal oxides, metal phosphates, chalcogenides; and even one-dimensional and zero-dimensional materials, such as (Mo₃Se₃⁻)ₙ, chains and clusters. Nanocomposites based on clay and layered silicates have been widely investigated due to the availability of clay starting materials and their well-known intercalation chemistry [26]. Depending on the nature of the components (layered silicate/clay, organic cation and polymer matrix), the method of preparation and the strength of interfacial interactions between the polymer matrix and the layered silicate/clay, three different types of nanocomposites may be obtained, as illustrated in Fig.1(a).1.
As shown in Fig. 1(a), when the polymer is unable to intercalate between the silicate/clay sheets, a phase-separated composite i.e. conventional composite is obtained, whose properties stay in the same range as that of traditional microcomposites.

The field of Polymer-layered nanocomposites gained impressive attention due to their improved properties, like high moduli, increased strength heat resistance and biodegradability [27-39], compare to the pure polymer and conventional micro and macrocomposites. Polymer-layered nanocomposites are obtained by intercalation of the polymer (or a monomer subsequently polymerized) inside the galleries of the layered host. Examples include graphite, metal chalcogenides, clays, layered silicate (montmorillonite, hectorite, saponite, fluoromica, fluorohectorite, vermiculite and kaolinite) and layered double hydroxides. The structural family called 2:1 phyllosilicate is the most commonly used layered silicate in polymer nanocomposites [Fig. 1(a)].
In recent years, there has been extensive study of the factors which control whether particular polymer nanocomposites can be synthesized as an intercalated or exfoliated structure. These factors include the exchange reactions with organic and inorganic cations, the polarity of the reaction medium and the chemical nature of the interlayer ionic species. Despite their relatively large molecular weights, electronically conducting polymers can play the role of intercalated guest molecules inserted within the Vander Waals gaps of layered inorganic phases resulting in a special class of intercalative nanocomposites, termed as “organic-in-inorganic nanocomposites”.

Depending upon the nature of association between the inorganic and organic components, these nanocomposites can also be classified into two categories:

i. **Inorganic-organic (I-O) nanocomposites**
   In this section, Inorganic nanoparticles can be introduced into the matrix of a host-conducting polymer either by some suitable chemical route or by an electrochemical incorporation technique.

ii. **Organic-inorganic (O-I) nanocomposites**
   A second group of nanocomposite material is constituted by those in which the organic polymer is confined into the inorganic layers for a broad range of applications. Since the inorganic layered materials exist in great variety possessing a well defined, ordered intralamellar space potentially accessible by foreign species they can act as matrices or hosts for polymers, yielding interesting lamellar “organic-in-inorganic nanocomposite” material. The
insertion of conducting polymers in layered inorganic host material and other structurally organized environments is a topic of considerable interest.

1(a).3.2 Application of Nanocomposites

From the foregoing, it becomes evident that nanocomposite may provide many benefits such as enhanced properties, reduction of solid wastes and improved manufacturing capability, particularly for packaging applications. As it can be observed, the promising applications of nanocomposite systems are numerous, comprising both the generation of new materials and the performance enhancement of known devices such as fuel cells, sensors and coatings. Although the use of nanocomposites in industry is not yet large, their massive switching from research to industry has already started and is expected to be extensive in the next few years.

Metal and ceramic nanocomposites are expected to generate a great impact over a wide variety of industries, including the aerospace, electronic and military [40].

CNT-ceramic composites, on their turn, are reported [41] to be potential candidates for aerospace and sports goods, composite mirrors and automotive spares requiring electrostatic painting. Such materials have also been reported [42] to be useful for flat panel displays, gas storage devices, toxic gas sensors, Li⁺ batteries, robust but lightweight parts and conducting paints. Despite these possibilities, there are only limited examples of industrial use of nanocomposite, mainly due to the challenges in processing and the cost involved, particularly for non-structural applications. However, the intense research in both metal- and ceramic-based nanocomposites suggests that the days are not far off when they will be actually in use.

On the other hand, polymer-based nanocomposites are in the forefront of applications due to their more advanced development status compared to metal and ceramic counterparts, in addition to their unique properties. Their major impacts appear in battery cathodes [43] microelectronics [44], nonlinear optics [45], sensors [46] etc. They can also replace corrosion-prone metals in the building of bridges and other large structures with potentially lighter and stronger capabilities[47]. Regarding the variety of applications of polymer nanocomposites, prominent impacts over the automotive industry is more highlighted [48]. Porous polymer nanocomposites can be employed for the development of pollution filters [49]. A new high-performance
anode structure based on silicon-carbon nanocomposite materials could significantly improve the performance of lithium-ion batteries used in a wide range of applications from hybrid vehicles to portable electronics.

![Schematic of silicon-carbon nanocomposite granule formed through a hierarchical bottom-up assembly process.](Image courtesy of Gleb Yushin, from google)](image)

**Fig.1(a).3** Schematic of silicon-carbon nanocomposite granule formed through a hierarchical bottom-up assembly process.

Annealed carbon black particles are coated by silicon nanoparticles and then assembled into rigid spheres with open interconnected internal channels.

Some newly emerging applications of nanocomposites are:

i. Electronic and optoelectronic devices [50-52]

ii. Electrochemical energy storage [53-58]

iii. Electro-catalysis [59,60]

iv. Magnetic applications [61,62]

### 1(a).4 Conducting polymers

Conducting polymers were first discovered in 1976. In the mid 1970s, the first polymer capable of conducting electricity, polyacetylene, was reportedly prepared by accident by Shirakawa. In 1976, Alan MacDiarmid, Hideki Shirakawa, and Alan Heeger, along with a group of young students found that conductivity of polyacetylene increased by up to 6 orders of magnitude when reacted with iodine (from $10^{-4}$S/cm to $10^{2}$S/cm); this phenomenon, known as doping, is as a result of
charge carriers. Since 1976, a number of conducting polymers, namely polypyrrole, polythiophene, and polyaniline, become the focus of much study. The importance of conducting polymers is exemplified by the awarding of the 2000 Nobel Prize in Chemistry to MacDiarmid, Shirakawa, and Heeger, for the discovery and development of conducting polymers [63]. This created a new field of research and a number of opportunities on the boundary between chemistry and condensed-matter physics. Some idea of the conductivities (σ) of the material is given in Fig.1(a.4).

Fig. 1(a).4 Electrical conductivities (Scm⁻¹) of some polymers

Electrically conducting polymers are designated as the fourth generation of polymeric materials. They can be classified in to different types on the basis of conduction mechanism that renders electrical conductivity to polymers:

a) Conducting polymer composites
b) Organometallic polymeric conductors
c) Polymeric charge transfer complexes
Chapter 1

1(a) Inherently conducting polymers

Leading on from this breakthrough, many small conjugated molecules were found to polymerize, producing conjugated polymers, which were either insulating or semiconducting in the oxidized or doped state.

The present study deals with the inherently conducting polymers polyaniline and polypyrrrole, a brief history of these materials are given here.

1(a).4.1 Polyaniline (PANI)

The continuously growing interest in the study of PANI over the years is mainly because of its diverse, but unique properties of PANI, allowing its potential applications in various fields. Among all the conducting polymers, polyaniline is known for its:

a. Ease of synthesis
b. Environmental stability and
c. Easy to dope by protonic acids.

The term Polyaniline corresponds to a class of polymers having up to 1000 repeat units (also called mers) and was first reported in 1862. Polyaniline is the oxidative polymeric product of aniline under acidic conditions and has been known since 1862 as aniline black [64]. There are several reports of polyaniline found in the literature over the decades about the structure and constitutional aspect of aniline polymerization [65]. In the year 1968, Surville et al reported the proton exchange and redox properties with the influence of water on the conductivity of polyaniline[66]. Polyaniline can be synthesized by both chemical and electrochemical oxidative polymerization [67,68]. Polyaniline exists in four main oxidation states viz.

(i) Leucoemeraldine base
(ii) Emeraldine base
(iii) Emeraldine salt
(iv) Pernigraniline,

Schematic representations for which are shown in the Fig.1(a).5.

1(a).4.1.1 Synthesis of Polyaniline

The most common synthesis of polyaniline involves oxidative polymerization, in which the polymerization and doping occurs concurrently, and may be accomplished either electrochemically or chemically. Electrochemical methods tend
to have lower yields than chemical yields [69]. This research work involves chemical synthesis of polyaniline.

1(a).4.1.2 Chemical Synthesis

Synthesis of polyaniline by chemical oxidative route involves the use of either hydrochloric or sulfuric acid in the presence of ammonium peroxy-di-sulfate as the oxidizing agent in the aqueous medium as shown below [70-73]. The principal function of the oxidant is to withdraw a proton from an aniline molecule, without forming a strong co-ordination bond either with the substrate / intermediate or with the final product.
Polyaniline becomes conducting when the moderately oxidized states, in particular the emeraldine base is protonated and charge carriers are generated. This process, is generally called as ‘protonic acid doping’, which makes polyaniline so unique, as no electrons have to be added or removed from the insulating material to make it conducting.

1(a).4.2 Polypyrrole (PPy)

Among known conducting polymers polypyrrole is most frequently used in the commercial applications due to the high conductivity, long term stability of its conductivity and the possibility of forming homopolymers or composites with optimal mechanical properties. It is known for its stability in the oxidised state and interesting redox properties. Conducting polypyrrole can be prepared by various methods such as chemical, electrochemical, vapor phase etc.

1(a).4.2.1 Chemical Synthesis

Chemical polymerization of pyrrole was first reported in the year 1916 by Angeli and his group [74]. They synthesized polypyrrole by the oxidation of pyrrole with H₂O₂. PPy powder as obtained was amorphous in nature and was known as pyrrole black. Generally, pyrrole black have been prepared in presence of various oxidizing agents like H₂O₂, PbO₂, Quinones or O₃. The materials thus obtained by this method are mainly insulating in nature with room temperature conductivity 10⁻¹⁰ to 10⁻¹¹ Scm⁻¹, but after doping with halogenic electron acceptor, the conductivity rises to 10⁻⁵ Scm⁻¹[75]. Various metallic salts such as FeCl₃, Fe(NO₃)₃, Fe(SO₄)₃, K₃Fe(CN)₆, CuCl₂ etc have been employed to polymerize pyrrole with conductivity between 10⁻⁵ to 200 Scm⁻¹. Ferric salts are the most commonly used oxidizing agents for the synthesis of highly conducting PPy, scheme for which is given below in Fig1(a).7:

\[
\begin{align*}
n \text{Py} & + 2n \text{FeCl}_3 \rightarrow \text{PPy} + 2n \text{FeCl}_2 + 2n \text{HCl}.
\end{align*}
\]

**Fig.1(a).7 Reaction scheme for PPy chemical synthesis**
The transition metal ions, being the electron acceptor, probably forms a donor acceptor complex with the \( \pi \)-system of pyrrole at the chain initiation step as well as the polymer intermediate at the final re-aromatization step.

Apart from conducting polymers polyaniline and polypyrrole, a nonconducting polymer poly(methyl methacrylate) (PMMA) is used in this research work.

1(a).5 Poly (methyl methacrylate)

PMMA is a member of a family of polymers which chemists call acrylates, but the rest of the world calls acrylics. The first acrylic acid was created in 1843. Methacrylic acid, derived from acrylic acid, was formulated in 1865. The reaction between methacrylic acid and methanol results in the ester methyl methacrylate. The German chemists Fittig and Paul discovered in 1877 the polymerization process that turns methyl methacrylate into polymethyl methacrylate. Rohm and Bauer polymerized methyl methacrylate (MMA) into transparent sheets in 1932 [76]. Pure, atactic poly(methyl methacrylate) (PMMA) is an amorphous plastic with a high surface gloss, high brilliance, a clear transparency of 92\% and a refractive index of 1.49. PMMA is classified as a hard, rigid, but brittle material, with a glass transition temperature of 105°C. PMMA has good mechanical strength, acceptable chemical resistance, and extremely good weather resistance. PMMA has favorable processing properties, good thermoforming, and can be modified with pigments, flame retardant additives, UV absorbent additives, and scratch resistant coatings [77] PMMA can be produced using a variety of polymerization mechanisms. The most common technique is the free radical polymerization of MMA. The free radical polymerization of acrylates and methacrylates is a chain polymerization across the double bond of the monomer [Fig.1(a).8]. The free radical polymerization of MMA can be performed homogeneously, by bulk or solution polymerization, or heterogeneously, by suspension or emulsion polymerization. The free radical polymerization of MMA is the predominant industrial mechanism to produce PMMA [78, 79].
PMMA has many biomedical uses because of its low \textit{in-vivo} immune response. Today, new derivatives of methacrylates, acrylates and dimethacrylates have biomedical applications in bone cements, dental fillings, and hard and soft contact lenses. The biggest biomedical use of PMMA, due to its excellent optical properties as well as its biomedical inertness, is in the human eye as a permanent implant for the intraocular lens following cataract surgery. Hard and soft contact lenses, and optical spectacles for eyeglasses, are all made commercially from homopolymers and copolymers of PMMA [80,81].

\textbf{1(a).6 Ion exchange chromatography (IEC)}

Ion-exchange chromatography (or \textit{ion chromatography}, IC) is a process that allows the separation of ions and polar molecules based on their charge. It can be used for almost any kind of charged molecule including large proteins. This separation method is based on ion-exchange process occurring between the mobile phase and ion-exchange groups bonded to the support material. In highly polarize ion, additional non-ionic adsorption processes contribute to the separation mechanism. It is often used in protein purification, water analysis, and quality control. In ion-exchange chromatography, the insoluble matrix carries ionic charges that retard the movement of molecules of opposite charge. For eg. Depending on the choice of matrix, proteins can be separated according to their charge (\textit{ion-exchange chromatography}), their hydrophobicity (\textit{hydrophobic chromatography}), their size (\textit{gel-filtration}
chromatography), or their ability to bind to particular small molecules or to other macromolecules (affinity chromatography) as shown in Fig.1(a).9.

Fig.1(a).9 Three types of matrices used for chromatography

1(a).6.1 History

The phenomenon of ion exchange is not of a recent origin. Many million years ago it had occurred in various sections of the globe. In Egypt and Greece as well as in China, ancient people were clever enough to use some soils, sands, natural zeolites and plants as the tools for improving the quality of drinking water by way of desalting or softening. Francis Bacon in 1623 brought the intentional use of ion exchange, without knowledge of its theoretical nature. Ion methods have been in use since 1850, when H. Thompson and J. T. Way, researchers in England, treated various clays with ammonium sulfate or carbonate in solution to extract the ammonia and release calcium [82,83]. In 1927, the first zeolite mineral column was used to remove interfering calcium and magnesium ions from solution to determine the sulfate content of water. Gans [84] developed the basis for the synthesis and technical application of inorganic cation-exchangers at the beginning of the 20\textsuperscript{th} century. The modern version of IEC was developed during the wartime Manhattan Project. A technique was required to separate and concentrate the radioactive elements needed to make the atom bomb. Researchers chose adsorbents that would latch onto charged transuranium elements, which could then be differentially eluted. Ultimately, once declassified, these techniques would use new IE resins to develop the systems that are often used today for specific purification of biologicals and inorganics. In the early
1970s, ion chromatography was developed by Hamish Small and co-workers at Dow Chemical Company as a novel method of IEC usable in automated analysis. This later led to the formation of Dionex Corp (Dow-Ion Exchange) who led the market in IC equipment and developments. IC uses weaker ionic resins for its stationary phase and an additional neutralizing stripper, or suppressor, column to remove background eluent ions. It is a powerful technique for determining low concentrations of ions and is especially useful in environmental and water quality studies, among other applications.

1(a).6.2 Principle

Ion exchange chromatography retains analyte molecules on the column based on coulombic (ionic) interactions. The stationary phase surface displays ionic functional groups (R-X) that interact with analyte ions of opposite charge. This type of chromatography is further subdivided into cation exchange chromatography and anion exchange chromatography. The ionic compound consisting of the cationic species M+ and the anionic species B- can be retained by the stationary phase.

Cation exchange chromatography retains positively charged cations because the stationary phase displays a negatively charged functional group:

\[ R-X^+ + M^+ \rightleftharpoons R-X+M^+ + C^- + B^- \quad \cdots \cdots 1.1 \]

Anion exchange chromatography retains anions using positively charged functional group:

\[ R-X^- + M^- \rightleftharpoons R-X^-+M^- + A^+ + B^- \quad \cdots \cdots 1.2 \]

Ion-exchange equilibrium may be described by two theoretical approaches viz (i) Based on law of mass action, and (ii) Based on Donnan theory.

1(a).7 Ion-Exchange Materials

Ion-exchangers are classified on the basis of their nature and active exchangeable sites. Classifications of ion-exchangres are listed below:

1. Inorganic Ion-Exchange Materials
2. Organic Ion-Exchange Materials
3. Chelating ion-exchange materials
4. Intercalation Ion-Exchangers
5. ‘Organic-Inorganic’ Composite Ion-Exchange Materials
1(a).7.1 Applications of ion exchange

Applications for ion exchange have many current forms, and some of these could expand as increased awareness of ion exchange processes continues. In addition, as the field of materials engineering continues to produce an ever-increasing variety of substances, the potential for creating new, useful ion exchange materials grows.

![Ionic interactions between the charged molecules and ion exchange resin.](image)

**Fig. 1(a).10** Ionic interactions between the charged molecules and ion exchange resin.

The current uses of ion exchange are long and numerous, some important are listed below:

- An application that can hit close to home is in the treatment of water for drinking, use (commercial, industrial, and residential), and wastewater treatment.
- Ion exchangers can soften the water, deionize it, and even be used in desalination.
- Preparation of various acids, bases, salts, and solutions is also aided by ion exchange.
- The recovery of valuable metals is also possible with resins.
- Industrial drying of treatment of gases is accomplished often with ion exchange.
- The food industry uses ion exchange in a variety of ways, ranging from wine-making to sugar manufacture.
- In the medical world, dozens of important manifestations of the benefits of ion exchange can be found, from development and preparation of key drugs and antibiotics, such as streptomycin and quinine, to treatments for ulcers, TB,
kidneys, and much more. Ion exchange is used to prevent coagulation in blood stores and in dextrose, as well.

The list keeps growing with each passing year.

**1(a).8 Electroanalytical application of ‘organic-inorganic’ composite materials**

Research aimed at exploring and understanding the analytical and electroanalytical application of ‘Organic-Inorganic’ Composite Ion-Exchange Materials. Recent challenge is to analyse the threat to human life and other living things due to hazardous effect of environmental pollutants. The importance of monitoring environmental pollutants has recently led to increasing interest in the development of novel sensors for the detection of toxic metals.

**1(a).8.1 Toxic effect of heavy metal ions**

Human exposure to heavy metals has risen dramatically in the last 50 years, however, as a result of an exponential increase in the use of heavy metals in industrial processes and products [Fig 1(a).11]. The most often implicated in human poisoning are mercury, nickel, lead, arsenic, cadmium, aluminum, chromium and copper. Mercury and lead fulfils no essential function in the human body, it can merely do harm after uptake from food, air or water. In today's industrial society, many occupations involve daily heavy metal exposure, over 50 professions entail exposure to mercury alone like physicians, pharmaceutical workers, any dental occupation, cosmetic workers etc. Toxicity studies confirm that these metals can directly influence human behavior by impairing mental and neurological function, influencing neurotransmitter production and utilization and altering numerous metabolic body processes. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis.

Ion exchanger-incorporated potentiometric membrane sensors are well-established analytical tools routinely used for the selective and direct measurement of a wide variety of different ions in environmental samples. The key ingredient of any potentiometric ion-selective sensor is its ion-selective membrane.
1(a).9 Membrane: An Introduction

A complete definition of membrane is given by Soliner [85], according to him it is a phase or structure interposed between two phases or compartments, usually heterogeneous, acting as barrier to the flow of molecular and ionic species present in the liquids and for vapors containing two surfaces [86]. The term heterogeneous has been used to indicate the internal physical structure and external physico-chemical performance. From this point of view, most of the membranes in general are to be considered heterogeneous, despite the fact that, conventionally, membranes prepared from coherent gels have been called homogeneous. The heterogeneous precipitate ion-exchange membranes consists of suitable colloidal ion-exchanger particles as electroactive materials embedded in a polymer (inert) binder, i.e., poly(vinyl chloride) (PVC), epoxy resin (Araldite), or polystyrene, polyethylene, nylon etc., have been extensively studied as potentiometric sensors and used for the measurement of a wide variety of different ions, directly in complex biological and environmental samples [87,88] as it offers great advantages such as speed, ease of preparation and procedure, non-destructive analysis, wide dynamic range and low cost. Ion sensors employing inorganic ion exchangers have been reviewed by Arnold [89] and Buck [90].
Recently, composite materials are used for the fabrication of various electrometric sensors for analytical purposes [91,92].

The usefulness of a membrane in a mass separation process is determined by its selectivity, by its chemical, mechanical and thermal stability and its overall mass transport rate. The chemical nature of the membrane material is of prime importance when components with more or less identical molecular dimensions and similar chemical or electrical properties have to be separated. The chemical, mechanical and thermal stability of the membrane determines to a large extent its useful lifetime, especially when the feed solution contains strong solvents, strong oxidants and extremely low or high pH values, when the process has to be carried out at elevated temperatures or when frequent cleaning procedures of the membrane are required. The mechanical properties of a membrane are of special significance in pressure driven process such as reverse osmosis, ultra filtration, etc. It should be noted that plasticizer acts as membrane solvent affecting membrane selectivity and also provide mobility of the membrane constituents within the membrane phase.

1(a).9.1 Ion-Selective Electrodes (ISE)

1(a).9.1.1 Historical Background

Discovery of the glass electrode for hydrogen ions by Cremer in 1906 stimulated the making of chemical measurements with physicochemical instrumentation. James Ross and Martin Frant of Orion Research are the founding fathers of ISEs. The calcium and fluoride ISEs they developed in the mid-1960s were the big bang that started a new era in potentiometric analysis.

In the early 1960s, Erno Pungor published his first paper on AgI-based electrodes and filed a patent on heterogeneous selective membranes with his co-workers Klara Toth, Jeno Havas, and Geza Madarasz, which were the basis for the first commercial solid-state ISEs. Wilhelm Simon, an eminent organic chemist at ETH in Zurich (Switzerland), studied on the structure selectivity relationships of many synthetic ionophores, plasticizers, and additives allowed him to fabricate novel ISEs [93,94]. The idea to incorporate all membrane ingredients into a PVC matrix and control site density came from the work of Rene Bloch, Adam Shatkay, and H. A. Sharoff in 1967. The most important procedure for compounding, casting, drying, and mounting PVC sensor membranes was developed by J. D. Ron Thomas and Gwylm J.
Moody in 1970 [95]. Progress in the field has been described in (Ion-) Selective Electrode Reviews over 1979 to 1992 [96] and other reviews [97,98].

1(a).9.1.2 Theory

Ion-selective electrodes are mainly membrane-based devices; consist of perm-selective ion-conducting materials, which separate the sample from the inside of the electrode. On the inside is a filling solution containing the ion of interest at a constant activity. The membrane is usually non-porous, water insoluble and mechanically stable.

The Ion-Selective Electrodes (ISEs) are commonly known as “Ion Sensors” or “Electrochemical Sensors”. Depending on the nature of the used membrane material, the ion-selective electrodes (ISEs) can be divided into three groups: glass membrane, crystal or solid membrane, and polymeric or liquid membrane. Many ISEs are commercially available and routinely applied in various fields. This is a very simple and practical electroanalytical method, making the application of these devices trouble-free and useful. Schematic arrangement of an ISE measurement is shown in Fig.1(a).12.

1(a).9.2 Physico-chemical properties of ion-selective electrodes

The properties of an ISE are characterized by parameters like:

1) Membrane potential  
2) Detection limit  
3) Response time  
4) pH effect  
5) Selectivity  
6) Lifetime  
7) Reproducibility

Fig.1(a).12 Diagrammatic presentation of ISE set up.
Electrode response or membrane potential

The development and application of ion-selective electrodes (ISEs) continue to be exciting and expanding areas of analytical research [99]. The use of ion-selective electrodes depends on the determination of potentials. The membrane potential is expressed in equation:

\[
E_m = \frac{RT}{Z_A F} \left[ \ln \left( \frac{a_{A}^{2}}{a_{A}^{1}} \right) - (Z_Y - Z_A) \int_{1}^{2} a_{\pm} \, dt \ln a_{\pm} \right]
\]

Where \( A = \) counter ion, \( Y = \) co-ion, \( Z = \) charge on ions, \( t_Y = \) transference number of co-ions in the membrane phase, \( [a_A]_1 \) and \( [a_A]_2 = \) activities of the counter ions in the solution 1 and 2, \( a_{\pm} = \) mean ionic activity of the electrolyte.

If the membrane is considered to be ideally perm-selective membrane (\( t_y = 0 \)) then equation (1.1) takes the form of the well-known Nernst Equation as follows:

\[
E_m = \pm \frac{RT}{Z_A F} \ln \left( \frac{[a_A]_2}{[a_A]_1} \right)
\]

The membrane potential measurement is carried out using a cell set up of the following type:

**Solution 2**

<table>
<thead>
<tr>
<th>External Saturated Calomel Electrode (SCE)</th>
<th>Test or External Solution</th>
<th>Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( E_L(2) )</td>
</tr>
</tbody>
</table>

**Solution 1**

<table>
<thead>
<tr>
<th>Internal Solution</th>
<th>Internal Saturated Calomel Electrode (SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( E_L(1) )</td>
</tr>
</tbody>
</table>

The e.m.f. of this potentiometric cell is given by the following expression:

\[
E_{cell} = E_{SCE} + E_{L(2)} + E_m + E_{L(1)} - E_{SCE}
\]

where \( E_{SCE}, E_L \) and \( E_m \) refer to Calomel Electrode, junction and membrane potentials, respectively. On combining equation (1.1) and (1.2), the following equation takes the form-

\[
E_{cell} = E_{SCE} - E_{SCE} + E_{L(2)} + E_{L(1)} + \frac{RT}{Z_A F} \ln \left( \frac{[a_A]_2}{[a_A]_1} \right)
\]

For cation-exchange membrane,
Furthermore, the values of \( E_{L(1)} \) and \( E_{L(2)} \) are negligible (due to salt bridge in use), the cell potential in above equation may approximately be taken as membrane potential. The equation (1.5) reduces to:

\[
E_{cell} = E^0 + \frac{RT}{Z_A F} \ln [a_A]_2
\]

…………………… 1.8

It is quite clear from equation (1.6) that the cell potential would change with the change in concentration (or activity) of the cation in external or test solution 2. At 25 \(^\circ\)C, value of \(\frac{RT}{Z_A F}\) comes out to be 0.059/\(Z_A\) volts. The membrane is said to give Nernstain response if the slope of a plot between cell potential and log activity comes out to be 0.059/\(Z_A\) volts. A potentiometric sensor is said to be behaving in a Nernstian or close to Nernstian fashion, if the slope is \(\pm 1-2\) mV of the theoretical value. Below this range, it is sub-Nernstian and above it, it is hyper-Nernstian. Sensors, which are outside the Nernstian range, can still be useful analytically.

Pungor et al. [100-103] have discussed the parameters detection limit, pH effect and response time in details.

1(a).10 Electrical Properties of Materials

One of the most important aspects of a material is most probably its electrical property. This is because of the advances in the electrical properties that have put electronic and electrical appliances in our daily life. The electrical behaviours of the various materials are divers. In order to explore the electrical properties of materials, that is, their responses to an applied electric field, it is necessary to discuss the phenomenon of electrical conduction: the parameters by which it is expressed, the mechanism of conduction by electrons which involves the charge transfer within the composite matrix.

1(a).10.1 Four – probe resistivity measurement

Electrical conductivities of composite materials were determined from the measurement of resistivity of the samples using the four-probe method for
semiconductors. This is the most satisfactory method as it overcomes difficulties which are encountered in conventional methods of resistivity measurement (i.e., two probe), e.g., the rectifying nature of the metal–semiconductor contacts and the injection of minority carriers by one of the current-carrying contacts, which affects the potential of the other contacts and modulates the resistance of the material, etc. In this method, four sharp probes are placed on a flat surface of the material, the current is passed through the two outer electrodes, and the floating potential is measured across the inner pair. The experimental circuit used for measurements is illustrated schematically in Fig. 1(a).13.

![Schematic circuit presentation of four-probe set up](image)

**Fig. 1 (a).13** Schematic circuit presentation of four-probe set up

### 1(a).10.2 Electrical Conduction in Materials

Electrical conductivity ($\sigma$) used to specify the electrical character of a material. It is simply the reciprocal of the resistivity, or

$$\sigma = \frac{1}{\rho} \quad \text{...............1.9}$$

and is indicative of the ease with which a material is capable of conducting an electric current. Materials show electrical conduction due to the movement of charge carriers on application of voltage as given by the equation:

$$\sigma = qn\mu \quad \text{...............1.10}$$

Where $\sigma$ is electrical conductivity of material, $n$ is the number of charge carriers, $q$ is the charge and $\mu$ is drift mobility of charge carriers. Drift mobility characterizes the ease with which the charge carriers can move under the influence of applied...
material. Electrons and holes in the electronic contribute and cations in ionic conductors.

1(a).10.3 Applications of Electrically Conducting Polymers and Composites

Research shows that conducting polymers exhibit conductivity from the semiconducting range ($\sim 10^{-5}$ S/cm) right up to metallic conductivity ($\sim 10^4$ S/cm). With this range of electrical conductivity and low density coupled with low cost polymeric conductor pose a serious challenge to the established inorganic semiconductor technology. The commercial applications are based on the promise of a novel material with a combination of properties such as light weight, high processibility and good electrical conductivity. Some of the most important potential applications of conducting polymers are briefly discussed below:

- **Optical devices**
  
  Optics was certainly one of the first applications of hybrid materials [104-106]. Thus, organic: inorganic/ organic: organic hybrid materials with high transparency are expected to be new optical materials such as optical fiber, wave-guide and optical lens.

- **Electrochromic displays**
  
  This utilizes the electrochemical doping and undoping of conducting polymers. The phenomenon of electrochromism can be defined as the change of the optical properties of a material due to the action of an electric field. In architecture electrochromic devices are used to control the sun energy crossing a window. In automotive industry rearview mirrors are a good application for electrochromic system.

- **Electromechanical Actuators:**
  
  Conducting polymer actuators were proposed by Baughmann and coworkers [107]. Oxidation induced strain of polyaniline and polypyrrole based actuators has been reported.

- **Drug release systems:**
  
  Another application for conducting polymers is controlled release devices. Principle used in this application is potential dependence ion transport. This potential
dependence ion transport is an interesting way to deliver ionic drugs to certain biological systems. One can deliver selective ions depending on the requirement.

➢ **Polymeric batteries**

One of the applications of conducting polymers, which is also a focus of attention worldwide, is lightweight batteries. Amongst the conducting polymers, the use of conducting PANI blends and composites in rechargeable batteries such as lithium batteries is very promising. Recent years have witnessed aggressive interest in lithium batteries.

➢ **Sensors**

Since electrical conductivity of conducting polymers varies in the presence of different substances, these are widely used as chemical sensors or as gas sensors. Organic or inorganic semiconductors have been reported to change their conductivities when exposed to variety of organic and inorganic vapours [108-110], the composite materials were found to give more significant and reversible decrease in electrical resistance in comparison with sensors constructed solely of tin dioxide or polypyrrole.

Some other important applications of conducting composite materials are:

- Solar cells
- Conducting textiles
- Display devices
- Optoelectronics
- Adhesives
- Electroplating
- Bio-sensor
- Photovoltaic cell
- Photo catalysis
- Filler
Chapter 1

During the last 15 years, the development of ‘organic-inorganic’ hybrid materials has been an important enterprise for people from very diverse origins. Illustrative examples of this versatility are their high-added-value applications as coatings for corrosion protection and abrasion resistance, artificial membranes for ultra- and nano-filtration, pervaporation and gas separation, catalysts and nanoscopic reactors, adsorbents of toxic compounds, biomaterials for osteo-reconstructive surgery or ophthalmic, materials with specific optic, electrical and/or magnetic properties for telecommunications or information displays, etc.

One of the important electroanalytical application of these composites is their use to fabricate Ion-selective electrode (ISEs) for sensing toxic metal ions. The ability to make direct or indirect measurements in complex samples without concern about sample color or turbidity and the fact that such measurements require relatively inexpensive equipment make ISE based techniques attractive to scientists in many disciplines. A large number of ion-selective electrodes using ion-exchangers have been developed during the past 25 years. The research work on these ion-selective electrodes has begun in 1920’s but there systematic studies started after Pungor et al. in 1961.

Literature survey shows the rapid progress in these fields. Although its very difficult to compile all the results as numerous work has been done, but attempt has been taken to tabulate important of them.

Indeed, an exhaustive literature survey in this chapter puts into:

- Synthetic inorganic ion exchanger based on zirconium, titanium and cerium.
  [Table 1(b).1]
- Chronological overview of important ‘Organic-Inorganic’ Composite materials
  [Table 1(b).2]
- Chronological overview of important ISEs and their selectivity
  [Table 1(b).3]
Table 1(b).1
Synthetic ion-exchanger based on zirconium, titanium and cerium prepared so far & their salient features

<table>
<thead>
<tr>
<th>S.No</th>
<th>Ion exchanger</th>
<th>Nature / Empirical formula</th>
<th>Application</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Nano-zirconium vanadate</td>
<td>Amorphous Zr(OH)$_2$(HVO$_4$)$_2$·2H$_2$O</td>
<td>High thermal and radiation stabilities</td>
<td>111</td>
</tr>
<tr>
<td>2.</td>
<td>Zirconium(IV) antimonotungstate</td>
<td>-</td>
<td>Removal of iron metal</td>
<td>112</td>
</tr>
<tr>
<td>3.</td>
<td>Zirconium titanium phosphate</td>
<td>Crystalline</td>
<td>Proton conductance</td>
<td>113</td>
</tr>
<tr>
<td>4.</td>
<td>Zirconium vanadate</td>
<td>Zr(OH)$_2$(HVO$_4$)$_2$·2H$_2$O</td>
<td>Removal of cesium, cobalt and nickel</td>
<td>114</td>
</tr>
<tr>
<td>5.</td>
<td></td>
<td>Amorphous</td>
<td>Solid acid catalyst</td>
<td>115</td>
</tr>
<tr>
<td>6.</td>
<td>CdS/Mesoporous Zirconium titanum phosphate</td>
<td>Amorphous</td>
<td>Photocatalyst</td>
<td>116</td>
</tr>
<tr>
<td>7.</td>
<td>Cellulose acetate-Zr(IV) molybdophosphate</td>
<td>Amorphous</td>
<td>Separation of heavy metal ions</td>
<td>117</td>
</tr>
<tr>
<td>8.</td>
<td>Poly-o-methoxyaniline Zr(IV) molybdate</td>
<td>Electrically conducting</td>
<td>Cd(II) selective</td>
<td>118</td>
</tr>
<tr>
<td>9.</td>
<td>Zirconium titanate</td>
<td>Amorphous Zr/Ti = 1.18</td>
<td>Cs(I), Zn(II), Eu(III) selective</td>
<td>119</td>
</tr>
<tr>
<td>10.</td>
<td>Zirconium phosphate</td>
<td>Amorphous Zr(OH)$_2$(PO$_4$)</td>
<td>Cs(I), Rb(I) selective</td>
<td>120</td>
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<tr>
<td>11.</td>
<td></td>
<td>Amorphous ZrO(HPO$_4$)$_2$</td>
<td>Sr(II), Co(II) selective</td>
<td>121</td>
</tr>
<tr>
<td>12.</td>
<td></td>
<td>Amorphous Zr$_3$(PO$_4$)$_2$</td>
<td>Ni(II), Zn(II), UO$_2$(II) selective</td>
<td>122</td>
</tr>
<tr>
<td>13.</td>
<td></td>
<td>Amorphous Zr(HPO$_4$)$_3$·H$_2$O</td>
<td>Li(I), K(I), Cs(I) selective</td>
<td>123</td>
</tr>
<tr>
<td>14.</td>
<td></td>
<td>Crystalline Zr(HPO$_4$)$_2$·H$_2$O</td>
<td>Na(I), Ag(I), Ca(II), Sr(II), Ce(III) selective</td>
<td>124</td>
</tr>
<tr>
<td>15.</td>
<td>Zirconium (IV) tungstophosphate</td>
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<td>16.</td>
<td>Zirconium tungstophosphate</td>
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<td>Hg(II) Selective</td>
<td>126</td>
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<td>17.</td>
<td>Zirconium (IV) phosphate</td>
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<td>127</td>
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<td>18.</td>
<td>Zirconium phosphate hemihydrate</td>
<td>Amorphous ion exchanger</td>
<td></td>
<td>128</td>
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<td>19.</td>
<td>Tetracycline HCl sobbed Zr(IV) tungstophosphate</td>
<td>Chelating exchanger</td>
<td>La(III)</td>
<td>129</td>
</tr>
<tr>
<td>20.</td>
<td>Zr (IV) tungsstomolybdate</td>
<td>Amorphous (ZrO) (OH)$_2$ (H$_2$WO$_4$)$_4$ (H$_3$MoO$_4$)$_3$·8H$_2$O</td>
<td>Heavy toxic metals selective</td>
<td>130</td>
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<td>21.</td>
<td>Styrene Zr(IV) tungstophosphate</td>
<td>Amorphous</td>
<td>Phosphamidon Adsorption</td>
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<td>22.</td>
<td>Poly-o-toluidine Zr(IV)</td>
<td>Semicrystalline</td>
<td>Hg(II) selective</td>
<td>132</td>
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<tr>
<td>No.</td>
<td>Material Description</td>
<td>Structure</td>
<td>Selectivity</td>
<td>Page</td>
</tr>
<tr>
<td>-----</td>
<td>----------------------------------------------------------</td>
<td>-----------</td>
<td>---------------------------</td>
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<td>Ti(IV) iodovanadate</td>
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<td>Pb(II) selective</td>
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<td>24</td>
<td>Polyaniline Titanotungstate</td>
<td>-</td>
<td>Cs(I) ion selective</td>
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<td>25</td>
<td>Polyaniline Titanium(IV)phosphate</td>
<td>Semicrystalline</td>
<td>Methanol sensor</td>
<td>135</td>
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<tr>
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<td>Sodium iron titanate</td>
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<td>Titanium antimonite</td>
<td>Semi crystalline</td>
<td>V (II) selective</td>
<td>138</td>
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<tr>
<td>28</td>
<td>Titanium antimonite</td>
<td>Semi crystalline</td>
<td>H₂TiO₂SbO₃(OH)₂</td>
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<td>Titanium (IV) phosphate</td>
<td>Crystalline</td>
<td>Cu²⁺, Co²⁺ &amp; Ni²⁺ selective</td>
<td>140</td>
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<td>Titanium (IV) phosphate</td>
<td>TiO₁.26(OH)₀.₄₇(H₂PO₄)₀.₇₇(HPO₄)₀.₁₃·2.₃H₂O</td>
<td>Cu²⁺ &amp; Pb²⁺ selective</td>
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<td>Titanium (IV)tungstosilicate</td>
<td>Ti WP</td>
<td>Heavy metals selective</td>
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<td>32</td>
<td>Titanium(IV)tungstophosphate</td>
<td>Ti WSi</td>
<td>Heavy metals selective</td>
<td>143</td>
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<td>Titanium (IV) molybdosilicate</td>
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<td>Fe³⁺ &amp; Zn²⁺ selective</td>
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<td>Titanium arsenate</td>
<td>Amorphous</td>
<td>Pb(II), Cu(II), Zn(II), Cd(II) selective</td>
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<td>Titanium molybdate</td>
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<td>Pb(II), Ba(II), K(I) selective</td>
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<td>Silicotitanate</td>
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<td>Diffusion coefficients</td>
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<td>Titanosilicate ETS-4</td>
<td>Microporous</td>
<td>Cd(II) selective</td>
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<td>Triton X-100 based cerium(IV) phosphate</td>
<td>Fibrous</td>
<td>Hg(II) selective</td>
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<td>Polyaniline Ce(IV) molybdate</td>
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<td>Cd(II) selective</td>
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<td>Cerium(IV) iodotungstate</td>
<td>Crystalline</td>
<td>Separation of the ^⁸⁹Sr–⁹⁰Y pair</td>
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<td>Cerium tungstate</td>
<td>Amorphous</td>
<td>Co(II) &amp; Eu(III)</td>
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<td>Cerium arsenate</td>
<td>Micro-crystalline</td>
<td>Li(I), Na(I), Cs(I)</td>
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<td>Cerium phosphate sulphate</td>
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<td>Na(I), Ag(I), Sr(I), Ca(II)</td>
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<td>44</td>
<td>Ceric phosphate</td>
<td>Granular</td>
<td>Bi, Pb isotopes</td>
<td>155</td>
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<td>45</td>
<td>Acrylonitrile Cerium(IV) phosphate</td>
<td>-</td>
<td>-</td>
<td>156</td>
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Table 1(b).2
Chronological representation of important ‘Organic-Inorganic’ Composite materials prepared so far

<table>
<thead>
<tr>
<th>Year</th>
<th>Organic polymer</th>
<th>Inorganic material</th>
<th>Application</th>
<th>References</th>
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<tbody>
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<td>Titanotungstate</td>
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<td>Poly-o-toluidine</td>
<td>Stannic molybdate</td>
<td>Heavy metals</td>
<td>156</td>
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<tr>
<td></td>
<td>Polyaniline</td>
<td>Titanium(IV)phosphate</td>
<td>Methanol sensor</td>
<td>157</td>
</tr>
<tr>
<td></td>
<td>Polyaniline</td>
<td>Zirconium titanium phosphate</td>
<td>Hg(II) selective</td>
<td>158</td>
</tr>
<tr>
<td></td>
<td>Polypyrrole</td>
<td>Zirconium titanium phosphate</td>
<td>Th(IV) selective</td>
<td>159</td>
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<tr>
<td></td>
<td>Poly-o-methoxyaniline</td>
<td>Zr(1 V) Molybdate</td>
<td>Kinetic studies</td>
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<td></td>
<td>Polyaniline</td>
<td>Zirconium tungstoiodo phosphate</td>
<td>Cu(II) selective</td>
<td>161</td>
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<tr>
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<td>Poly-o-anisidine</td>
<td>Sn(IV) arsenophosphate:</td>
<td>Pb(II) selective</td>
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<td>Sn(IV) tungstate</td>
<td>Pb(II) selective</td>
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<td>Poly(methyl methacrylate)</td>
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<td>Pb(II) selective</td>
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<td>Clay</td>
<td>Reinforcing properties</td>
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<td>Ce(IV) molybdate</td>
<td>Cd(II) selective</td>
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<td>poly-o-methoxyaniline</td>
<td>Zr(1V) molybdate</td>
<td>Cd(II) selective</td>
<td>118</td>
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<td>Polyaniline</td>
<td>Palladium nanoparticles</td>
<td>Catalytical activity-oxidation of hydrazine</td>
<td>166</td>
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<td>Polyaniline</td>
<td>MnO₂ nanoparticles</td>
<td>Electrochemical capacitor</td>
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<td>CdS</td>
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<td>Polyaniline</td>
<td>Humic acid</td>
<td>Hg (II) selective</td>
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<td>Ag nanoparticles</td>
<td>Humidity sensing</td>
<td>170</td>
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<td>Polyaniline</td>
<td>Cu-montmorillonite</td>
<td>Electrical properties</td>
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<td>Polyaniline</td>
<td>Co₀.₅ Zn₀.₅ Fe₂O₄</td>
<td>Microwave absorption properties</td>
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<tr>
<td></td>
<td>Polyaniline</td>
<td>Magnetite</td>
<td>Magnetic properties</td>
<td>173</td>
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<td></td>
<td>Polyaniline</td>
<td>Chitosan</td>
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<td>Silica</td>
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<td>Selective for alkaline metal ions</td>
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<td>Polyaniline</td>
<td>Heteropolyanion</td>
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<td>Nylon-6,6</td>
<td>Sn(IV) phosphate</td>
<td>Hg(II) selective</td>
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<td>Acrylonitrile</td>
<td>stannic(IV) tungstate</td>
<td>Pb(II)selective</td>
<td>181</td>
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<td>Poly-o-anisidine</td>
<td>Sn(IV) phosphate</td>
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<td>Acrylamide</td>
<td>stannic silicomolybdate</td>
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<td>Dye adsorption</td>
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<td>Ammonium</td>
<td>Rb(I) and Cs(I) selective</td>
<td>186</td>
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<tr>
<td>Material</td>
<td>Function</td>
<td>Year</td>
<td></td>
<td></td>
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<tr>
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<td>----------</td>
<td>------</td>
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<tr>
<td>Molybdophosphate–calcium alginate</td>
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<td>Polyacrylamide</td>
<td>Apatite</td>
<td>Pb(II), UO₂(II) and Th(IV)</td>
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<td>B₂O₃/TiO₂ nano composite</td>
<td>Preconcentration and separation of cadmium</td>
<td>188</td>
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<td>Macroyclic diamide</td>
<td>Sulfur</td>
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<td>189</td>
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<td>Nafion</td>
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<td>190</td>
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<td>Poly (acrylic acid)</td>
<td>Chitosan</td>
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<td>191</td>
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<td>Poly(vinyl alcohol)</td>
<td>α-zirconium phosphate</td>
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**2008**

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<tr>
<td>Poly-o-toluidine</td>
<td>Zr(IV) phosphate</td>
<td>Hg(II) selective</td>
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<td>Cellulose acetate</td>
<td>Zr(IV) molybdophosphate</td>
<td>Heavy metal separation</td>
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<td>Polyacrylamide</td>
<td>Thorium (IV) phosphate</td>
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<td>Triton X-100</td>
<td>Cerium(IV) phosphate</td>
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<tr>
<td>Polyvinyl acetate</td>
<td>SiO₂</td>
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<tr>
<td>Carbon nanotubes modified by polyaniline</td>
<td>MnO₂</td>
<td>Enhanced electrochemical stability</td>
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<tr>
<td>Polynvinylpyrrolidone</td>
<td>Barium titanate</td>
<td>Dielectric properties</td>
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<td>Carbon black</td>
<td>Metallophthalocyanine</td>
<td>Organic vapors and NH₃ sensing</td>
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<tr>
<td>Polyaniline</td>
<td>TiO₂</td>
<td>QCM sensor</td>
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<tr>
<td>Poly(2,5-dimethoxyaniline)</td>
<td>WO₃</td>
<td>Humidity sensitive</td>
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<td>Polyaniline derivatives</td>
<td>Molybdenum trioxide</td>
<td>Aldehyde gases sensors</td>
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<td>PMMA</td>
<td>TiO₂</td>
<td>Organic vapor absorption</td>
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<td>Nafion</td>
<td>[(ZrO₂)·(SiO₂)₀·₆₇]</td>
<td>Proton conducting</td>
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<td>Parachlorophenol</td>
<td>Tin antimonate</td>
<td>Bi(III) and Cu(II) selective</td>
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<td>Zn–Al layered double hydroxide</td>
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**2007-2000**

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<tr>
<td>Poly(o-toluidine)</td>
<td>Th(IV) phosphate</td>
<td>Hg(II) selective</td>
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<tr>
<td>Poly(o-toluidine)</td>
<td>Sn(IV) phosphate</td>
<td>Hg(II) selective</td>
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<tr>
<td>Poly(o-toluidine)</td>
<td>Sn(IV) tungstoarsenate</td>
<td>Hg(II) selective</td>
</tr>
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<td>Poly(o-toluidine)</td>
<td>Th(IV) phosphate</td>
<td>Pb(II) selective</td>
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<tr>
<td>Poly(o-toluidine)</td>
<td>Sn(IV) tungstoarsenate</td>
<td>Cd(II) selective</td>
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<tr>
<td>Poly(o-toluidine)</td>
<td>Sn(IV) arsenophosphate</td>
<td>Pb(II) selective</td>
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<td>PMMA</td>
<td>Forsterite</td>
<td>Machining property</td>
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<td>Hydroxyapatite</td>
<td>Biomedical Applications</td>
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<td>PMMA</td>
<td>Clay</td>
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<tr>
<td>Poly(o-toluidine)</td>
<td>Manganese oxide</td>
<td>Used in capacitor</td>
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<tr>
<td>Porasil</td>
<td>8-Hydroxyquinoline</td>
<td>Metal ion</td>
</tr>
</tbody>
</table>
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---|---|---|---
PAN [1-(2-pyridylazo 2-naphthol)]  | Zinc silicate  | Pt(IV), Au(III)  | 220
Phenyl α & γ Zirconium phosphate  | Intercalated exchanger [α-Zr(PO₄)₂(H₂PO₄).2H₂O]  | 221
n-phenyl amine  | Zirconium phosphate  | -  | 222
Diethanol amine  | Tin(IV), Fe(III)  | -  | 223
Monoamine  | α-Sn(HPO₄)₂.H₂O  | -  | 224
Phenyl Zirconium diposphonate phosphate  | Cs(I)  | 225
p-chlorophenol & o-chlorophenol  | Zr(IV) tungstate  | -  | 226
Pyridinium Tungstoarsenate  | Rb(II), Cs(I)  | 227
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**Table 1(b).3**
Chronological representation of important Ion-selective electrode (ISE) prepared so far

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<th>Year</th>
<th>Material</th>
<th>Selectivity</th>
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<tr>
<td><strong>2010</strong></td>
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<tr>
<td>Polyaniline Zirconium titanium phosphate</td>
<td>Hg(II) selective</td>
<td>158</td>
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<tr>
<td>Polypyrrole Zirconium titanium phosphate</td>
<td>Th(IV) selective</td>
<td>159</td>
<td></td>
</tr>
<tr>
<td>Poly(methyl methacrylate)Ce(IV) molybdate</td>
<td>Cd(II) selective</td>
<td>164</td>
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<tr>
<td>Poly-o-anisidine Sn(IV) arsenophosphate:</td>
<td>Pb(II) selective</td>
<td>162</td>
<td></td>
</tr>
<tr>
<td>Poly-o-Toluidine Sn(IV) tungstate</td>
<td>Pb(II) selective</td>
<td>163</td>
<td></td>
</tr>
<tr>
<td>Polyaniline Humic acid</td>
<td>Hg (II) selective</td>
<td>169</td>
<td></td>
</tr>
<tr>
<td>Carbon composite PVC-based membrane</td>
<td>Pb(II)</td>
<td>229</td>
<td></td>
</tr>
<tr>
<td>1,3-bis(N′-benzoylthioureido)benzene and 1,3-bis(N′-furoylthioureido)benzene</td>
<td>Pb(II)</td>
<td>230</td>
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<tr>
<td>2-amino-1,4-naphthoquinone</td>
<td>Indium(III)</td>
<td>231</td>
<td></td>
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<tr>
<td>3-deoxy-d-erythro-hexos-2-ulose bis (thiosemicarbazone)</td>
<td>Ba(III)</td>
<td>232</td>
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<tr>
<td>1-(2-thiazolylazo)-2- naphthol</td>
<td>Tm(III)</td>
<td>233</td>
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<tr>
<td>1-phenyl-3-pyridin-2-yl-thiourea</td>
<td>Fe(III)</td>
<td>234</td>
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<tr>
<td>5-(4′-nitrophenylazo)25,27-bis(2-propyloxy)26,28-dihydroxycalix[4]arene</td>
<td>Cs(I)</td>
<td>235</td>
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<tr>
<td>N,N′-propanediamide bis(2-salicylideneimine)</td>
<td>Al(III)</td>
<td>236</td>
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<tr>
<td>Chelating ion exchanger</td>
<td>Pb(II)</td>
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<tr>
<td>1,12,14-triara-5,8-dioxo-3(4),9(10)-dibenzoylcyclopentadeca-1,12,14- triene</td>
<td>Zn(II)</td>
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<tr>
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<td>Ce(IV)</td>
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<tr>
<td>Substance</td>
<td>Metal</td>
<td>Year</td>
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<tr>
<td>2-amino-3-(α-N-phenylmethyl-2′-amino-1′,4′-naphthoquinonyl)-1,4 naphthoquinones</td>
<td>Ga(III)</td>
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<tr>
<td>N,N'-bis(4-hydroxy salicylidene)-1-3-phenylenediamine</td>
<td>Praseodymium</td>
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<td>1,1'-(iminobis(methan-1-y1-yl-1-yldene))dinaphthalen-2-ol</td>
<td>Fe(III)</td>
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<tr>
<td>Trihexadecylalkylammonium iodides</td>
<td>Iodide selective</td>
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<td><strong>2009</strong></td>
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<tr>
<td>Nylon 6,6-Sn(IV) phosphate</td>
<td>Hg(II) selective</td>
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<td>Carbon composite–PVC based membrane</td>
<td>Chromium</td>
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<tr>
<td>Sulfur-containing macrocyclic diamide</td>
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<td>Benzo-substituted macrocyclic diamides</td>
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<tr>
<td>Pendant armed macrocycle</td>
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<tr>
<td>N-Phenylaza-15-Crown-5</td>
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<tr>
<td>Coated graphite electrode</td>
<td>Gd(III)</td>
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<tr>
<td>1,3-bis(2-methoxy benzene)triazene</td>
<td>Hg (II) selective</td>
<td>250</td>
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<tr>
<td>1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide</td>
<td>Hg(II) selective</td>
<td>251</td>
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<tr>
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<td>Dy(III)</td>
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<tr>
<td>Bis-benzilthiocarbohydrazide</td>
<td>Fe(III)</td>
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<tr>
<td>N,N'-bis (salicylidene)-1, 2-cyclohexanedi amine</td>
<td>Al(III)</td>
<td>254</td>
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<td><strong>2008</strong></td>
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<tr>
<td>Poly-o-toluidine Zr(IV) phosphate</td>
<td>Hg(II) selective</td>
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<td>PVC membrane-based thoron</td>
<td>Zirconium</td>
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<td>N, N-Dimethyl-N', N''-bis(4-methoxyphenyl)phosphoramidate</td>
<td>Terbium(III)</td>
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<tr>
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<td>Co(II)</td>
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<td>Cd(II) Schiff base complexes</td>
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<td>Poly(4-vinyl pyridine)</td>
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<td>Polyaniline–carboxylated PVC composites</td>
<td>Ammonia sensor</td>
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<td><strong>2007-2000</strong></td>
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<td>Polyaniline Sn(IV) arsenophosphate</td>
<td>Pb(II)</td>
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<td>Poly-o-toluidine Th(IV) phosphate</td>
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<td>Polyaniline Sn(IV) tungstoarsenate</td>
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<td>Polyaniline Sn(IV) tungstoarsente</td>
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From the literature survey, it can be inferred that ‘organic-inorganic’ composite has given fire to the research of composite materials. Furthermore, the explosive growth in computer power during the last 15 years helps materials engineers work much more efficiently in developing useful compounds. This literature review summarized the most considerable ISEs practical applications concerning the anionic and cationic determination. Rapidity and simplicity in operation and preparation, low cost, comparatively fast responses, very low detection limit, wide dynamic ranges and satisfactory selectivity were among the ISEs advantages.
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