# **Chapter 1**

General introduction to sensor materials, scope and objectives

#### **1.1 Introduction**

Global research and development (R&D) activities in the field of artificial sensors have expanded enormously during last three decades in terms of financial investment, published literatures, and the number of active researchers for identification and control of tastes and smells of materials used for living. The control and monitoring of toxic gases and vapors and other contaminations of industrial effluent gases and liquids and run-off from agriculture fields have become the crying need of the present time. Thus very useful sensor devices for environmental, biochemical and medical technology have been an utmost need to combat the challenges. In this regard, tremendous efforts have been put forth in the field of sensor researches. An artificial sensor is basically maneuvered to provide information about our physical, chemical, and biological environment.

Amongst the five senses of human such as touch, sight and sound (physical senses), senses of taste and smell (chemical senses) are the most critical and difficult to reproduce, as the sensing mechanisms of these two senses in biological system are not yet fully understood. In particular, the research and development of an artificial taste sensor is somewhat behind that of artificial odour sensor due to the complex human gustatory system and the intricate interactions of large number of taste related substances [1].

At the advent of the modern civilization accompanied with the complexity of life, malnutrition, allergy, chronic diseases, stress-induced heart diseases and obesity, etc. have become very alarming for the potential growth of human civilisation. Therefore, the selection of newer materials as food supplements and additives with proper hygiene, soothing smell or fragrance and particularly good tastes of food, drinks and pharmaceutical drugs have become extremely important. So also is required for the security reasons to determine the smells and tastes for preventing ingestion of toxic substances and different other health-incompatible or uncomfortable newer materials. Also as there is a requirement of huge quantity of foods, drinks and beverages for humans with proper quality, it has become very essential to manufacture that huge quantity of foods, drinks, beverages and drugs with the precise control of tastes and hygiene in automatic plants. Hence the use of artificial sensors for monitoring and control of the tastes and smells of all those items have become very essential during automated processing or manufacturing. Raw foods and drinks are natural which are neither all beneficial irrespective of tastes nor all good to the taste irrespective of benefits.

Over the last few decades, sensor devices were developed using classical semiconductors [2], solid electrolytes [3], insulators [4] and metals [5]/metal oxides [6]. Polymer based sensors [7, 8] and actuators [9] have gained a tremendous importance in sensor technology. Polymer based chemical sensors [10] and biosensors [11, 12], which are also a kind of chemical sensor, measure chemical substances by means of biomaterials or related materials [13]. An artificial electronic taste sensor composed of several kinds of lipid/polymer membrane [14], closely mimicking the mammalian tongue, was fabricated. The artificial taste sensors are all far from reproducing the human senses and most of them are for qualitative analysis used particularly for assessment of taste [15], freshness [16] and safety [17] of foods and drinks [18]. The key to a successful artificial tongue may be found in smart taste sensors consisting of chemical sensors using intellectual data processors [19, 20] and pattern recognition technique [21]. The multichannel sensor device was further miniaturized by using FET (flied-effect transistor), which gives the same characteristics as the above taste sensor by measuring the gate-source voltage [22].

Polymers have attracted serious attention of the modern scientists and technologists due to the tremendous development of modern polymeric materials. Polymers have gained much importance in the construction of sensor devices by virtue of their tailorability with different functional groups for physical and chemical interaction with the environment. Polymers possess easy processability in regard to their physical forms like film, powder, liquid, etc. shape and other physical properties. Although a majority of the polymers are unable to conduct electricity, their insulating properties are utilized in electronic industry. It has been found in literature that polymers have acquired a major position as materials in various sensor devices among other materials. Either some intrinsically conducting polymer is being used as coating/encapsulating materials on electrode surfaces or non-conducting polymers are being used for immobilization of specific receptor agents in the sensor device.

#### **1.2 Principles of sensing**

The sensory organs of human or any living system, which collect the information from the environment, are responsible for sensing all sorts of basic parameters of the environment required particularly for safety and security of the species. The basic need for survival is to sense the inconvenient changes of the basic environmental parameters like temperature, pressure, vibrations, light or radiations, taste and smell of materials, etc. The degree and sensitivity of sensing vary from one creature to the other depending on the physical and biological features of the creatures.

However, the basic principle is similar in all the creatures. The changes in the environmental parameters, inconvenient to the particular species, shall be initially sensed by the specific and respective sense organs of that creature. Then the received information shall be communicated through the nervous system to the intelligent system present in the brain of that creature and analysed there itself. The output information and hence the command shall be transmitted for execution to the respective functional organs of the creatures for protective measure and the whole of the process shall be memorised in the memory system of the creature. In majority of the cases, the different parameters and principles of sensing present in living systems are being mimicked in artificial sensor devices for convenience. In this regard, it is convenient to mention that different sensing systems used for identifying different senses make use of different basic principles of transduction as discussed earlier but different in receiving and processing.

Depending on the mode of transduction or the recognition element used in the sensor device the sensing principle can be classified into three broad categories: electrochemical, electromagnetic and thermal. Electrochemical sensing principle can be further subdivided into amperometry, conductometry and potentiometry. Optical and acoustic measurements come under electromagnetic principles. Detail discussion on principles of these various categories is beyond the scope of this thesis. Sensing of tastes of food materials comes under potentiometry, Voltametry and conductometry principles. In a taste sensor device, basically an open circuit potential is measured across a membrane, which is the actual recognition element in the sensor device. Some electrolyte

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solution, viz., KCl remains in touch with the both side of the membrane electrode. The substance (may be electrolytic or non electrolytic), for which the taste measurement is required, is added to this electrolyte solution on one side of the membrane electrode. Addition of such taste substance to the electrolyte solution, initially present, alters the electric potential across the membrane. Variation in the concentration of the taste substance varies the potential and hence a potential-concentration pattern is obtained. Recently a new principle, viz., impedentiometry technique has been reported for the measurement of taste by an electronic tongue, which measures variations of electric impedance of the polymer membrane in contact with the solution of the substance for taste measurement [23]. A general principle of sensing of an analyte is shown in Figure 1.1.



Figure 1.1: A general sensing principle

## 1.3. Materials in sensor devices

## **1.3.1 Classical materials**

The principle of solid-state sensor devices is based on their electrical response to the chemical environment for which the sensing measurement needs to be done. Classical semiconductor materials, solid electrolytes, insulators, metals and catalytic materials, different types of organic membranes are normally used in the fabrication of solid-state sensors. Catalytic reactions helps functioning of such solid-state sensors, for example, sensors based on semi conducting oxides [24]. Either the semiconductor oxide or an externally added catalyst provides sensitivity, selectivity and rapid response to changes in composition of the ambient gas/vapor. Si, GaAs based semiconductor sensor devices were constructed for detection of  $H^+$  ion,  $O_2$ ,  $CO_2$ ,  $H_2S$  and propane gases [25]. Semiconducting  $SnO_2$  was used for detection of reducing gases in air [26]. Ytria (Y<sub>2</sub>O<sub>3</sub>) stabilized zirconia  $(ZrO_2)$  [27] was used for the detection of oxygen in exhaust gases of automobiles, boilers, etc. Ion-exchange membranes [28-31], neutral carrier membranes [32-34] and charged carrier membranes [35,36] were used for the detection of various ions. Apart from inorganic semiconductor materials, organic semiconductor materials [37-40], viz., polyphenyl acetylene, pthalocyanine, polypyrrole, polyamides and polyimides were used for the detection of gases like CO, CO<sub>2</sub>, CH<sub>4</sub>, NO, NO<sub>2</sub>, NH<sub>3</sub> and various chlorinated hydrocarbons.

# **1.3.2** Polymers as sensing materials

# 1.3.2.1 Different useful aspects of polymers in sensor applications

Polymers have found wide applications in various sensor devices. Special characteristics of polymers, which have placed them as most suitable materials today in various sensor applications, are good film forming ability, easy processability and tailorability. Although majority of polymers are electrically insulating in nature but some polymers having extended  $\pi$ -electron conjugation have found most important place in sensor applications. Due to having high tailorability, chemically modified polymers, polymer electrolytes, copolymers, polymer nanocomposites, polymer blends, interpenetrating polymer

networks (IPN) and both doped and undoped conducting polymers are available today for providing improved sensor properties. **Table 1.1** shows some examples of polymers used in various sensor applications. Elaborate information on application of polymers in the fabrication of different sensor devices can be available from one of our review articles [41]. Utilizing polymers in sensor devices needs some understanding in polymer science and technology. Since there is no scope for elaborate discussion on these aspects, it will be appropriate here providing some basic information related to polymer classification, synthesis and modification, etc.

Sensor	Polymers	Fields of applications	Special features
Biosensor	Polyaniline	Estimation of glucose, urea, triglycerides	Electrochemical deposition of polymer and enzyme immobilization
	Nafion	Estimation of glucose	Sensor based on polymer modified electrodes optimized by chemometrics method
Chemical	Polyaniline and its	Sensing aliphatic	Extent of change governed by
sensor	derivatives,	alcohols	chain length of alcohol and its
	Polyvinyl pyrrolidone,		chemical
	Polyacrylamide		
Ion	Polyvinyl chloride,	Detection of sodium ion	All-solid-state ion-selective
selective	Polyelectrolytes		electrode based on calixerene
sensor			ionophore in PVC membrane
			with polypyrrole solid contact
pH sensor	Polyaniline	pH sensing	Optical method
Odor	Poly (3-ethylthiophen),	Discriminate among	Doping agents used
sensor	Polypyrrole,	different virgin olive	
	Polyaniline	oils	
Gas sensor	Polyaniline,	Sensing $CO_2$ , $N_2$ , $CH_4$	Nanocomposites of iron oxide
	Polypyrrole	gases at varying	polypyrrole were prepared by
	nanocomposite	pressures	simultaneous gelation and
TT 114			polymerisation
Humidity	Polyvinyl alcohol,	Optical humidity	Crystal violet and Methylene blue
sensor	rylate)	sensing	are incorporated in PVA/H <sub>3</sub> PO <sub>4</sub>
Optical	Polyvinyl alcohol,	Optical sensing of	Fluorescence quenching of
sensor	Polyvinyl chloride,	nitro-aromatic	benzo[K]fluoranthene in PVA
	poly(tetrafluoroethylene),	compounds	film
	Nafion <sup>®</sup> , Nylon		
Taste	Polyvinyl chloride,	Can detect sour, salty,	Sensing membrane was prepared
sensor	polyvinyl alcohol,	bitter, sweet and umami	immobilizing lipids in PVC.
	polyaniline,		
	poly (m-aminophenol)		

Table 1.1: Few exan	ples of polymers	used in different	types of sensors	[41].
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## 1.3.2.2 Classification of polymers

Polymers are classified according to their origin, thermal response, mode of formation, line structure, application, tacticity and crystallinity, etc. From the genesis point of view there are three classes: natural polymers, semisynthetic and synthetic polymers. The sources of natural polymers are plants and animals. Common examples are: natural rubber, cellulose, natural silk, proteins, starch, etc. Semisynthetic polymers are basically chemically modified natural polymers. Regenerated cellulose, cellulose nitrate, esters and ethers of cellulose and halogenated natural rubbers are few examples.

Synthetic polymers are artificially prepared from different organic compounds, known as monomers, which are obtained as by-products of petrochemicals. Polyethylene, polystyrene, polyvinyl chloride, polyacrylonitrile, polycarbonate, polyaniline, polyvinyl alcohol, polyesters, phenol-formaldehyde resins, styrene butadiene rubber, polychloprene rubber, nitrile rubber, butyl rubber, silicone rubber, polytetrafluroethylene, etc. are examples of synthetic polymers. On the basis of application and physical properties polymers are classified into rubbers, plastics and fibers. Depending on the degree of alignment of molecules, i.e., on the degree of crystallinity, the same polymer can be converted to plastic, rubber or fiber. The order of their crystallinity is fibers > plastics > rubbers. Based on the mode of formation, the polymers are classified as addition polymers and condensation polymers. On the basis of thermal response, polymers are classified as thermoplastics and thermosets. Thermoplastic polymers soften on heating and hardens on cooling whereas, thermoset polymers set permanently to a three-dimensional network structure on heating but once formed they do not soften further on cooling.

# **1.3.3 Principles of polymer formation**

One of the most important advantages of polymers over other classical materials used in sensor devices is their ability of *in situ* formation/deposition directly from respective monomers. Polymers are, in general, prepared/synthesized following two basic principles, viz., addition polymerization and condensation polymerization.

# 1.3.3.1 Addition polymerization

Addition polymerization is applicable to olefinic or vinyl monomers having double bonds  $(CH_2=CHX)$ . Some initiator is required to initiate the polymerization by opening the double bond. The sequences of events that occur during this polymerization are: initiation, propagation and termination. This polymerization is very fast and formation of one polymer molecule completes from its initiation to termination within a fraction of second time. The termination of growing chain occurs either by combination or disproportionation reactions. Scheme 1.1 shows radical polymerization of monomers containing olefinic unsaturation.

## **Initiator decomposition:**

$$I \xrightarrow{k_d} 2R^{\cdot}$$

Where, I denotes initiator molecule and  $R^{-}$  is initiator radical and  $k_{d}$  is rate constant for initiator decomposition.

#### **Initiation:**

$$R^{\cdot} + M \xrightarrow{k_i} RM_1^{\cdot}$$

Where, M is monomer,  $k_i$  is initiation rate constant and  $RM_1^i$  is initiated monomer radical.

# **Propagation:**

 $RM_{1}^{\cdot} + M \xrightarrow{k_{p}} RM_{2}^{\cdot}$   $RM_{2}^{\cdot} + M \xrightarrow{k_{p}} RM_{3}^{\cdot}$   $RM_{n-1}^{\cdot} + M \xrightarrow{k_{p}} RM_{n}^{\cdot}$ 

Where,  $RM_2^i$ ,  $RM_3^i$ ,  $RM_n^i$ , etc. are growing polymer chain radicals formed during propagation.  $k_p$  is rate constant for chain propagation.

# **Termination:**

$$RM_{m}^{\cdot} + RM_{n}^{\cdot} \longrightarrow R - M_{m+n} - R$$
 (Dead polymer)  
 $\xrightarrow{k_{tc}} RM_{m} + RM_{m}$  (Dead polymer)

Where,  $k_{tc}$  is the rate constant for termination by coupling of two growing chain radicals and  $k_{td}$  is the rate constant for termination by disproportination of two growing chain radicals.

Scheme 1.1 Addition polymerization of olefinic monomers

## 1.3.3.2 Condensation polymerisation

Condensation polymerization occurs by reaction between two reactive functional groups attached to a molecule used for polymerization. For condensation polymerization to occur at least two different reactive functional groups should be present in one compound or two different compounds. Exclusively a linear polymer will be formed if two bifunctional monomers are reacted in stoichiometric quantity. During condensation of two functional groups of opposite nature a biproduct molecule is eliminated. These ways monomers are converted in steps to dimer, trimer, tetramer, pentamer and so on till adequate length of the molecule is achieved beyond a threshold value. For this reason this type of polymerization is known as step polymerization, which is slow in nature as compared to addition polymerization. One typical example of a condensation polymerization to form a polyester is shown below:

# $n \text{ HO-R-OH} + n \text{ HOOC-R'-COOH} \longrightarrow \text{HO-[ROOC-R'-COO]-H} + (2n-1) \text{ H}_2\text{O}$

# **1.3.4 Polymerization techniques**

Polymers can be prepared by any of the following major techniques [42]. These techniques are followed for both laboratory preparation and commercial manufacture of different polymers.

## 1.3.4.1 Bulk polymerization

In bulk polymerization the polymer is formed from its monomer in presence of a suitable monomer-soluble initiator without using any diluent. This technique provides purest form of polymer. Thus, the polymer produced will be free from contaminants excepting traces of unreacted monomers. The polymer formed gets soluble in the monomer and consequently the viscosity of the polymer-monomer mass increases with increase in the extent of polymerization. As a result proper heat transfer system should be used in order to avoid runaway reaction and deterioration of the quality of the product.

## **1.3.4.2 Solution polymerization**

This is a homogenous polymerization system. In this polymerization technique the monomer is dissolved in a suitable solvent including the initiator. During polymerization the polymer gets dissolved in the solvent. Due to the presence of the solvent the viscosity of the polymer solution remains controlled and using a condenser can easily do heat transfer. This also allows more efficient agitation of the system effecting better heat dissipation. Solution polymerization method often involves handling of flammable or hazardous solvents. As complete removal of the solvent used may not occur, purity of the polymer may be inferior as compared to that obtained by bulk polymerization. Solution polymerization is advantageous in cases where polymer has to be applied in solutions, such as paints and surface coatings applications, etc.

# **1.3.4.3 Suspension polymerization**

This is a case of heterogeneous polymerization in contrast to two previously described techniques. This technique involves dispersion of the liquid monomer into tiny droplets (>  $10^{-4}$  cm) in a large continuous mass of a dispersion medium, which is immiscible with the monomer, by efficient agitation. Being cheapest, water is invariably used as the dispersion medium for all water insoluble monomers because of ready availability, non-toxic nature, ease of storage and handling without the necessity of recovery. But the boiling point of water limits the polymerization temperature of vinyl polymerizations at

100 °C. A low concentration of water-soluble polymer like carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA), gelatin, etc., is used as stabilizers to prevent the suspended droplets to coalesce together during the intermediate course of polymerization. In suspension polymerization, monomer-soluble initiators, e.g., organic peroxides, hydroperoxides or azocompounds, etc. are used. Thus each tiny droplet behaves as a miniature bulk polymerization system. Finally, polymers appear as tiny beads looking like pearls, which are filtered, washed properly to remove the stabilizers as far as possible, and dried.

#### 1.3.4.4 Emulsion polymerization

This is also a heterogenous polymerization technique. In emulsion polymerization, a monomer is emulsified in water as the dispersion medium with the help of a suitable emulsifier. Here also the monomer should be immiscible with water and water soluble initiator should be taken. In general, this technique provides fastest polymerization rate and highest molecular weight as compared to other techniques. The monomer is dispersed in fine droplets ( $< 10^{-4}$  cm) in water with a soap or detergent as emulsifier by agitation to obtain a monomer emulsion. Fatty alcohol, e.g., cetyl alcohol can be used to minimize fluctuations in surface tension. A low concentration of water-soluble polymer like carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA), gelatin, dextran etc., is used as emulsion stabilizers. Using selected efficient redox initiator systems; emulsion polymerization is conveniently done at ambient or slightly elevated temperatures (5-50 °C) giving simultaneously very high rates and degrees of polymerization. After polymerization to optimum conversion, appropriate dose of a short-stop or inhibitor is added to stop further conversion. Breaking the emulsion by using salt or acid, coagulating, filtering, washing and drying, the polymer is isolated. This technique is extensively employed for the polymerization of isoprene, butadiene, vinyl monomers (like vinyl chloride, vinyl acetate, styrene, various acrylates and methacrylates) and for making different copolymers of these monomers and other related monomers.

#### **1.3.4.5 Electrochemical polymerization**

Electrochemical polymerization is done for the synthesis of conducting polymers for direct deposition of the polymer on the electrode or a suitable substrate. Conducting polymer films [43] were grown electrochemically by anodic oxidation of a solution containing the monomer and a supporting electrolyte salt. It is usually carried out in a single compartment cell with a three-electrode system containing a working electrode (Pt or any other electrodes according to requirement), a reference electrode (calomel electrode) and a secondary or counter electrode (Pt, Ni or carbon). The polymer film gets deposited on the working electrode. Although organic solvents can be used in electrochemical polymerizations, aqueous solutions of monomers are also convenient. Oxidation can be accomplished by different methods, viz., under a constant potential, under a constant current or by a cyclic voltametry. The deposited polymer film is usually a dense film, which can sometimes be separated from the electrode as a freestanding flexible film.

## 1.3.4.6 Plasma polymerization

This technique is also used for direct deposition of a thin conducting polymer film on a substrate. Plasma polymerization [44] is a method of preparation of polymers by using plasma state of monomers, or reactive species created in the plasma chamber. The plasma used in the formation of polymeric materials can be either 'low temperature plasma' or 'low pressure plasma', where thermal equilibrium is not maintained among electrons, ions and neutral species. Low temperature plasma can be generated in various ways, viz., electric glow discharge created by using power sources as varied as DC and microwave, which is the most practical for the formation of polymeric materials in laboratories and in industrial applications. In low-pressure plasma, the population of ions is less than the neutral species. There are two major categories of plasma polymerization: plasma-state polymerization and plasma-induced polymerization. Plasma-state polymerization is the condensed phase polymerization of monomers (liquid and solid) initiated by the action of plasma.

This process is used in polymerization of vinyl monomers (like styrene, acrylic acid, etc.) and the saturated vinyl compounds (like ethyl benzene, propionic acid, etc.).

## **1.3.5 Chemical modification of polymers**

For application in sensor devices, the polymers can be suitably modified according to the need in a variety of ways like, isomerizations, additions, grafting, cross-linking, chelations, substitutions, eliminations and chain cleavages [45]. Suitable functional group can be substituted on a substrate polymer to make it suitable for a specific application. Chlorination, esterification and hydrolysis, amination and quaternization, Friedel-Crafts reaction, sulphonation and phosphorylation are some of the examples of substitution reactions for polymer modification. For application in sensor devices chemically modified polymers can be cast into films or membranes or the formed films/membranes can be chemically modified suitably using appropriate reagents, techniques and conditions. Such modified polymers can also be deposited on an electrode surface by using a solution of the polymer in an appropriate solvent. Similarly, a water soluble polymer film can be made insoluble by cross-linking of the polymer molecules in the film by using a suitable cross-linking agent.

# 1.3.6 Preparation of polymer film

It is an important technique needed for the fabrication of a sensor device using polymer. Film preparation is easy with polymers having adequate solubility in a suitable solvent. But for insoluble polymers, viz., majority of conducting polymers, film preparation is rather difficult. For such cases, techniques like direct film deposition by electrochemical polymerization or plasma polymerization is convenient. Such techniques can provide high quality thin films of polymers. In general, polymer films can be prepared by solution casting, electrodeposition, self-assembly (SA) technique, Langmuir-Blodgett (LB) technique, spin casting, etc. In order to prepare films by solution casting, polymer needs to be dissolved in a suitable solvent. Then the solution is cast on a suitable substrate. The substrate may be a polymer sheet, glass, or even an electrode surface. A freestanding film is obtained by evaporation of the solvent. If required, polymer films can Chapter 1

be cross-linked by applying heat in presence of a suitable cross-linking agent in a thermostatic chamber under an inert atmosphere. These techniques generally produce thick films (e.g., 40-500  $\mu$ m) and the thickness is not well controlled. But for sensor device preparation, thin films are generally preferred to obtain better sensitivity. Spin casting technique [46] uses the casting of a polymer solution on a substrate, which is kept rotated at high speed. In fact, the centrifugal force spreads the polymer solution on the substrate, and after solvent evaporation a thin layer of film remains on the substrate. Generally, thinner films (ranging from 0.1 to 50  $\mu$ m) can be prepared by this technique. There are reports on the electrodeposition casting of polymers from aniline, pyrrole, etc. on the working electrode surface [47]. Applying suitable cycles of potential can control the thickness of the conducting polymer films. LB and SA techniques are widely used to prepare ultrathin films.

# 1.4 Polymer applications in major sensors

Polymers have been found to be used in various sensor devices, viz., gas sensor, pH sensor, ion selective sensor, humidity sensor and biosensors, which include enzyme sensor, odor sensor and taste sensor. **Table 1.1** shows some examples of sensors and polymers used. A brief overview is presented below on the application of polymers in various sensor devices. To improve the electrical properties of the sensor devices conducting polymers like polyaniline, polypyrrole, etc. and solid polymer electrolyte (Nafion) are widely used. Polymethylmethacrylate (PMMA), polyvinyl chloride (PVC), polyvinyl alcohol (PVA) are also used after modification in the fabrication of different types of sensors due to their good film forming properties. Hydrophilic polymers like PVA, poly(hydroxyethylmethacrylate) [poly(HEMA)], sodium polystyrene sulfonate (PSSNa), poly (N,N-dimethyl-3,5-dimethylene piperidinium chloride), sodium salt of poly (2-acrylamide-2-methyl propane sulphonic acid), IPN of cross-linked 2-hydroxy-3-methacryloyloxypropyl trimethyl ammonium chloride (HMPTAC) polymer and cross-linked ethylene glycol dimethacrylate (EGDMA) polymer, poly (2-acrylamido-2-methylpropane sulfonate) (poly-AMPS), etc. are used in the fabrication of humidity

sensors. Besides these polymers, polyethylene oxide, polyethylene glycol, epoxy resin, polyisoprene, etc., are also found to be used in sensor device fabrication [41].

#### 1.4.1 Gas sensor

Analytical gas sensors offer a solution to problems related to hazardous gases in the environment. Gaseous pollutants such as  $SO_2$ ,  $NO_x$  and other toxic gases are emitted from related chemical industries. Sensors are, therefore, needed to detect and measure the concentration of such gaseous pollutants in the environment. Conducting polymers such as polyaniline(PAn), polyacetylene [48,49], polypyrrole [40] etc. were used for the sensing of gases having acid-base characters like HCl, NH<sub>3</sub>, etc., or oxidizing characteristics like that of NO<sub>2</sub>. Ultrathin PAn-isopolymolybdic acid nanocomposite films [50] were used for detection of NH<sub>3</sub> and NO<sub>2</sub> gases.

# 1.4.2 pH sensor

Measurement of pH of a solution is required for carrying out a chemical reaction in a proper manner and also maintaining a pH has a significant effect in chemistry, biochemistry, clinical chemistry and environmental science. Ferguson et al. [51] used a poly (hydroxyethyl methacrylate) hydrogel containing acryloyl fluorescein as pH indicator. Among various organic materials, polyaniline has shown to be most suitable for pH sensing in aqueous medium [52]. Also the use of conducting polymers in the preparation of optical pH sensor has eliminated the need for organic dyes.

# 1.4.3 Ion selective sensors

Ion selective sensors are suitable for determination of specific ions in a solution in presence of other interfering ions. The quantitative analysis of ions by ion-selective electrodes (ISEs) is a widely used analytical method since these sensors find wide application in medical, environmental and industrial analysis. ISEs also used in measuring the hardness of water. In measurements with ISEs, chemical transduction is based on selectivity of ion conveyed by ionophore-ion-exchange agents, charged carriers and neutral carriers-doped in polymeric membranes. In addition to organic salts, several

macrocyclics, such as antibiotics, crown ethers and calixerenes, are also used as neutral carriers, which function by host-guest interactions [53]. PVC is a common polymer matrix in ISEs. Silicone rubber and a PU/PVC copolymer [54] were reported to be good screen-printable ion-selective membranes for sensing arrays. In Ca<sup>+</sup> ion sensing, PAn [55] was used as the membrane matrix that transforms ionic response to an electronic signal.

# 1.4.4 Humidity sensor

The measurement and control of humidity are necessary in paper, food and electronic industries, domestic environment, etc. Use of different polymers in the fabrication of humidity sensors is extensively reviewed [41]. Composites of acrylate resin with BaTiO<sub>3</sub>, modified inter penetrating network (IPN) of hydrophilic and hydrophobic methacrylate polymers, sulphonated polystyrene grafted to polytetrafluroethylene (PTFE) were used in humidity sensor devices. Ions containing polymeric systems were used in humidity sensor devices based on variation of the electrical conductivity with water vapor. Polymer electrolytes containing polymeric cation/anion with its counter ions and mixtures or complexes of inorganic salts with polymer are the major materials for fabrication of humidity sensor.

#### 1.5 Taste sensor

In living system, the biological membrane of the gustatory system is composed of proteins and lipid bilayer. The lipid molecules have a self-organising property because of the presence of hydrophilic tail and hydrophobic head at the two ends of a long chain organic compound. The hydrophilic parts are water loving and hydrophobic ends are water repelling and due to this the lipid molecules can automatically form the lipid bilayer by gathering the hydrophobic chains inside and facing the hydrophilic group towards the water phase. This self-organization of lipids have been utilised in developing biomimetic devices. The sense of taste is a chemical sense induced when chemical substances interact with the taste buds of a mammalian tongue [56]. Toko [57] pioneered on the development of taste sensor composed of several kinds of lipid/polymer

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membranes for transforming information of taste substances into electrical signal. Chemical substances having different taste qualities such as saltiness and sourness show different patterns as sensor output. Such taste sensor can detect and quantify taste interactions such as suppression effect between bitterness and sweetness.

The detail insight of the gustation mechanism has brought out the fact that different types of proteins present in the cell membrane primarily maintain the unbalanced electric potential between the inside and outside of the biological membrane in an environment of electrolytes where inside of the cell contains  $K^+$  ions and outside Na<sup>+</sup> ions. Under the action of an external stimulus, the nerve cell shows series of transient action potentials. This phenomenon has been exploited in the fabrication of artificial taste sensors using different lipids immobilized in a suitable polymer matrix. Different Japanese researchers have done much advancement in lipid based taste sensor development. In doing so, they have explored the basic science of taste sensing using lipid membranes [56].

Some of the functionality of mammalian taste bud cells has been mimicked to develop a taste sensor using lipid membranes in combination within electrodes [57,58]. Mammalian tongue consists of sandy grains called papillae [59]. One papilla contains a few hundred taste buds, which vary from species to species. One adult human has about 9000 taste buds 60-80  $\mu$ m in length and maximum 40  $\mu$ m in diameter. One taste bud contains several taste (gustatory) cells. On receipt of chemical substance at the biological membrane the membrane potential of a taste cell changes at the first stage of chemical reception. It has been proposed that a nerve fiber connected to the taste cells shows excitation. The taste buds are located in depressions on tongue, where the molecular and ionic analytes get restricted to allow time for their identification [60,61].

Lavigne et al. [62,63] developed a chip-based chemically derivatized polymeric microspheres localized in micromachined cavities suitable for the digital analysis of taste of complex fluids mimicking many of the features exhibited by the human sense of taste. A major focus of this development is that multianalyte mixtures can be analyzed. For discriminating different basic tastes Sehra et al. [17] fabricated a novel analytical sensing system based upon a dual shear horizontal surface acoustic wave (SH-SAW) device.

They fabricated 60 MHz SH-SAW dual delay-line sensors on  $36^{0}$  rotated Y-cut X propagating LiTaO<sub>3</sub> and placed below a miniature PTFE housing containing the liquid under test. This artificial electronic tongue could classify correctly the tastes of sour, salt, sweet and bitter substances without a selective biological or chemical coating. L- $\alpha$ -phosphatidylcholine dipalmitoyl phospholipid based Langmuir-Blodgett membrane was prepared for detection of five basic taste substances by measuring the impedance change of the membrane [64]. Multichannel taste sensor was developed by immobilizing lipids, viz., n-decyl alcohol, oleic acid, dioctyl phosphate, trioctyl methyl ammonium chloride and oleyl amine lipids in PVC for the sensing of tastes such as sour, salty, bitter, sweet and umami [14,65].

Majumdar et al. [66] grafted polyacrylic acid and polyacrylamide [67] on cellulose membrane for measurement of taste sensing characteristics in terms of membrane potential with a good repeatability. Similar kind of taste response was also obtained from a functionalized polymer membrane without using any lipid molecule as sensor element. In fact cross-linked polyvinyl alcohol was phosphorylated to attach phosphoric acid functional group onto polyvinyl alcohol, thus mimicking the function of phospholipids [68]. Phosphorylated cellophane membrane also responded to the measurement of tastes of NaCl, HCl, glucose, QHCl and monosodium glutamate [69,70]. Japanese groups [71,72] also constructed membranes from cellulose ester impregnated with dioleyl phosphate (DOPH) and measured their changes in electrical characteristics according to variations in the concentration of a salt such as NaCl or KCl. DOPH is a synthetic lipid obtained by phosphorylating oleyl alcohol with phosphorus oxychloride and was first made by Kobatake et al. [73]. The structure of DOPH is



Taste sensor device measures electric potential between two detecting electrodes immersed in 10 mM KCl (containing taste substances) and 1 M KCl solution isolated by lipid/polymer membrane. Due to the increase in the ion concentration of the 10 mM KCl

solution with increasing taste substances added, the output shows different patterns for the different substances. Thus the electric potential measurement shows sensitivities to electrolytes such as sour and salty substances and insensitivities to non-electrolytes such as sweet substances. To overcome such problem measurement of admittance and optical transmittance along with electric potential is a good approach. In order to improve the sensitivity to sweet taste substances, the measurement of the admittance and optical transmittance of the taste-substance containing 10 mM KCl solution was done by Ishii and Tsubakihara [74]. They reported that the addition of the sweet substances such as glucose and sucrose decreased the admittance and increased the transmittance of about 950 nm band. The reason behind this is, as pointed out, that the sweet substances adsorb the ions in the solution and break up the hydrogen bonds localized at 950 nm band.

Cui et al. [75] studied the selectivity control in a sweetness sensor with lipid/polymer membranes for sucrose, fructose, and glucose, which are nonelectrolytes and therefore, are susceptible to interference from electrolytes and/or adsorptive substances. They focused on suppressing the adsorption of bitter and astringent substances on a membrane surface designed to be electrically neutral to avoid interference from electrolytes. The dynamical behavior of lipid bilayer membranes was experimentally studied by Nomoto et al. [76] under superposition of random, periodic membrane-potential fluctuations or constant membrane potential. An analysis of the mutual information revealed that, in less than 10 Hz of random fluctuations, each of the time series of the mutual information of the transmembrane current for the five chemical substances (five basic tastants) had its inherent pattern, but not in a periodic fluctuation. Phospholipids such as phosphatidic acid exert a bitterness-masking effect without changing other taste qualities. Shimakawa et al. [77] detected and qualified the suppression of bitterness using a taste sensor whose transducer was composed of several kinds of lipid/polymer membranes with different characteristics. They observed that the response to quinine hydrochloride decreased with increasing phospholipid concentration in a manner similar to human gustatory sensation. In this study they detected the adsorption of quinine hydrochloride on the membrane surface and the masking effect of phospholipids by using an atomic force microscope (AFM). Through AFM

measurements they confirmed that blocking the adsorption of bitter substances onto to the membrane caused the masking effect. Lipid-coated quartz-crystal microbalance (QCM) system can objectively measure the body, smoothness, bitterness, and astringency of a beer. Objective evaluation systems for beer tastes were developed by Hirotaka et al. [78] using a lipid-coated QCM. They reported that the adsorption and desorption on the lipid membrane in a water flow system showed a good correlation with beer body or smoothness in a sensory evaluation, respectively. Specifically the lipid-coated QCM responded to astringent tannins in presence of gelatin.

Instead of PVC silicone rubber (SR) was used as a substrate for the study of taste sensing behaviour. Tanaka et al. [79] developed lipid membranes using SR by mixing only lipids in SR. They prepared three kinds of lipid membranes and investigated their response characteristics for five basic taste qualities. Taste substances with the same basic taste showed similar response patterns constructed from outputs of three kinds of membranes, whereas those with the different taste showed different patterns. Response patterns for sweet substances were a little similar to those for umami taste substances. The saltiness of sodium chloride was evaluated in presence of bitter substances such as magnesium sulfate, magnesium chloride and calcium chloride [80]. In this study model samples consisting of sodium chloride with bitter substances were measured using a taste sensor with lipid/polymer membranes. Gotoh [81] constructed a single use disposable taste biosensor by using screen printed five Ag/AgCl electrodes on a PET film and lipid layers which are deposited in a dry form on each electrodes. An Ag/AgCl reference electrode was also printed on the same PET film. Each lipid layer provided response to each taste, for example, bitterness, sweetness etc. Using this device the taste of many kinds of beverages were evaluated by the potential pattern of five electrodes, where according to the kind of beverages, the potential pattern changed apparently. The advantage of such single use disposable taste biosensor against the conventional taste sensor is that there is no contamination by measurement. The tastes of 20 bottled Japanese commercial nutritive drinks were evaluated both in human gustatory sensation tests and using a multi-channel taste sensor [18]. In the gustatory sensation tests, seven trained healthy human volunteers were employed to score the drinks in terms of the

intensities of four basic tastes (sweetness, saltiness, sourness, and bitterness), for overall palatability (ease of drinking), and for nine components of palatability (astringency, pungency, fruitiness, tasting of a medicinal plant, refreshing, irritating to the throat, seeming beneficial, good aftertaste, and the desire to drink again). A linear correlation was obtained between the intensities of sourness and bitterness determined by the human volunteers and those predicted by the multi-channel taste sensor.

#### 1.6 Non-lipid taste sensor

Apart from using polymers, people fabricated taste sensor with monophthalocyanines (including Co and Cu phthalocyanines) and lanthanide bisphthalocyanines (comprising europium, gadolinium and lutetium bisphthalocyanines and the octa-tertbutyl substituted praseodymium bisphthalocyanine) following two different methods: Langmuir-Blodgett and carbon paste electrode (CPE) techniques [82]. They obtained similar responses from both types of electrodes, although the LB films showed better peak resolution with a very good repeatability. Whereas, the reproducibility of the LB film electrodes was lower than that of the CPE electrodes. In place of lipids Kim [83] immobilized electroactive materials such as valinomycin in plasticized poly (vinyl chloride) (PVC) and fabricated an 8-channel device for taste sensation and applied for discriminant analysis of marketed liquor. This biomimetic polymer membrane was prepared through a casting procedure by employing PVC, bis (2-ethylhexyl) sebacate as plasticizer and electroactive materials such as valinomycin in the ratio of 33:66:1, and was attached over the sensitive area of ion-selective electrodes to construct the corresponding taste sensor array. The signal data from the sensor array for 3 groups of marketed liquors like Maesilju, Soju and beer were analyzed by principal component analysis after normalization. It was observed that the 1st, 2nd and 3rd principal components were responsible for most of the total data variance, and the analyzed liquor samples were discriminated well in 2 dimensional principal component planes composed of the 1st-2nd and the 1st-3rd principal components. Abraham et al. [84] fabricated highly sensitive microsensor using horizontally polarized surface acoustic wave (SH-SAW) microsensors on 36<sup>o</sup>-rotated Y cut X propagating LiTaO<sub>3</sub> (36YX.LT) substrate. The design consists of a dual delay line

configuration in which one line is free and other one is metalized and shielded. Due to high electromechanical coupling of 36YX.LT, it could detect difference in electrical properties for distinguishing different soft drinks. Different soft drinks were tested using this sensor device, which could distinguish between two popular soft drinks like Pepsi and Coca cola.

Tsuji et al. [85] evaluated the degree of bitterness of commercial dry syrup preparations of three kinds of macrolide antibiotic, including erythromycin dry syrup (EMD), clarithromycin dry syrup (CAMD) and azithromycin dry syrup (AZMD) when suspended in various beverages (water, tea and acidic sports drinks) by human gustatory sensation testing and taste sensor measurements. An impedentiometry electronic tongue was developed [23] for the discrimination of basic tastes by measuring the variations of the electric impedance of a sensor array. In the case of electronic tongue, mainly three measurement techniques are used for sample analysis, viz., potentiometry, voltametry and conductometry. The array composed of five sensors of three different types based on carbon nanotubes or carbon black dispersed in polymeric matrixes and doped polythiophenes. Measurements were carried out on 15 different samples representing five basic tastes (sodium chloride, citric acid, glucose, glutamic acid and sodium dehydrocholate for salty, sour, sweet, umami and bitter respectively) at three concentration levels comprising the human perceptive range. A fairly good degree of discrimination was reported after analyzing the data by linear and nonlinear pattern recognition techniques. Firmino et al. [86] showed that self-assembled artificial membranes of poly(o-ethoxyaniline) with sulfonated lignin can be satisfactorily used in the distinction of 4 brands of coffee using a.c. measurements. A review on Multichannel taste sensors with lipid, lipid like - polymer Membranes has been written by Szpakowska et al. [87]. Two types of potentiometry taste sensors, one with lipophilic compoundpolymer membranes (ISE) and the other with lipid polymer membrane and a conducting polymer film (all solid state electrode, ASSE) were tested in appropriate taste solutions.

#### 1.7 Scope and objectives of the present investigation

## 1.7.1 Scope

Chemical sensors have been developed to identify the chemicals present in a foodstuff, but a foodstuff contains huge numbers of chemicals producing the taste. The chemical sensors are very selective and specific and therefore to identify the taste of a foodstuff, it is not practical to fabricate many chemical sensors for all the chemicals present in the foodstuff. Biosensors were developed to identify specific chemical involved in a biological event. Biosensor is also a kind of chemical sensor and is selective and hence can identify different chemicals present in a food but can not reproduce taste of the food. These difficulties of identifying tastes were overcome by the fabrication of lipid/polymer based artificial multi-channel taste sensor with global selectivity [14]. The different lipids used in the fabrication of a multi-channel taste sensor are dioctyl phosphate, cholesterol, oleic acid, decyl alcohol, trioctyl methyl ammonium chloride, oleyl amine, distearyl dimethyl ammonium bromide, trimethyl stearyl ammonium chloride. The lipids are self organised biomolecules and this fact is utilized in the hydrophilic and hydrophobic interaction of the lipid molecules in aqueous solution of the taste substances and the functional groups of the lipids are actually receptor in the taste sensing mechanism [13]. Majumdar et al. [68] developed different functionalised polymer membranes for studying the taste response towards different basic tastes. They used polyvinyl alcohol (PVA) cross-linked with 50 % by weight of PVA of maleic anhydride and phosphorylated the crosslinked PVA membrane. Besides this, they used cellophane and cellophane phosphate membrane, poly (acrylic acid) grafted cellulose, phosphorylated PVAcellulose grafted membrane and polyacrylamide grafted cellulose membrane. They have attempted at incorporating the basic functional groups like –OH, -COOH, -NH<sub>2</sub>, etc.

Literature survey reveals that different natural and synthetic polymers have been used in the development of taste sensors either as a conducting type alone or nonconducting type immobilised with different receptor agents like lipids or enzymes etc. Although chemically modified polymers have been attempted at large in the fabrication of taste sensors, but the reports of using polyvinyl alcohol (PVA)-conducting polymer composites, pure polyelectrolytes and their blends as taste sensors have not been reported in the literature. Moreover, Majumdar et al. [68] developed some functionalised polymer membranes without any optimisation of cross-linking of polyvinyl alcohol (PVA) and subsequent phosphorylation for using as taste sensing membranes. Polyvinyl alcohol is a polymer, which is known for its tailorability and easy processability and easy chemical modification with variety of functional groups. The presence of –OH groups in PVA makes it possible. Hence the PVA matrix can be optimally cross-linked to acquire the required physical and mechanical properties for taste sensing purpose thus leaving maximum scope for chemical modifications. The scope of optimizing the cross-linking density and degree of phosphorylation of PVA and preparation of PVA composites and blends with different conducting polymers and polyelectrolytes and conducting polymer composites respectively have been utilized in the present investigation to study the taste response behaviours of the membranes.

# 1.7.2 Objective

Based on the scope of research in taste sensor development the following points have been enumerated as objectives of the present investigation:

- 1. The basic objective of the present investigation is to develop an artificial taste sensor with functionalised polymer membranes as transducers.
- 2. Development of transducers based on chemically modified polymers and their composites.
- 3. Standardization of measuring device for taste sensing.
- 4. Measurement of taste sensing response of the developed membranes.
- Application of simple statistical techniques like principal component analysis (PCA) and multi discriminant analysis (MDA) in data processing for evaluating the membranes performances in taste sensing.

# 1.7.3 Plan of work

- 1. Preparation of membrane
  - (a) Preparation of PVA based polymer membrane with optimisation of the degree of cross-linking and maximum density of the active functional sites like phosphoryl group.

- (b) Preparation of polyacrylic acid (PAA) and PVA-PAA blend membranes.
- (c) Preparation of composite membranes of cross-linked PVA (PF2G) with polyaniline (PAn), cross-linked PVA (PF6G) with poly (m-aminophenol)(PmAP), PAA with PAn and PVA-PAA with PAn.
- Characterisation of the polymer membranes in terms of moisture absorption, water absorption, contact angle measurement, conductivity measurement, FTIR, XRD, FESEM analyses, etc. Analyses of elements like phosphorous and nitrogen to ascertain the chemical structure of the respective membranes.
- Fabrication of an electrochemical device for taste sensing measurement using Ag/AgCl electrodes and Keithley 6<sup>1</sup>/<sub>2</sub> digit multimeter.
- 4. Evaluation of taste sensing characteristics of the membranes, like temporal stability, response stability and reproducibility, taste response in terms of electric potential of different basic taste substances (analytes) and suppression or synergistic effect of mixture of analytes.
- 5. Analysis of the measurement outputs by graphical presentation, simple mathematical tools and statistical techniques (PCA and MDA).

# References

- 1. Chandrasekhar J., Hoon M. A., Ryba N. J. P., Zuker C. S. (2006), The receptors and cells for mammalian taste, Nature, Vol . 444, pp. 288-294.
- 2. Schwebel T., Frank J., Fleischer M., Meixner H., Kohl C-D. (2000), A new type of gas sensor based on thermionic charge carrier emission, Sensors and Actuators B: Chemical, Vol. 68, Issue 1-3, pp. 157-161.
- 3. Yamazoe N. and Miura N. (1996), Prospect and problems of solid electrolyte-based oxygenic gas sensors, Solid State Ionics, Vol. 987, pp. 86-88,.
- 4. Arai Y. (2006), Monolithic pixel detector in a 0.15μm SOI technology, IEEE Nuclear Science Symposium, Conference 3, pp. 1440-1444.
- 5. Borato C. E., Leite F. L., de Oliveira Jr. O. N., Mattoso L. H. C. (2006), Efficient taste sensors made of bare metal electrodes. Sensor Letters, Vol. 4, No. 2, pp. 155-159.
- 6. Panigrahi S., Balasubramanian S., Gu H., Logue C. M., Marchello M. (2006), Design and development of a metal oxide based electronic nose for spoilage classification of beef, Sensors and Actuators B: Chemical, Vol. 119, Issue 1, pp. 2-14.
- 7. Gangopadhyay R., De A., Ghosh G. (2001), Polyaniline-poly (vinyl alcohol) conducting composite: Material with easy processability and novel application potential, Synthetic Metals, Vol. 123, pp. 21-31.
- Gupta N., Sharma S., Mir I. A., Kumar D. (2006), Advances in sensors based on conducting polymers, Journal of Scientific and Industrial Research, Vol. 65, pp. 549-557.
- Radhakrishnan S. and Kar S. B., (2006), Response characteristics of conducting polypyrrole bi-layer actuators: Role of backing layer polymer, Sensors and Actuators B: Chemical, Vol. 119, Issue 1, pp. 94-98.
- 10. Li D., Jiang, Y. D., Wu Z. M., Chen X. D., Li Y. R. (2000), Self-assembly of polyaniline ultrathin films based on doping-induced deposition effect and applications for chemical sensors, Sensors and Actuators B: Chemical, Vol. 66, pp. 125-127.
- 11. Marx K. A. (2007), The quartz crystal microbalance and the electrochemical QCM: applications to studies of thin polymer films, electron transfer systems, biological macromolecules, biosensors, and cells, Springer Series on Chemical Sensors and Biosensors, Vol. 5(Piezoelectric Sensors), pp. 371-424.
- Sharma S. K., Suman, Pundir C.S., Sehgal N., Kumar A., (2006), Galactose sensor based on galactose oxidase immobilized in polyvinyl formal, Sensors and Actuators B: Chemical, Vol. 119, Issue 1, pp. 15-19.
- 13. Toko K., Biomimetic sensor technology, Cambridge university press, 2000, p. 77.
- 14. Hayashi K., Yamanaka M., Toko K., Yamafuji K. (1990), Multichannel taste sensor using lipid membranes, Sensors Actuators B, Vol. 2, pp. 205-213.
- 15. Szpakowska M., Magnuszewska A., Szwacki J. (2006), On the possibility of using liquid or lipid, lipid like-polymer membrane systems as taste sensor, Journal of Membrane Science, Vol. 273, pp. 116–123.
- 16. Maynor M. S. Nelson T. L., O'Sullivan, C., Lavigne J. J. (2007), A food freshness sensor using the multi-state response from analyte induced aggregation of a cross-reactive poly (thiophene), Organic Letters, Vol. 9, pp. 3217-3220.

- 17. Sehra G., Cole M., Gardner J. W. (2004), Miniature taste sensing system based on dual SH-SAW sensor device: an electronic tongue, Sensors and Actuators B, Vol. 103, pp. 233–239.
- Kataoka M., Miyanaga Y., Tsuji E., Uchida T. (2004), Evaluation of bottled nutritive drinks using a taste sensor, International Journal of Pharmaceutics, Vol. 279, pp. 107– 114.
- 19. Lavine B. K. and Workman J. R. (2004), Fundamental Review of Chemometrics, Analytical Chemistry, Vol. 76, No. 12, pp. 3365-3372.
- 20. Krishna Kumar P.T. (2006), Design of a discriminating taste sensor using mutual information, Sensors and Actuators B: Chemical, Vol. 119, Issue 1, pp. 215-219.
- Krantz-Rülcker C., Stenberg M., Winquist F., Lundström I. (2001), Electronic tongues for environmental monitoring based on sensor arrays and pattern recognition: a review, Analytica Chimica Acta, Vol. 426, Issue 2, pp. 217-226.
- 22. Toko K., (1998), Measurement Scence and Technology, Vol. 9, pp. 1919-1936.
- 23. Marchetti A., Ahluwalia A., Pioggia G., Serra G. De Rossi D., Di Francesco F., Domenici C. and Francesconi R. (2004), Development of an impedentiometric electronic tongue, Sensors and Microsystems, Proceedings of the Italian Conference, 8th, Trento, Italy, Feb. 12-14, 2003, Meeting Date 2003, pp. 328-333.
- 24. Madou M. J. and Morrison S.R. (1989), Chemical sensing with solid state devices, Academic Press, London, p.1-9.
- 25. Madou M. J. and Morrison S. R. (1989), Chemical sensing with solid state devices, Academic Press, London, Chapter 9.
- 26. Taguchi N. (1970), Gas detection semiconductor element, Ger Offen 2,005,497.
- 27. Kleitz M. and Fouletier J. (1976), In: Degn H., Balselv I., Brook R., eds., Measurement of oxygen, Elsevier, Amsterdam, p. 103.
- 28. Bloch R., Shatkay A., Saroff H. A. (1967), Fabrication and evaluation of membranes as specific electrodes for calcium ions, Biophysics Journal, Vol. 7, pp. 865-77.
- 29. LeBlanc O. H. Jr, Grubb W.T. (1976), Long-lived potassium ion selective polymer membrane electrode, Analytical Chemistry, Vol. 48, pp.1658-60.
- 30. Wang J. and Tuzhi P. (1986), Selectivity and sensitivity improvements at perfluorinated ionomer/cellulose acetate bilayer electrodes, Analytical Chemistry, Vol. 56, pp. 3257-61.
- 31. Szentirmay M. N. and Martin C. R. (1984), Ion-exchange selectivity of Nafion films on electrode surfaces, Analytical Chemistry, Vol. 56, pp.1898-902.
- Wuthier U., Pham H. V., Züend R., Welti D., Funck R. J. J., Bezegh A., Ammann D., Pretsch E., Simon W. (1984), Tin organic compounds as neutral carriers for anion selective electrodes, Analytical Chemistry, Vol. 56, pp. 535-8.
- 33. Stefanac Z. and Simon W. (1967), Ion-specific electrochemical behavior of macrotetrolides in membranes. Mikrochem Journal, Vol. 12, pp.125-32.
- 34. Koryta J. and Stulik K. (1983), Ion-selective electrodes, Cambridge University Press, Cambridge.
- Schulthess P., Ammann D., Krautler B., Caderas C., Stepanek R., Simon W. (1985), Nitrite-selective liquid membrane electrode, Analytical Chemistry, Vol. 57, pp.1397-401.

- 36. Stepanek R., Krautler B., Schulthess P., Lindemann B., Ammann D., Simon W. (1986), Aquocyanocobalt(III)-hepta(2-phenylethyl)-cobyrinate as a cationic carrier for nitrite-selective liquid-membrane electrodes, Analytica Chimica Acta, Vol. 182, pp. 83-90.
- 37. Hermans E. C. M. (1984), CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O sensing by polymer covered interdigitated electrode structures, Sensors and Actuators, Vol. 5, pp.181-6.
- 38. Bott B. and Jones T. A. (1986), The use of multisensor systems in monitoring hazardous atmospheres, Sensors and Actuators, Vol. 9, pp. 19-25.
- 39. Heiland G. and Kohl D. (1985), Problems and possibilities of oxidic and organic semiconductor gas sensors, Sensors and Actuators, Vol. 8, pp. 227-33.
- 40. Nylander C., Armgarth M., Lundström I. (1983), An ammonia detector based on a conducting polymer, Analytical Chemistry Symposia Series, Vol. 17, pp. 203-207.
- 41. Adhikari B. and Majumdar S. (2004), Polymers in sensor applications, Progress in Polymer Science, Vol. 29, pp. 699-766.
- 42. Ghosh P. (1990), Polymer science and technology of plastics and rubbers, Tata McGraw-Hill, New Delhi, pp. 139-147.
- 43. Bailey R. A. and Persaud K. C. (2000), Sensing volatile chemicals using conducting polymer arrays. In: Osada Y., De Rossi D. E. (Eds.), Polymer sensors and actuators, Springer-Verlag, Berlin, p.157.
- 44. Yasuda H. and Iriyama Y. (1989), Plasma polymerization. In: Eastmond G. C., Ledwith A., Russo S., Sigwalt P., (Eds.), Comprehensive polymer science The synthesis, characterization, reaction and applications of polymers, Vol. 4. Chain polymerization Part II, Pergamon press, Oxford, pp. 357-375.
- 45. Marechal E. (1989), Chemical modification of synthetic polymers. In: Eastmond G. C., Ledwith A., Russo S., Sigwalt P. (Eds.), Comprehensive polymer science. The synthesis, characterization, reaction and applications of polymers, Vol. 6, Polymer reactions, Pergamon press, Oxford, Chapter 1.
- 46. Fraden J. (2004), Handbook of modern sensors physics, designs and applications, Springer-Verlag, New York, p. 544.
- 47. Cooper J. C. and Schubert F. (1994), A biosensor for L-amino acids using polytyramine for enzyme immobilization, Electroanalysis, Vol. 6, pp. 957-961.
- Chiang C. K., Park Y. W., Heeger A. J., Shirakawa H., Louis E. J., MacDiarmid A.G. (1978), Conducting polymers: halogen-doped polyacetylene, Journal of Chemical Physics, Vol. 69, pp. 5098-5104.
- Shirakawa H., Louis E. J., MacDiarmid A. G., Chiang C. K., Heeger A. J. (1977), Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH)<sub>x</sub>. Journal of Chemical Society, Chemical Communications, pp. 578-80.
- 50. Li D., Jiang Y., Wu Z., Chen X., Li Y. (2000), Self-assembly of polyaniline ultrathin films based on doping-induced deposition effect and applications for chemical sensors, Sensors and Actuators B, Vol. 66, pp. 125-127.
- 51. Ferguson J. A., Healey B. G., Bronk K. S., Barnard S. M., Walt D. R. (1997), Simultaneous monitoring of pH, CO<sub>2</sub> and O<sub>2</sub> using an optical imaging fiber. Analytica Chimica Acta, Vol. 340, pp. 123-131.

- 52. Karyakin A. A., Vuki M., Lukachova L. V., Karyakina E. E., Orlov A. V., Karpachova G. P., Wang J. (1999), Processible polyaniline as an advanced potentiometric pH transducer. Application to biosensors, Analytical Chemistry, Vol. 71, pp. 2534-2540.
- 53. Suzuki K., Watanabe K., Matsumoto Y., Kobayashi M., Sato S., Siswanta D., Hisamoto H. (1995), Design and synthesis of calcium and magnesium ionophores based on double-armed diazacrown ether compounds and their application to an ion sensing component for an ion-selective electrode, Analytical Chemistry, Vol. 67, pp. 324-334.
- 54. Tsujimura Y., Yokoyama M., Kimura K. (1995), Practical applicability of silicone rubber membrane sodium-selective electrode based on oligosiloxane-modified calix[4]arene neutral carrier, Analytical Chemistry, Vol. 67, pp. 2401-2404.
- 55. Lindfors T., Ivaska A. (2001), Calcium-selective electrode based on polyaniline functionalized with bis [4-(1,1,3,3-tetramethylbutyl) phenyl] phosphate, Analytica Chimica Acta, Vol. 437, pp. 171-183.
- 56. Toko K. (2000), Biomimetic sensor Technology, Cambridge University press, Cambridge, pp. 1-29.
- 57. Toko K. (2006), Development of taste sensor, Hyomen Kagaku, Vol. 27, No. 1, pp. 34-38.
- 58. Hayashi K., Yamanaka M., Toko K., Yamafugi K. (1990), Multichannel taste sensor using lipid membranes, Sensors Actuators B, Vol. 2, pp. 205-213.
- 59. Toko K. (2000), Biomimetic sensor Technology, Cambridge University press, Cambridge, pp.29-63.
- 60. Schmale H., Ahlers C., Blaker M., Kock K., Spielman A. I. (1993), In: Chadwick D., Marsh J., Goode J., Eds., The molecular basis of small and taste transduction. Chichester, U. K., John Wiley and Sons, p. 167.
- 61. Toko K. (2000), Biomimetic sensor Technology, Cambridge University press, Cambridge, pp. 29-36.
- 62. Lavigne J. J., Savoy S., Clevenger M. B., Ritchie J. E., McDoniel B., Yoo S-J., Anslyn E. V., McDevitt J. T., Shear J. B., Neikirk D. (1998), Solution-based analysis of multiple analytes by a sensor array: toward the development of an 'Electronic Tongue', Journal of American Chemical Society, Vol. 120, pp. 6429-6430.
- 63. Goodey A., Lavigne J. J., Savoy S. M., Rodriguez M. D., Curey T., Tsao A., Simmons G., Wright J., Yoo S-J., Sohn Y., Anslyn E. V., Shear J. B., Neikirk D. P., McDevitt J. T. (2001), Development of multianalyte sensor arrays composed of chemically derivatized polymeric microspheres localized in micromachined cavities, Journal of American Chemical Society, Vol. 123, pp. 2559-2570.
- 64. Akiyama H., Toko K. and Yamafuji K. (1996), Detection of taste substances using impedance change of phospholipids Langmuir-Blodgett membrane. Japanese Journal Applied Physics, Vol. 35, pp. 5516-5521.
- 65. Mikhelson K. N. (1994), Ion-selective electrodes in PVC matrix. Sensors Actuators B, Vol. 18, pp. 31-37.
- 66. Majumdar S., Dey J., Adhikari B. (2006), Taste sensing with polyacrylic acid grafted cellulose membrane, Talanta, Vol. 69, pp. 131-139.

- 67. Majumdar S. and Adhikari B. (2006), Taste sensing with polyacrylamide grafted cellulose, Journal of Scientific and Industrial Research, Vol. 65, No. 3, pp. 237-243.
- 68. Majumdar S. and Adhikari B. (2006), Polyvinyl alcohol: A taste sensing material, Sensors and Actuators B Chemical, Vol. 114, pp. 747-755.
- 69. Majumdar S. and Adhikari B. (2005), Taste sensing with cellophane phosphate membrane, Analytica Chimica Acta, Vol. 554, Nos. 1-2, pp. 105-112.
- 70. Majumdar S. and Adhikari B. (2005), Polyvinyl alcohol-cellulose composite: a taste sensing material, Bulletin of Materials Science, Vol. 28, No. 7, pp. 703-712.
- Kobatake Y., Irimajiri A., Matsumoto N. (1970), Studies of electric capacitance of Membranes, I. A model membrane composed of a filter paper and a lipid analogue, Biophysics Journal, Vol. 10, pp. 728-744.
- Toko K., Nitta J., Yamafuji K. (1981), Dynamic Aspect of a Phase Transition in DOPH-Millipore Membranes, Journal of Physical Society, Japan, Vol. 50, pp. 1343-1350.
- 73. Yoshida M., Kobatake Y., Hashimoto M., Morita S. (1971), Journal of Membrane Biology, Vol. 5, p. 185.
- 74. Ishii S. and Tsubakihara H. (2005), Development of the taste sensor based on lipid polymer membranes, Kinki Daigaku Kogakubu Kenkyu Hokoku, Vol. 39, pp. 115-124.
- 75. Cui H., Habara M., Ikezaki H., Toko K. (2005), Selectivity control in a sweetness sensor using lipid/polymer membranes, Sensors and Materials, Vol. 17, No. 7, pp. 385-390.
- 76. Nomoto M., Nishikanbara M., Yoshimoto M. (2005), Development an artificial taste sensor which used the planar lipid bilayer membranes, Chemical Sensors, Vol. 21, Suppl. A, pp. 142-144.
- 77. Shimakawa, H., Habara M., Toko K. (2004), Bitterness-masking effect of phospholipids on lipid/polymer membranes, Sensors and Materials, Vol. 16, No.6, pp. 301-307.
- 78. Hirotaka K., Masachika T., Yoshio O. (2005), Development of Beer Taste Sensor Using a Lipid-Coated Quartz-Crystal Microbalance, Journal of American Society. Brew. Chem. Vol. 63, No. 3, pp. 89-95.
- 79. Tanaka K., Iwakura M., Toko K. (2003), Development of lipid membrane layer using silicone rubber as substrate for taste sensor, Research Reports on Information Science and Electrical Engineering of Kyushu University, Vol. 8, No. 1, pp. 91-95.
- 80. Chen R., Habara M. and Toko K. (2003), Study of saltiness using taste sensor with different lipid/polymer membranes, Sensors and Materials, Vol. 15, No. 3, pp. 155-163.
- 81. Gotoh M. (2004), Disposable taste biosensor Chemical Sensors, Vol. 20, Suppl. B, pp. 486-487.
- 82. Arrieta A., RodriguezMendez M. L., de Saja J. A. (2003), Langmuir–Blodgett film and carbon paste electrodes based on phthalocyanines as sensing units for taste, Sensors Actuators B, Vol. 95, pp. 357–365.
- 83. Kim N. (2005), Discriminant analysis of marketed liquor by a multi-channel taste evaluation system, Food Science and Biotechnology, Vol. 14, No. 4, pp. 554-557.

- 84. Abraham J. K., Karjathkar S., Jacesko S., Varadan V. K., Gardner J. W. (2005), Identification of soft drinks using MEMS-IDT microsensors, Proceedings of SPIE-The International Society for Optical Engineering, 5763 (Smart Electronics, MEMS, BioMEMS, and Nanotechnology), pp. 414-424.
- 85. Tsuji E., Takada M. and Uchida T. (2005), Effective bitterness evaluation of macrolide dry syrup formulations by a taste sensor. Iryo Yakugaku, Vol. 31, No. 3, pp. 186-193.
- 86. Firmino A., Junior A. R., Venancio E. C., Fonseca F. and Mattoso L. H. C. (2002), Development of taste sensors using natural polymers for evaluation and classification of coffees, Natural Polymers and Composites IV, Proceedings of the International Symposium on Natural Polymers and Composites, 4th, Sao Pedro, Brazil, Sept. 1-4, pp. 55-59.
- Szpakowska M., Szwacki J. and Marjanska E. (2008), Multichannel taste sensors with lipid, lipid like – polymer Membranes, Journal of Physics: Conference Series, Vol.127, 012013, doi:10.1088/1742-6596/127/1/012013.