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Original Research Article

ODOUR DETECTION: AN OVERVIEW OF SENSORS AND ITS PRESENT APPLICATIONS AND A FUTURISTIC APPROACH

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Abstract- Smell detection being one of the emerging techniques which was certainly an underrated technology in the past, has seen growth from the early 90's. This paper encapsulates the growth of smell detection, especially the sensing mechanism from a humongous machine of Gas Chromatography to simple sensors like Metal Oxide, Conducting Polymers, Optical Sensors and Piezoelectric sensors. It also explores the applications of odour detection in various facets of our day to day life like food and beverage quality control, detection of diseases, alcohol and wine detection, soil quality and fertility testing and also a few futuristic applications like detection of medicinal plants, detection of carcinogenic substances and various other applications too. This technology has been an attempt to mimic the biological nose which has far reaching effects in the mere future.

Key words: Smell Detection, Electronic nose, Gas Chromatography, Sensors, Applications.

Introduction

Smell being one of the least acute of the senses that humans possess, our nose can detect as many as 10,000 different odours. Rather our tongue can invariably detect only 5 distinguishable tastes, and rest of the tastes that we perceive is due to "SMELL". An electronic nose is basically an attempt to mimic our biological nose. So let us first study, in brief, how our bio-nose works. The molecules of the odorant enter the superior nasal concha which is a part of the nasal passage. Through this passage, the molecules

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get diffused in the mucus. Mucus is a host to some odorant binding proteins. The molecules interact with these proteins which further get interlocked with the olfactory receptors present in our dendrites. The receptors are encoded by a specific gene which helps us in sensing a particular smell. In short, our nose breathes in the air which activates the receptors in our nasal cavity. These receptors act like sensors and transmit a signal to the neurons in the brains through our nerves. The brain then interprets the signal and makes a decision about the smell which is known as odour coding. The electronic nose has a similar approach as that of a biological nose i.e. sample handling, sensing and pattern recognition/neural network. To understand the efficiency and the working behind an e-nose we emphasise more on sensors. But this includes right from using the gas chromatography/mass spectrometry to MOX, conducting polymers, optical sensors and also piezoelectric crystal sensors.[1,6] The paper also includes an approach to visualize the smell detection techniques in various facets and application.

Sensing mechanism

Detection of odour molecules in e-nose is done with the use of sensors which sense physical changes such as conductivity, mass, optical characteristic, work function and reaction of gas/solid interaction.[5]

Gas Chromatography

Gas Chromatography is a technique used to separate out the compounds from a mixture of gases. A GC model consists of the following:

An injection port.
A vaporising chamber.
A carrier and a stationary phase.
A thermostat oven.
Detection system.

An air sample is injected into the GC instrument using a micro syringe. The calibration on the syringe helps to inject the required amount of sample. Because an unnecessarily higher amount of sample leads to tailing of the peak. This sample further goes down to a heating chamber where the gas is vaporised i.e. its temperature is increased further which makes it more volatile and hence quickens the process.[11] Typically, the temperature of the heating chamber is maintained by 50 degree celcius higher than the lowest boiling point of a mixture of gases. Modern techniques often use heated sampling port where the process of injection and heating happens almost simultaneously. Next is the carrier phase. Here, a hydrogen or inert gas is used todirect the sampled air for further processing. The type of inert gas used depends on the type of detector. While helium can be used with almost all the traditional detectors like ECD, FID etc. (elaborated in due course); MS uses argon or nitrogen. Selection of the carrier depends on many factors like molecular weights, thermal conductivity, flow rates etc. The carrier gas is used in its pressurized forms and requires high purity (99.995-99.9995%). The oxygen and hydrocarbon links should be less than 0.5 ppm. The carrier system has a molecular sieve which filters out the water and other impurities from the pressurized tanks. The gas is then passed to a column oven which is the stationary phase. The main part of separation happens here. The principle of separation of compounds is very similar to the principle of fractional distillation. Thermostatted oven maintains and serves to raise or reduce the temperature of the column by isothermal or programmed method. As the temperature of the column is varied, different elements elute out as sharp peaks as they reach their boiling points. In temperature programming method, the temperature is either increased or reduced; continuously or in steps. This method is more suitable for a broader range of boiling points. Also, the column is coated with a solid or liquid layer. Accordingly, it is named as gas-solid or gas-liquid chromatography. The only difference between the two is the state of the element used in the stationary phase. The solid or the liquid phase is adsorbed onto the inner surface of the capillary column. Compounds from the mixture dissolve in this layer (liquid or solid) to a different extent. Lesser is the solubility, faster the results. This module gives us a better idea about the separation and measurement techniques and also its applications. Column length also affects the separation. Longer columns give better results, however it might also lead to back diffusion into the stationary phase. However Gas solid chromatography has limitations of severe peak tailing and the semipermanent retention of polar compounds within the column. Its extensibility for different applications is severely low. Hence Gas Liquid Chromatography is a more widely used technique and is often referred to as simply GC for convenience.

Moving on to the detection techniques, following detectors can be used

1) Flame ionization detector (FID):

This detector is sensitive for organic compounds as compared to the inorganic bonds between nitrogen, oxygen, hydrogen etc. FID involves pyrolysis i.e. burning of the gas sample. Hence when a carbon bond passes through this detector, cations are formed in the effluent stream which is further processed to get the required results. But due to the burning process this method can't be used in preparative GC. Also, compressed air is oftenly required to operate an FID.

2) Electron capture detector (ECD):

Two electrodes and a radiation source is fitted in a cavity. The source emits b-radiation. If the compound contains electronegative atoms, collision between electrons and carrier gas results in the formation of anions. This happens due to the "capturing" of electrons from the compound. Hence the name. This reduces the collection of electrons. It is generally used for analysis of chlorinated compounds like pesticides.

3) Thermal Conductivity (TCD):

It is less sensitive as compared to an FID, but the sample is not destroyed and hence can be used for preparative applications. Detection is done by comparing two gas streams, one with the mixture of carrier and sample gas and the other being pure gas. Carrier used is hydrogen or helium due to their high conductivity. The two gases are then passed onto two thin tungsten wires, and the difference between the temperatures of reference and sample cell filaments is monitored by a Wheatstone bridge. Ensuring high surface to mass ratio will help in achieving equilibrium quickly.

Some other techniques are: Atomic Emission (AED) ,Chemiluminescence (CS) and Photoionization (PID).

4) Mass spectrometry (MS):

This is the most commonly used technique for detection technique. Many GC instruments are coupled with a mass spectrometer. The GC separates the compounds from each other, while the mass spectrometer identifies them based on their fragmentation pattern. MS works on a similar principle as a cathode ray tube. As the name suggests, this technique detects gas based on the mass of the particular molecule.

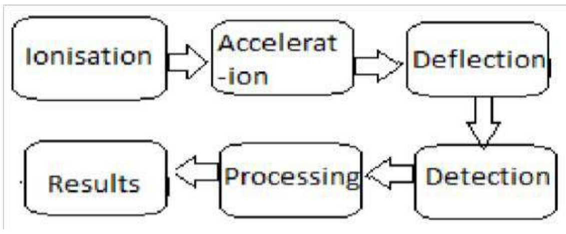

Fig 1: Block diagram of Mass spectrometry

Principle: Atoms are, as a whole, electrically neutral. Hence, they cannot be deflected by any magnetic field. For this reason, the atoms in the molecules are ionized by removal of electrons producing positively charged ions. Mass spectrometry does not deal with negatively charged ions.

After ionisation, the ions are accelerated in an acceleration chamber which is maintained at a very high voltage level of 10,000V.[9]

Electromagnets are used to deflect the ions. Each type of ion is deflected to a different extent depending upon its mass, velocity and its positivity. This deflection is measured in the form of variations in current. This is computed and plotted in the form of a graph and the smell is detected.

B] Metal oxide gas sensors

As explained by RuiGao et al. the metal oxide gas sensor has a characteristic feature of reversible interaction of the gas with the surface of the material. Usually non transition metal oxides like TiO2, V2O5, WO3, ZnO and SnO2 are commonly used. The mechanism behind sensing is that, when oxygen molecules are adsorbed on the surface of MOX they tend to pull electrons from the conduction band and trap them on the surface in the form of ions. This results in the band bending effect leading to the formation of an electron depleted region (space charge region). Thus decreasing conductivity. Now when the analyte reacts with the oxygen species resulting into reduction or adsorption and replacement of the adsorbed oxygen by other molecules, the decrease in band bending takes place. The conductivity increases due to the release of electron back into the bulk material. The underlying principle is that the conductance of the metal oxide material changes with the concentration of the gas. The operating temperatures of such sensors are 300450 degree celcius which also avoids the effects due to humidity.

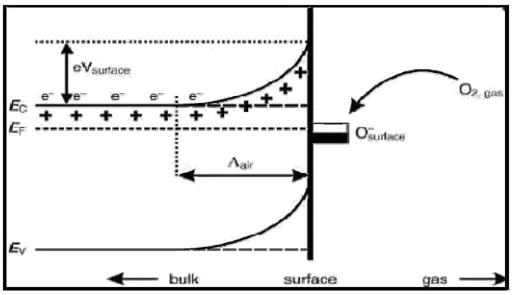

Fig 2: Working principle of MOX sensor [5]

Conducting polymers

Conducting polymer composites is basically made of insulating polymer and conducting element and works on the principle of percolation theory.[1] On exposure to vapours the insulating polymer swells up(e.g. carbon black). The swelling of the polymer leads to the increase in resistance. It would not be economical if a sensor would be capable of sensing only a single smell. Hence a solution to this is using an array of sensors, it includes various different polymers that respond to a particular smell in a particular way. This indicates that the smell vapours would have its own fingerprint as the array of polymers would have its variable swelling to the vapours i.e. what we get is a pattern of variable resistances. On absence of vapours swelling is reduced and resistance of each polymer film returns back to its original value. The advantage of this method is that is much more rapid and disposable too. But the disadvantage is its response to complex signatures, the films have limited environmental stability and also sensitive to humidity.[12]

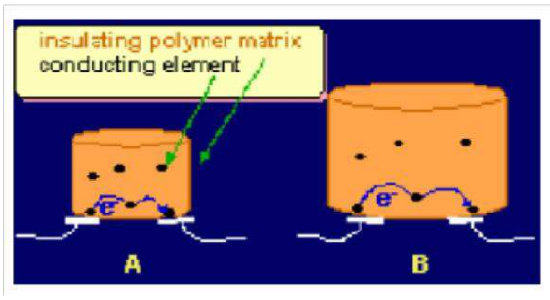

Fig 3: Working principle of conducting polymer sensor[12]

Using piezoelectric crystal

Piezoelectric crystals used for detection of smell are sub-divided into:

1. Surface acoustic wave (SAW): The SAW produces wave along the surface of the crystal. The principle used here is that it detects the mass of the vapours that are absorbed by a chemically selective layer that causes a change in the resonant frequency.[3] This sensitive membrane is placed between two transducers, at the input transducer an ac signal is applied that creates a 2 dimensional acoustic wave that propagates through the surface of the crystal. The vapour or the analyte is adsorbed on the crystal leading to an alteration of frequency due to change in the mass. The change in frequency is directly proportional to the concentration of the analyte. The substrate materials (piezoelectric in nature) that are commonly used are quartz, lithium niobate and ZnO. But one of its critical problems is that it has a poor signal to noise ratio due to its high frequencies at which they operate. They offer a high sensitivity and a comparatively fast time response and their fabrication being compatible with currently used IC technologies.

2. Quartz crystal microbalance (QCM) The QCM follows a similar principle as that of the SAW but the main difference is that it produces a wave that travels across the bulk of the crystal sensor. Similar to SAW an ac signal is applied to the input transducer the material oscillates at its resonant frequency. It follows the same philosophy of adsorption of analyte, increase in mass alters the resonant frequency for detection of vapours. It also has a fast response time typically 10 seconds but has the some disadvantages like poor SNR and complex

fabrication. [3]

Using optical sensors

An optical sensor works on the principle that when the analyte interacts with the fluoroscent dye results in change in the dye's optical properties such as spectrum change, intensity change, or shift in wavelength.[1] It has a faster response time than piezoelectric crystals, compact, light weight and very importantly is immune to electromagnetic interference, however on the other hand it has a short lifespan due to photo-bleaching and due to the complex software associated for its usage it incurs a lot of capital.

Applications

Food and Beverage quality control:

Food and beverage quality control is one of the many important applications of odour detection. We broadly classify this application into various subclasses of quality control:

a] Quality Monitoring by production of CO2 and O2: Excess production of CO2, usually deteriorates the quality of food by increasing metabolic rate and thus reducing its shelf life.[4] This can be done by using CO2 sensors as explained previously. Similarly Oxidative degradation may pose to be one of the most prime factors that cause food spoilage.

b] Quality monitoring of low shelf life food stuff. Meat, poultry and fish usually have very low shelf life which gives out a typical decay smell when it gets spoilt. Thus amines are formed which is a result of enzymatic actions of amino acids and protiens.

This detection can be done by using GC-MS.

c]Quality monitoring by use of carbon nanotubes : Use of carbon nanotubes may a better option but is still in its developing stage.[7] They are extremely sensitive to the slightest changes in concentrations of the gas. Carbon nanotubes basically form thin films forming a conductive network that behave like electrodes. This film certainly works like the sensors, by following the same principle of adsorption of gas and hence resulting in variation of resistance. The most important keypoint, where it outdoes other sensors like MOX, composite polymers, SAW etc is its reliability, reproducibility and also the low cost incurred in its fabrication. The carbon nanotates are now being thought to be used with the plastic substrate so as to use them as the packaging material (i.e. using disposable gas sensors).

d] Quality monitoring of various other foods with reference to its signature pattern: Here we propose to use smell detection and pattern recognition in order to keep a check of quality input, quality output, quality statistics based on quality degradation etc.

For example the coffee beans usually need to be of excellent coffee, and pertaining to this various coffee manufacturing companies employ people to do this task. To be extremely specific in quality one can use smell detection so at various points like before beans come in processing, after beans are roasted, after the beans have been powdered. This would give a clear understanding of the quality check in the product.

Detection of diseases:

Smell detection can be used in diagnosis of diseases, perhaps prevention in many cases. Microbial or fungal infections like pneumonia can be detected. Not only symptomatic diseases but also diseases like lung cancer which shows later signs can be detected. The human breath or even the smell from our armpit for that matter emanates a complex mixture of organic volatile compounds. During illness the body has a distinct release of a particular dominating compound i.e. the affected organs emits characteristic chemical signature. The smell samples can be taken from exhalation(breath), armpit, urine and also the feet. Many theories say canines are also used to detect illness in person by giving it training, using the same philosophy the smell detectors can diagnose diseases.

Detection of trimethylamine in kidney diseases and uremia, dimethylsulphide in case of liver infections, acetones in case of diabetes and hydrocarbons in oxidative stress.

Similar to fingerprints-that no two individuals have the same fingerprint, also no two individuals can have the same body odour emanation.[2] After experimentations, where 2 people asked to follow the same daily routine, in the same environmental conditions and using the deodrant and also the same amount gave varied and extremely different patterns showing that smell detection gives and individualistic approach where it outdoes fingerprinting, as we can also find the disease, emotional state etc. of an individual.

The residents living near industrial areas or the workers working in factories have the threat inhaling toxic or harmful gases like chlorine, nitric acid, sulphur dioxide and ammonia. We can collect samples of the air throughout the city and an odourbased system can be made in order to categorize and segregate different classes of the city as, less harmful air, moderately harmful and very harmful. The map will also help in taking immediately and fast actions to be taken in order to decrease and reduce its ill effects. The sample collection, verifying whether the air is toxic or polluted can be done at the work station in case of use of mass spectrometry-gas chromatography but owing to technologic advancement we also can also have portable and handy devices to do the same either using typical application based sensors or miniature built in MSGC advanced equipments.

We also propose in using detection of formaldehyde. We have put stress on detection of formaldehyde especially because it has proved to be one of the greatest causing carcinogenic chemical.

Formaldehyde has an extremely putric and irritating smell. It is released from various things that we use and see around us, many of which being paints, fertilizers, preserved foods, tobacco, building materials, carpets etc. People working in industries are exposed to such highly toxic atmosphere. Here employment of such devices can be used to detect concentrations of formaldehyde.

Soil and plants:

Smell detection in soil is used in order to have a qualitative analysis of the soil based on its fertility, the proportions of various gases needed (%nitrogen,%sulphuretc).The toxic content can also be understood in soil in order take precautionary measures. It can also help us in indicating the right crop suited to the soil.

Biogenic VOCs (R.Baghi et al.) performed a detailed study of the biogenic voc emissions during the flowering period. Emissions due to insect pollination and the contribution of flowering trees to the urban environment.

We propose to use smell detection for searching for plants that have medicinal values. We have easily identified plants like asparagus, turmeric, basil and neem by their smell and their physical appearance, but there are innumerable other plants that have a peculiar smell and extremely high medicinal values, just to name a few are Wattle bark, Gum arabic and Devil's Nettle. Of course this would mean investing a lot of time to collect smell samples of these plants, but once it is done it would prove to be a very useful tool.

Alcohol detection:

Alcohol detection is one of the most wide-spread application of smell detection. We've all seen the police taking tests for drunk driving using a device. This device is called breathalyzer. This is how it works:

The reason we can detect alcohol levels in our body is that inspite of being absorbed by our throat, lungs and intestines into our bloodstream, it is not digested by the body. Even in the bloodstream, it is not chemically reacted upon. So the vapours of alcohol move along with the blood throughout our body. Now, a breathalyzer takes in these vapours and reacts with it chemically which changes the colour .This process is explained in more detail as follows: The air sample is collected by asking the person to blow into the mouthpiece of the breathalyzer. This air sample is directed into a glass vial which contains a mixture of sulphuric acid, potassium dichromate, silver nitrate and water. The air sample reacts chemically with this mixture to produce sulphates of potassium and chromium along with acetic acid and water[10]. Alcohol (especially ethanol) is separated out from air by sulphuric acid which reacts with potassium dichromate. Silver nitrate is used as a catalyst because it is vital to get quick alcohol results in this case.

Another method to detect alcohol is using intoxilyzer. Intoxilyzer uses an infrared light which is absorbed by the vibrating molecules in the alcohol. Generally we have C-H, C-C, C-O and O-H bonds in any organic compound. Each of these bonds stretches or bends upon absorbing the IR light. This is because each type of bond absorbs the light at different wavelengths. The study of bonds will then help us identify the presence of alcohol.

Upcoming Technology:

As seen earlier Mass spectrometry and gas chromatography have certain limitations like its high cost, non portability and bulky nature due to which it cannot be implemented in various fields. But if these drawbacks are eliminated then there can be a revolutionary change in the field of odour detection. We can think of numerous such applications where this technique can be used. If this technique comes down to a penny sized device then it can be placed anywhere as desired and any kind of smell with its variable concentration can be measured. We can place these devices on buildings or public transports to detect radioactive emissions before it causes drastic hazards. Pollutants which are harmful to health can be detected. It can be used for security reasons or in place of metal detectors in cinemas or shopping mall and many such places to detect explosives or alcohol or any such substance that is prohibitated. It can also be used for food quality check. It can determine the freshness of the food stuff and can give its true expiry date which will benefit the consumer. Research can be made in the field of medicine by which all the dangerous diseases can be determined at their initial stages. Also we can find out the age of a particular plant or a tree using smell. Smell detection can be replaced with the technique of carbon dating as well.

Research is going on in various parts of the world so as to downsize the instruments of mass spectrometry and gas chromatography. The penny sized sensor has an extremely small sized vacuum pump for sample collection. Research shows that this technology have been tried to fit into smart phones. It is known as the world's first MEMS (micro-electromechanical systems) vacuum pump. The Researchers suggests that quality of air can be found and along with it one can know when and where the user was exposed.

Conclusion

In this paper a detailed review of all kinds of sensors is given which includes an evolution of the sensor technology from Gas chromatography-Mass Spectrometry to the latest penny sized GC/MS. Also the applications of smell detection in various fields which already exist and the future possible applications have been discussed.

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