Evaluating Polymeric Materials for Sensing of Gaseous Analytes

by

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A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Applied Science
in
Chemical Engineering

Waterloo, Ontario, Canada, 2019

Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Polymers have been widely used in gas sensing applications especially for detecting Volatile Organic Compounds (VOCs). Some of these applications consist of disease diagnosis and breathalyzers as well as evaluation of indoor air quality and detecting toxic analytes.

A sensing material requires to be highly sensitive to small amounts of gas. Selectivity is another essential characteristic, which has to be evaluated since many vapours/gases exist in small quantities (ppm or ppb) in houses and work places at the same time.

The goal was to evaluate poly (methyl methacrylate) doped with metal oxides as a potential sensing material for detecting acetone (diabetic applications). Afterwards, other polymeric sensing materials were examined for gas sorption capabilities toward formaldehyde, acetaldehyde, and benzene. The experiments were all operated at room temperature through a highly specialized and sensitive Gas Chromatograph test system.

Some of these polymeric sensing materials were commercially available and were used as received, whereas some others were synthesized in our lab. Poly (methyl methacrylate) (PMMA) has been used as doped and un-doped with metal oxides to evaluate its potential sensing capabilities toward acetone. Polyaniline (PANI), poly (2,5-dimethyl aniline) (P25DMA), poly(4-vinyl phenol) (P4VP), and poly (acrylic acid) (PAAc) have also been investigated as potential sensing material for formaldehyde sorption. After selecting the promising sensing material in single gas evaluations, selectivity of each sensing material has been studied. In order to evaluate selectivity, the target analyte has to be in a mixture with interferents (other gas analytes). Benzene and acetaldehyde were chosen as interferent analytes. Several gas concentrations and gas mixture ratios have been investigated to have a complete set of experiments and comparable data. In addition, one of the promising sensing materials for formaldehyde detection, PANI, was doped with NiO and In_2O_3 to further evaluate whether metal oxides can enhance sensing capabilities. At the final characterization step, Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) were used for additional information about the topology and the composition of the polymeric samples as well as incorporation of metal oxides into polymers.

Acknowledgements

Dedication

To my wonderful parents for their unstoppable love and support

&

To my lovely sister, Yasi

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1. Outline and Objectives

1.1 Motivation

Sensing volatile organic compounds (VOCs) is important in many applications; for example, acetone detection in disease diagnosis such as diabetes, and formaldehyde and benzene detection in indoor air quality. Higher amounts of acetone are emitted from diabetic patients' breath or skin, compared to a non-diabetic person. It has been found that patients with higher blood glucose levels had much higher breath acetone levels (Tassopoulos et al. 1969). Formaldehyde, even at very low concentrations, can cause respiratory problems and a general feeling of un-wellness. Thus, sensing small amounts of these analytes at room temperature is of high interest.

This research focuses on evaluating polymeric materials as sensing materials for acetone, formaldehyde, acetaldehyde, and benzene detection at ppm levels. There is preference for using polymeric materials as they are inexpensive and with tailorable properties. In any application, multiple gas analytes are present and will interact with both the sensing materials and the other analytes. This makes the identification of highly selective sensing materials desirable but difficult at the same time.

1.2 Objectives

There have been several long-term research studies in our group, evaluation polymeric sensing materials as sensitive and selective detectors for gaseous analytes for different applications (Stewart and Penlidis 2012- 2017). This MASc study is complementary to previous research and at the same time, is expanding the scope of previous research. More specifically:

a) Poly (methyl methacrylate) (PMMA) of different molecular weights (commercially available) was deposited for testing as a sensing material for acetone (A). To improve the sensitivity of a sensing material, metal oxides are widely used (Stewart et al. 2015). PMMA doped with three metal oxides, zinc oxide (ZnO), tungsten trioxide (WO_3), and tin (IV) oxide (SnO_2) at three levels of 5, 10, and 20 wt. % have been deposited and tested through a very sensitive gas chromatograph (GC) set-up to evaluate any potential analyte sorption.

b) Two different molecular weights of PMMA were synthesized, doped with 10% wt. ZnO, and evaluated for acetone detection in three different concentrations of 5 ppm, 100 ppm, and 1100 ppm acetone at room temperature.

c) In another study, polyaniline (PANI), a derivative of PANI, poly (2,5-dimethyl aniline) (P25DMA), poly(4-vinyl phenol) (P4VP), and poly (acrylic acid) (PAAc) in three different molecular weights were chosen as potential sensing materials for formaldehyde (F) and benzene (B) as toxic gas analytes. Benzene was used as interferent for selectivity studies of sensing materials toward formaldehyde. In general, the more analyte a sensing material sorb, the higher the sensitivity to that analyte.

1.3 Thesis Outline

Chapter 1 contains an introduction to the thesis. It discusses the motivation and objectives of this work, and also outlines what is to follow.

Chapter 2 includes relevant literature background. Gas sensing materials for volatile organic compounds (VOCs), specifically, acetone, formaldehyde, acetaldehyde, and benzene are discussed. Furthermore, sensing characteristics, including sensitivity and selectivity, are defined. Chapter 2 wraps up with discussing metal oxides used as sensing materials for gas analytes.

Chapter 3 covers the experimental procedures that were used. An experimental test system was used to evaluate sensing materials. The test system consists of a highly specialized gas chromatograph (GC) with a photon discharge helium ionization detector (PDHID). Chapter 3 also includes the sensing material preparation, synthesis of the polymers, and doping polymers with metal oxides. For ease of reading, the results and discussion part has been broken down into three chapters: evaluating sensitivity of sensing materials (Chapter 4), evaluating selectivity of sensing materials (Chapter 5), and polymeric sensing material analysis (Chapter 6).

Chapter 4 contains sensitivity results of sensing materials with regards to several gas analytes including acetone, formaldehyde, benzene and acetaldehyde.

Chapter 5 discusses selectivity results of sensing materials with regards to formaldehyde by using benzene and acetaldehyde as intereferents. This gave a basis for better evaluation of a specific sensing material when various gas analytes are present.

Chapter 6 contains sensing material analysis and further characterization by Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Analysis (EDX). In addition, it includes possible sensing mechanisms that occur when polymeric sensing materials and gas analytes, specifically VOCs, interact.

Finally, Chapter 7 includes concluding remarks, as well as recommendation for future work.

2. Literature Background

2.1 Volatile Organic Compounds (VOCs)

Volatile organic compounds (VOCs) are organic compounds/chemicals that have a high vapor pressure at room temperature. This high vapor pressure results from a low boiling point. They can commonly affect the human body through inhalation (breathing) or skin contact. Short-term exposure to various VOCs may cause irritation of the eyes and respiratory tract, headaches, dizziness, etc. Long-term exposure to various VOCs may cause irritation of the eyes, nose, and throat, nausea, fatigue, and damage to the liver, kidneys and central nervous system. It is important to detect toxic gas analytes in a variety of applications, including ethanol detection to prevent a person from driving while intoxicated (Winther-Jensen et al. 2014); or acetone detection in disease diagnosis such as diabetes (Choi et al., 2013); or formaldehyde and benzene detection for evaluating indoor air quality (González-Chavarri et al. 2015).

2.1.1 Acetone as a Volatile Organic Compound

Acetone is produced in the liver and evacuated from the body through urine and lungs (Wang et al. 2013). Excessive acetone circulating in the blood system is excreted from the lungs. Higher acetone concentration ranges from 1.7 ppm to 3.7 ppm could be detected in the breath of diabetic patients, while the breath of a healthy human typically contains less than 0.8 ppm (Deng et al. 2004). As a result, acetone can be regarded as a biomarker of diabetes prognosis and diabetes staging. Breath analysis has the potential for early stage detection and monitoring of illnesses to drastically reduce the corresponding medical diagnostic costs and improve the quality of life of patients suffering from chronic illnesses. In particular, the detection of acetone in the human breath is promising for non-invasive diagnosis and painless monitoring of diabetes (no finger pricking) (Righettoni et al. 2012). Gas sensors with sub-ppm acetone detection capacity play an important role in the development of non-invasive monitors or early diagnosis of potential diabetic patients.

2.1.2 A comparison of sensing material for detecting Acetone

Table 2.1 provides a variety of sensing materials used in acetone detection. From now on, the term "detections limit" represents the sensitivity of a sensing material toward a certain analyte. In addition, temperature of detection is the temperature in which the sensing material was able to detect the target gas analyte.

When metal oxides are used as sensing materials, sensitivity to acetone is achieved, but at higher temperatures (above 200 °C). PMMA combined with some metal oxides has shown sorption to acetone at room temperature (see Table 2.1).

Table 2.1 A comparison of sensing material for detecting acetone

Sensing Material	Detection Limit	Oper. Temp.	Reference
PANI/WO_3 doped with cellulose	10 ppm	Room temp	Aparicio-Martinez et al. (2018)
PMMA	29 ppm	-	Do & Wang (2013)
PMMA/Ammonium dihydrogen phosphate	-	Room temp	Devikala & Kamaraj (2011)
PMMA/TiO_2	-	Room temp	Devikala et al. (2016)
SnO_2- reduced graphene oxide	10 ppm	Room temp	Zhang et al. (2015)
WO_3	100 ppm	200 °C	Zhang et al. (2013)
ZnO	2 ppm	310 °C	Li et al. (2013)
ZnO	-	200 °C	Chen et al. (2016)
In_2O_3	25 ppm	400 °C	Vomiero et al. (2007)

2.1.3 Formaldehyde as a Volatile Organic Compound

Formaldehyde is one of toxic volatile organic compounds (VOCs) that pollute indoor air. It is the simplest of the aldehydes. Formaldehyde is used in a variety of products including plywood, glues, resins, insulating materials, adhesives, fabrics, and pulp and paper products (WHO. 2001; Wang et al. 2009). The main way people are exposed to formaldehyde is by inhaling it. The liquid form can be absorbed through skin. Materials containing formaldehyde can release it as a gas or vapor into the air. Automobile exhaust is a major source of formaldehyde in outdoor air.

Formaldehyde concentrations in dwellings vary according to the age of the building, since the release of formaldehyde decreases with time, the air exchange rate, and the season (Raw et al. 2004), as well as temperature and relative humidity (Haghighat et al. 1998).

Occupational short-term exposure limits for formaldehyde in Ontario workplaces is 1ppm with the ceiling limit of 1.5 ppm. The concentration of formaldehyde measured as an 8-hour-weighted average should be less than 0.75 ppm. The International Agency for Research on Cancer (IARC) has declared formaldehyde as carcinogenic to humans.

2.1.4 A comparison of sensing material for detecting Formaldehyde

Stewart et al. (2012) developed a formaldehyde sensing material based on polyaniline and modified polyaniline with several metal oxides as dopants. They could detect formaldehyde in very small amounts (<1ppm) using these sensing materials. The sensors were tested at room temperature and over several other gas analytes as interferents. A sensor array of SnO_2 thin film doped with metal catalysts of Au, Cu and Pt could detect formaldehyde presence down to 0.06 ppm at 150-350 °C (Lv et al. 2007). Many sensors that use platinum in acidic solutions also worked well at low concentrations of formaldehyde (Mascaro et al. 2004).

A comparison of sensing materials used in formaldehyde detection is provides in Table 2.2.

Table 2.2 A comparison of sensing material for detecting formaldehyde

Sensing Material	Dopant	Detection Limit	Temperature of detection	Reference
PANI	MoO_3	-	30 °C	Wang et al. (2006)
PANI	NiO (15 wt. %)	0.3 ppm	21 °C	Stewart et al. (2012)
PANI	NiO (5 wt. %) Al_2O_3 (15 wt. %)	1 ppm	21 °C	Stewart & Penlidis (2016)
Single-wall carbon nanotubes	Polyethyleneimine	24 ppb	-	Song et al. (2018)
Cu_2O	-	6 ppb	250 °C	Park et al. (2014)
Graphene	ZnO	180 ppb	Room Temperature	Mu et al. (2014)
In_2O_3	Ag (8 wt. %)	2 ppm	100 °C	Wang et al. (2009)
SnO_2	-	10 ppb	215 °C	Xing et al. (2013)

2.1.5 Acetaldehyde as a Volatile Organic Compound

Acetaldehyde is considered as carcinogenic and toxic. The main sources of acetaldehyde are essentially incomplete combustions or emissions from paints, linoleum, and varnishes (Pichard et al. 2005). Several technologies were considered for its detection by using metal oxides (Shalini et al. 2016) or quartz crystal microbalance (QCM) coated with polymers (Hirayama et al. 2002), just to mention a few.

2.1.6 A comparison of sensing material for detecting Acetaldehyde

Polymeric sensing materials that have been used for the detection of acetaldehyde include polyaniline and its derivatives (Stewart et al. 2012). Also, several metal oxides have been used in detecting acetaldehyde. Among those, ZnO was used with cobalt as dopant to detect acetaldehyde at room temperature (Mani and Rayappan, 2016). Mixing a metal oxide with a metal, Indium (III) oxide with gold, had sensitivity of about 10 ppm towards acetaldehyde at 250 °C (Han and Sohn, 2011). Table 2.3 provides more information on some sensing materials used in acetaldehyde detection.

Table 2.3 A comparison of sensing material for detecting acetaldehyde

Sensing Material	Dopant	Det. Limit	Oper. Temp	Reference
PANI	Dodecyl-hydrogen sulfate salt & maleic acid	10 ppm	Room temp	Palaniappan & Saravanan (2010)
TiO_2	-	5 ppm	Room temp	Muthukrishnan et al. (2015)
Poly (2,5-dimethyl aniline)	MoO_3	0.96 ppm	40 °C	Itoh et al. (2007)
ZnO	F (4 wt. %)	100 ppm	Room temp	Gunasekaran et al. (2018)
In_2O_3	Au	10 ppm	250 °C	Han & Sohn (2011)
In_2O_3	-	1 ppm	300 °C	Chava et al. (2019)
ZnO	Co	10 ppm	Room temp	Mani & Rayappan (2016)

2.1.7 Benzene as a Volatile Organic Compound

Benzene is an aromatic compound with a single six-member unsaturated carbon ring. Benzene has a relatively low boiling point of 80.1 °C and a high vapor pressure, causing it to evaporate rapidly at room temperature. It is slightly soluble in water and is miscible with most organics. Benzene in indoor air can originate from outdoor air and also from sources indoors such as building materials and furniture, heating systems, stored solvents and activities such as cleaning (Kim et al. 2001). Tobacco smoke is also considered as one of the main indoor sources of benzene. Smoking cigarette emits 430 to 590 μg benzene per cigarette (Singer et al. 2003).

Outdoor benzene concentrations are mainly due to traffic sources and are affected by season. Some other outdoor sources of benzene are certain industries concerned with steel, oil, natural gas, and chemicals (Jia et al. 2008). Benzene is also present in plywood, paints, adhesives and some furnishing materials (Yu et al. 2003). Therefore, recently made buildings are associated with high concentrations of benzene from house furniture and materials. A study estimated a daily benzene exposure of 102 μg/day/person, where this number was attributed to 36% indoor home, 32% indoor work, 2% outdoor and 30% in transit (Bruinen et al. 2008).

Many organic analytes, such as benzene, are not reactive at room temperature. Therefore, detecting them by their chemical reactions with conducting polymers is difficult. However, they may show weak physical interactions with the sensing polymers, involving absorbing or swelling the polymer matrixes, etc. These interactions do not change the oxidation levels of conducting polymers, but can influence the properties of the sensing materials and make these gases detectable (Bai and Shi 2007).

2.1.8 A comparison of sensing material for detecting Benzene

Polymeric sensing materials that have been used for benzene detection include a specialty polymer SXFA and polyaniline (Chen et al. 2015; Stewart et al. 2018). These polymers have also been doped with various metals and metal oxides to improve sensitivity and/or selectivity. Table 2.4 provides a variety of sensing materials used in benzene detection, most of which are active at high temperatures.

Table 2.4 A comparison of sensing material for detecting benzene

Sensing Material	Dopant	Detection Limit	Temperature of detection	Reference
SnO_2	Au	150 ppb	30 °C	Gràcia et al. (2008)
SnO_2	-	300 ppm	Room temp	Panchal et al. (2015)
ZnO	Au	1 ppm	340 °C	Wang et al. (2013)
Bi4SnV2O13	-	~100 ppb	150 °C	Fan et al. (2016)
SXFA	-	625 ppm	Room temp	Chen et al. (2015)
WO_3	Pt	0.2 ppm	300 °C	Ke et al. (2009)
Pd- SnO_2		1 ppm	400 °C	Kim et al. (2016)

2.2 Polymeric Sensing Materials

2.2.1 Introduction

Sensing material is the material that interacts with the target gas through sorption, which is defined as a gas sticking to the surface of the sensing material.

The two main categories of sensing materials currently used are polymers and metals and metal oxides (Stewart and Penlidis 2016). Polymers are ideal sensing materials since they work at low temperatures (Mabrook and Hawkins 2001), possess high toughness, can be tailor-made to attract a specific gas analyte, therefore can have high selectivity (Talwar et al. 2014), and are recyclable (Yi et al. 2008). Polymeric sensing materials are usually used as thin films; in this case a higher surface area to volume ratio is achieved. This provides more available active sites on the surface of a sensing material in order to sorb gas (Finks 2012).

Conducting polymers show chemical selectivity, which allows them to act as excellent materials for gas sensors.

2.2.1 Chemistry and properties of PMMA

Poly (methyl methacrylate), PMMA, is a hard, rigid, glassy but brittle, polymer with a glass transition temperature of about 100 °C. It is used in many applications, e.g., intraocular lenses and

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hard contact lenses, bone cement in joint replacement surgery, coatings, "glass" production, etc. PMMA consists of a non-polar backbone (i.e., a hydrocarbon backbone), with somewhat polar pendant ester groups. The overall polymer is hydrophobic. PMMA blends with reduced graphene oxide have been used for gas sensing application at room temperature (Chuang. 2015).

2.2.2 Chemistry and properties of PANI

Polyaniline (PANI) is made from aniline oxidation. It exists in five oxidation states. Although none of the states are conductive, protonated forms of the moderately oxidized states, especially emeraldine, are conductive and are the most stable form of PANI due to the high conjugation. PANI is unique since no electrons need to be added or removed from the material to make it conductive (Feast et al. 1996; Hosseini et al. 2005).

Aniline is processed easily, inexpensive and produces a stable and conductive polymer (Feast et al. 1996). Of the many polymeric materials available, polyaniline (PANI) and its derivatives are particularly sensitive to formaldehyde (Itoh et al. 2006).

2.2.3 Chemistry and properties of P25DMA

Poly (2,5-dimethyl aniline) (P25DMA) is a derivative of PANI with many of the same desirable sensing material aspects as PANI. P25DMA is more tailorable than PANI since its chains are not packed as closely, which increases the size of the interstitial spaces meaning easier access to more active sites in the polymer. This results in sensitivity improvements.

2.2.4 Chemistry and properties of PAAc

Poly (acrylic acid) (PAAc) is hygroscopic, brittle and colorless in nature with T_g of about 106 °C. It has free carboxylic functional groups, which leads to the high sensitivity and selectivity toward amine compounds. PAAc is employed as a thickening agent for adhesives and cosmetic products. Also, electrospun fibrous polyacrylic acid membranes have been studied as sensing material for ammonia detection at very low concentrations (Ding et al. 2005).

2.2.5 Chemistry and properties of P4VP

Poly (4-vinylphenol) (P4VP) with glass transition temperature of about 150 °C is structurally similar to polystyrene. Some of its applications are in electronic displays and adhesives. It has also

been used as a nanogap electrode coating material for acetone detection at low concentrations (Minh et al. 2017).

2.3 Dopants and Metal Oxides

Dopants are small amount of additives to the sensing material used to improve sensitivity and/or selectivity properties of a sensing material. Dopants include metals and metal oxides, acids, and surfactants (Talwar et al. 2014). Furthermore, sensing materials can be doped by adding a small amount of an impurity as desired, which can significantly change some of the sensing material's properties (Stewart 2016). They usually need to operate at high temperatures for catalytic activity. Several technologies for monitoring and detecting gases such as ethanol and acetone have been developed. One type of these technologies is based on semiconductor materials such as metal oxides and metal nitrides. Another type is based on conducting polymers, which represent several advantages including operation at room temperature, short response time, high sensitivity, and ease of fabrication. Among these polyaniline has attracted considerable attention because of its ease of fabrication, versatility in use, environmental stability, low cost, and high mechanical strength (Fratoddi et al. 2015; Li et al. 2009; Gao et al. 2003; Mojtabavi et al. 2016)

Besides metal oxides, external factors such as temperature and humidity, also play an important role in the testing of sensitivity. Humidity will decrease the sensitivity and be harmful to repeatability. Fortunately, it can be eliminated by heating to high temperatures (usually >400 °C; Wang et al. 2010).

In gas sensors, metal and metal oxides are sometimes used for their electronic conductivities and their surface catalytic properties as oxidation catalysts (Dirksen et al. 2001). The specific surface area of a conductive polymer is increased by the addition of metal particles, thus improving the catalytic efficiency of the sensing material (Choudhury 2009). Sensitivity and selectivity of the dopant in contact with a gas analyte will increase when small grain size of metal oxide is being used. This is also due to the increased surface area of the dopant (Lee et al. 2007).

2.3.1 Zinc Oxide (ZnO)

ZnO is one of the most extensively used metal oxides for gas sensing applications (Shafiei et al. 2010). It is a desirable sensing material due to its high chemical stability, non-toxicity, and low cost (Liu, 2012). In addition, ZnO can be combined with other metal oxides to improve both its sensitivity and selectivity. The high sensitivity of ZnO can be related to its catalytic activity and

small particle size. By reducing the particle size, the specific area (surface area to volume ratio) is increased, therefore more active sites are available to sorb analyte (Xu et al. 2000).

Table 2.5 provides some applications of ZnO in gas dectection.

Table 2.5 ZnO as a sensing material for gas detection

Material	Dopant	Detection limit	Selectivity	Oper. Temp	Reference
ZnO	-	10 ppm	-	400 °C	Singh et al. (2008)
ZnO	-	50 ppm	-	220 °C	Choopun et al. (2007)
ZnO	-	5 ppm	Acetone; Formaldehyde; Nitrogen dioxide; Ammonia; Hydrogen gas; Carbon monoxide; Hydrogen sulfide		Zou et al. (2013)
ZnO	NiO	0.3 ppm	Formaldehyde; Acetone; Carbon monoxide; Benzene	450 °C	Na et al. (2012)
ZnO	Ti	50 ppm	-	250 °C	Hsu et al. (2014)
ZnO	-	250 ppb	Acetone	230 °C	Jia et al. (2014)
ZnO	Co (5 wt%)	10 ppm	Acetone	Room temp.	Mani & Rayappan (2016)
ZnO	-	1 ppm	Ethanol	320 °C	Wang et al. (2012)
Graphene	ZnO	180 ppb	Formaldehyde	Room temp.	Mu et al. (2014)

2.3.2 Tin Oxide (SnO$_2$)

SnO$_2$ is a widely-used metal oxide material for gas sensing applications of small organic molecules because of its low cost and high chemical stability. However, wide application of SnO$_2$-based gas sensors is limited by low sensitivity, slow response, lack of selectivity and the effects of aging

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(Zhang et al. 2005). SnO_2 is not very selective on its own. Therefore, other dopants has been used to improve its selectivity. A number of gas sensing applications can be found in Table 2.6.

Table 2.6 SnO₂ as a sensing material for gas detection

Material	Dopant	Detection Limit	Selectivity	Oper. Temp.	Reference
SnO_2		50 ppm	Ammonia	Room temp	Khun Khun et al. (2009)
SnO_2	NiO	5 ppm	Acetone; Benzene; Carbon monoxide	300 °C	Liu et al. (2011)
SnO_2	NiO	6.7 ppm	Formaldehyde; Carbon dioxide; Methane	280 °C	Lou et al (2012)
SnO_2	In (10%)	200 ppb	Acetone	200 °C	Cindemir et al. (2016)
SnO_2	In (4.43%) Pd (0.66%)	5 ppm	Formaldehyde	160 °C	Lin et al. (2015)

2.3.3 Tungsten Oxide (WO₃)

WO_3 has been proposed as one of the most suitable materials for acetone sensing (Shi et al. 2011). WO_3 has been successfully applied to gas sensors for detecting H_2, NO_2, H_2S, and NH_3. Table 2.7 provides some applications of WO_3 as sensing material in gas detection.

Table 2.7 WO₃ as a sensing material for gas detection

Material	Detection Limit	Selectivity	Oper. Temp.	Reference
WO_3	40-100 ppm	Ethanol	400 °C	Khadayate et al. (2007)
WO_3		H_2		Shaver (1967)
WO_3		H_2S		Lin et al. (1994)
WO_3		NH_3	250-300 °C	Llobet et al. (2000)
WO3	31-80 ppm	NO & NO_2	300 °C	Akiyama et al. (1991)
PANI/Cellulose/WO_3	10 ppm		Room temp	Aparicio-Martinez et al. (2018)

2.3.4 Indium Oxide (In_2O_3)

Indium oxide (In_2O_3) is a low resistance material and has a high capability in testing oxidizing gas (Huang et al. 2009). In_2O_3 as metal oxide sensing material has been used for formaldehyde detection (Wang 2009). It has also been used for acetaldehyde detection doped with Au at 250 °C (Han and Sohn 2011). Therefore, incorporating In_2O_3 into a polymeric sensing material may improve sensing performance (see Table 2.8).

Table 2.8 In₂O₃ as a sensing material for gas detection

Material	Dopant	Detection Limit	Selectivity	Oper. Temp.	Reference
In_2O_3			NO_2	Room temp	Roso et al. (2016)
In_2O_3	Pt (4.5 wt.%) La_2O_3 (1.35 wt.%)		Ethanol		Zhan et al. (2007)
In_2O_3	SnO_2 17%	200 ppm	Methanol	Room temp	Patel et al. (2003)
In_2O_3	Au	10 ppm	Acetaldehyde	250 °C	Han & Sohn (2011)
In_2O_3	Ag (8 wt.%)	2 ppm	Formaldehyde	100 °C	Wang et al. (2009)

2.3.5 Nickel Oxide (NiO)

NiO as sensing material has been used for formaldehyde detection by several researchers (Lee et al. 2007; Campanella et al. 2006; and Wang et al. 2009). It has also been used as dopant with PANI to detect formaldehyde (Stewart et al. 2012; 2016).

Although most metal oxide sensors operate at high temperatures above 100˚C, NiO can detect ethanol at room temperature (Stewart et al. 2015; Li 2016). This gives NiO further potential to sense analytes at both high and low temperatures.

Ni is in the same group as Pt and Pd, all good oxidation catalysts for small organic molecules (Safavi et al. 2009). Comparison of the catalytic activity towards the oxidation of formaldehyde of many metals illustrated that NiO has the highest catalytic activity towards formaldehyde among them (Dirksen et al. 2001).

Table 2.9 NiO as a sensing material for gas detection

Material	Dopant	Detection Limit	Selectivity	Oper. Temp.	Reference
PANI	NiO		Formaldehyde Acetaldehyde Ethanol Benzene	Room temp	Stewart et al. (2012)
NiO		5 ppm	Acetone Carbon monoxide	300 °C	Kaur et al. (2016)
NiO		10 ppm	-	Room temp	Li (2016)
NiO	TiO$_2$	2000 ppm	Methanol	Room temp	Lyons et al. (2004)
NiO		0.8 ppm	Formaldehyde		Lee et al. (2007)

2.4 Sensing Characteristics

2.4.1 Sensitivity

Sensitivity is defined as the lowest concentration a sensor or sensing material can detect when exposed to a target analyte. The more sensitive the sensor, the lower the concentration of analyte

the sensor can detect. The sensitivity of a sensing material is defined as the concentration of analyte sorbed onto the sensing material divided by the total concentration of the analyte present (see Equation 2.1).

$$Sensitivity = \frac{[Gas]\ total - [Gas]\ residual}{[Gas]\ total}$$
(Equation 2.1)

Sensitivity is affected by the morphology of a sensing material. Thin films and highly ordered structures increase sensitivity. Also, sensing materials with higher surface areas, therefore more sensing sites available for analyte sorption, increase sensitivity (Nair and Alam 2007).

2.4.2 Selectivity

Selectivity is a value indicating how much the target analyte is favoured over interferent analytes (for the same or very similar concentrations). The ratio between the concentrations of target analyte (that sorbs onto the polymer) over the interferent analyte is the selectivity value (see Equation 2.2). The larger the ratio between the target analyte and an interferent analyte, the higher the selectivity. A material is called selective when the selectivity ratio is greater than 1.75 (Stewart et al. 2012).

$$Selectivity = \frac{[Target\ analyte\ sorbed]\ ppm}{[Interferent\ analyte\ sorbed]\ ppm}$$
(Equation 2.2)

3. Experimental: Gas Test System and Sensing Materials

3.1 Experimental Apparatus

Evaluation of potential sensing materials was through gas sorption tests. Each sensing material was exposed to a certain concentration of gas analyte in a balance of nitrogen. The amount of analyte sorbed onto the sensing material was measured by the gas test system.

Sensitivity of the sensing material is higher when more analyte is sorbed onto that sensing material. The gas test system evaluated sensing materials at room temperature (21-23°C) and at atmospheric pressure of 15 psi. Mixtures of gas analytes were produced using an inline passive mixer, after which the gas line was split using an MKS RS-485 mass flow controller on one side and an MKS 640A pressure controller and MKS 1179A flow meter on the other to ensure a 50:50 volumetric split.

The sensing materials were tested using a flow rate of 200 standard cubic centimeters per minute (sccm). In the case of gas mixtures, a total flow rate of 200 sccm was also used. The gas stream (200 sccm) was directed into a 100 ml round butom flask containing sensing material and subsequesntly into a specialized Varian 450 gas chromatograph (GC) with a photon discharge helium ionization detector (PDHID) with the measuring capability down to the ppb level (Stewart et al. 2012). A schematic of the test system, where MFC, PC, and FM stand for mass flow controller, pressure controller, and flow meter, respectively, is shown in Figure 3.1.
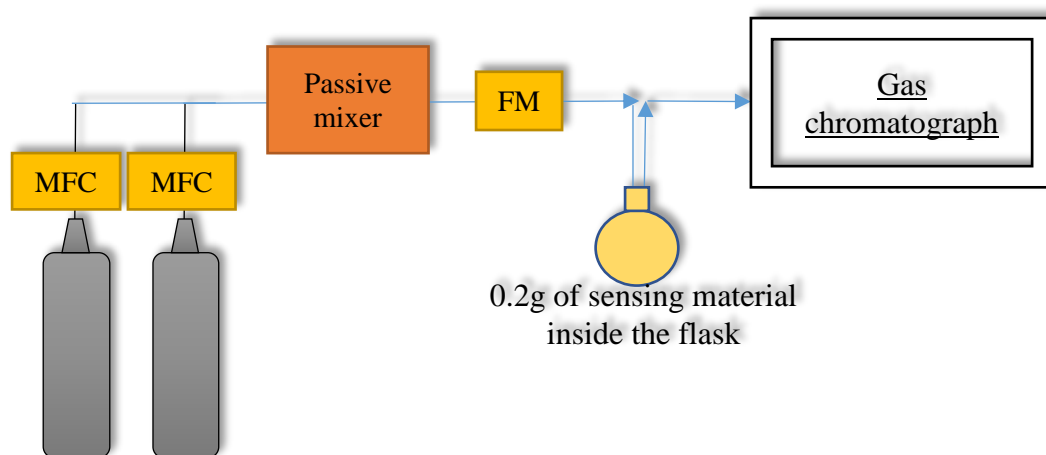
Figure 3.1 Schematic of the gas test system

3.1.1 Gas Chromatograph (GC)

A gas chromatograph is used to identify components in either a liquid or a gas sample. The components of the sample are separated based on their retention times, as they flow through a column, which contains a suitable packing material. The packing material is chosen based on what components are known to be in the sample. As the components of a sample pass through the column, they sorb (adsorb or absorb) onto the packing material at different rates based on each component affinity. The retention times indicate which components are in a sample. The data of a gas chromatograph can be represented graphically and appear as peaks on a voltage versus time graph. The peaks are integrated and compared to those of a standard with a known concentration to determine the concentration of each component in a sample quantitatively (Barry 2004).

The specialized highly sensitive gas chromatograph used in this study needed to separate very chemically similar compounds and detect very low concentrations. The separation was achieved using a Varian CP-Sil 5 CB with a capillary column of dimensions 60 m x 0.32 mm x 8 μm (the CP-Sil 5 CB GC column is packed (100%) with poly(dimethylsiloxane) or PDMS).

The GC uses a very sensitive pulsed discharge helium ionization detector (PDHID) which can detect in the parts per billion (ppb) range. Pulsed direct current (DC) discharge causes the helium to ionize. When helium turns back to its normal state, photons are released and ionize the sample as it moves down the column, producing electrons. Then, these electrons generate a response towards the detector. The detector is very sensitive and because of that, it is encased in helium (Collin et al. 2006).

3.1.2 Evaluation of Sorption Amounts

The GC produced chromatograms (see Figure 3.2 for a typical one) from which the concentration of residual gas (gas that was not sorbed onto the sensing material) was determined. This value was subtracted from the initial concentration of gas to determine the amount of gas sorbed onto the sensing material (see Equation 3.1).

$$[Gas]sorbed = [Gas]initial - [Gas]residual \qquad \text{(Equation 3.1)}$$

In Figure 3.2, the pink line represents a "blank" sample, whereas the blue line is when a polymer sample was exposed to a gas analyte. The difference between these two peaks gives the amount of analyte sorbed onto the sensing material in ppm.

In the case of gas mixture experiments, the polymer would ideally sorb a higher concentration of the target analyte and a lower concentration of the other gases (interferents).
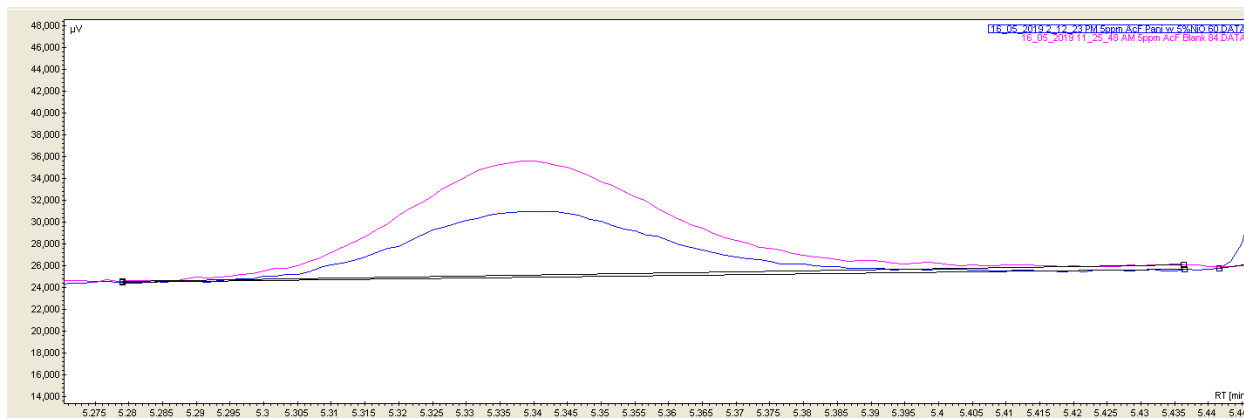
Figure 3.2 A typical chromatogram produced from GC

During a "blank" trial, an empty flask without any absorbent polymer in it was exposed to the gas analyte. This was performed before the first (real) sample and also in the middle/end of the day (for a specific analyte at a specified concentration) in order to verify that the blanks did not change during the day and concentration values were reliable for all the polymers measured. These 'blanks' were used to ensure there was no baseline drift throughout the measurements. In case of baseline drift during the day, there would have been fluctuations between the blank measurements, which result in a high variance. For the ideal case, the expected response from the blank should be equal to zero, which means that all the gas passed through (did not sorb onto) the test system at that concentration. The equations for the average and the variance are given below (see Equations 3.2 and 3.3, respectively), where X is the measured variable and n represents sample size.

$$\bar{X} = \frac{1}{n}\sum_{i=1}^{n} X_i \tag{Equation 3.2}$$

$$S^2 = \frac{\sum_{i=1}^{n}(X_i - \bar{X})^2}{n-1} = \frac{1}{n-1}\left\{\sum_{i=1}^{n} X_i^2 - \frac{1}{n}\left(\sum_{i=1}^{n} X_i\right)^2\right\} \tag{Equation 3.3}$$

3.1.3 Reproducibility of Results

According to the manufacturer of this very specialized GC, the GC has an error of 1%, which accounts for some of the variance. The rest of the variance (if at all present) is due to other sources of uncertainty that contribute to overall variability.

The polymer samples tested were independent replicates. The error within the replicates was expressed as the coefficient of variation (CV). The coefficient of variation, which is a ratio between

18

the standard deviation (s) over the mean (x̄), is a normalized measure that can be used as an indicator of the overall error (see Equation 3.4).

$$Coefficient\ of\ Variation\ (CV) = \frac{s}{\bar{x}}$$ (Equation 3.4)

The CV values for each polymer at each concentration for each gas were determined from the concentration sorbed onto the polymer. For many of the polymers for each gas, the coefficient of variation was 0.05 or less; meaning the error between the replicates was 5% or less and the GC had reproducible results.

3.2 Gas Analytes Tested

In total, four gas analytes (acetone, formaldehyde, benzene, and acetaldehyde) were evaluated in the gas test system (see Table 3.1 for the concentrations of each gas analyte available). All of these gases were specialty gas mixtures (standard grade) in a balance of nitrogen gas (Praxair, California, USA). In addition, other concentrations of each of these gases could be achieved by dilution with 5.0 grade nitrogen (Praxair, Mississauga, Ontario, Canada).

Table 3.1 Gas analytes and concentrations used

	Tank concentration (ppm)			
Analyte	5	10	100	1100
Acetone (A)	✔		✔	✔
Formaldehyde (F)	✔	✔		
Acetaldehyde (Ac)		✔		
Benzene (B)	✔			

In the case of evaluating gas mixtures, certain analytes were combined together. For example, to obtain a 5 ppm formaldehyde and benzene mixture, 2 ±0.5 ppm formaldehyde and 2 ±0.5 ppm benzene streams were combined (50-50). The same procedure was followed at higher concentrations, for example, combining 10 ppm F and 10 ppm B, which resulted in a mixture containing 5 ±0.5 ppm of each gas.

Gas mixtures directed in the gas stream were calculated using ideal gas law. In the case of similar concentrations of analytes in the GC gas stream, gas masses were calculated by knowing the molecular weights of each gas. The calculated values were then slightly adjusted based on experimental observations to achieve the desired overall concentration. A brief example of the related calculations is provided in Appendix A.

Structures of the gas analytes, metal oxides, and polymers investigated in this thesis are shown in Appendix B.

3.3 Sensing Materials for Acetone (A) Detection

In the selection of proper sensing material for the target analyte (acetone), Hildebrand solubility parameters values have been considered. Also, the glass transition temperature (T_g) of the sensing material is important. Since the operational temperature for our sensing materials is room temperature (21-23 °C), we need to choose a sensing material which remains rigid throughout the application. This means that the glass transition temperature of the sensing material should be significantly higher than room temperature. Hildebrand solubility parameter values for acetone and PMMA are 20.3 and 22.8 $MPa^{1/2}$, respectively. Therefore, these two materials have a very promising range of solubility parameters and PMMA can be chosen for further evaluations.

3.3.1 Polymers and Dopants for Acetone Sorption Evaluation

- Commercially available polymers: PMMA with molecular weight averages of 15,000 and 120,000 were purchased from Sigma Aldrich and used as received.
- Synthesized polymers: PMMA with molecular weight averages of 500,000 and 1,000,000 were synthesized in our lab. In addition, zinc oxide (ZnO) particle size <100 nm, 50 wt. % in water was purchased from Sigma-Aldrich, Oakville, Ontario, Canada, and used as received.
- Three metal oxides including zinc oxide (ZnO), tungsten trioxide (WO_3) particle size <100 nm, and tin (IV) oxide (SnO_2) particle size <100 nm were used to dope PMMA in three weight percent concentrations of 5, 10, and 20.

3.4 Sensing Material for Formaldehyde (F) and Benzene (B) detection

Hildebrand solubility parameter values for formaldehyde and benzene and the corresponding sensing materials are provided in Table 3.2.

Table 3.2 Hildebrand solubility parameters for analytes and polymers

Analyte	δ (MPa$^{1/2}$)	Sensing material	δ (MPa$^{1/2}$)
Formaldehyde	24.7	Poly (acrylic acid) (PAAc)	19.2
Benzene	18.6	Polyaniline (PANI)	22.2
Acetaldehyde	21.1	Poly(methyl methacrylate) (PMMA)	22.8
		Poly (2,5-dimethyl aniline) (P25DMA)	21
		Poly (4-vinylphenol) (P4VP)	25.6

3.4.1 Polymers and Dopants for Formaldehyde and Benzene Sorption Evaluation

- Commercially available polymers: Poly (4-vinylphenol) (P4VP) was purchased from Sigma Aldrich. The average molecular weight of the polymer is ~25,000. Poly (acrylic acid) (PAAc) in three different molecular weight averages was investigated: Mn = 130,000 (number-average molecular weight) and Mv = 450,000 (viscosity-average molecular weight) (both from Sigma Aldrich) and Mw = 1,000,000 (weight-average molecular weight) (from Polysciences, Inc.). These polymers were purchased and used as received.

- Synthesized polymers: Polyaniline (PANI) with molecular weight average of about 200,000 and poly (2,5- dimethyl aniline) (P25DMA) with molecular weight average of 180,000 were synthesized in our lab.

- Two metal oxides, indium (III) oxide (In_2O_3) particle size of <100 nm and nickel oxide (NiO) particle size of <50 nm, were chosen as promising candidates for doping PANI. Doping PANI with metal oxides can improve sensitivity and selectivity, electrical conductivity, thermal stability and mechanical stability (Stewart, 2012).

3.5 Sensing Materials for Acetaldehyde (Ac) detection

3.5.1 Synthesized Polymers and Dopants used in Acetaldehyde Sorption Evaluation

Polyaniline (PANI) with molecular weight average of about 200,000 was synthesized (as described in Section 3.9.2), and evaluated for acetaldehyde sorption.

In$_2$O$_3$ was selected as a metal oxide as it has been used to successfully detect acetaldehyde (Hang, 2011). PANI was doped with 5% indium (III) oxide and 5% nickel oxide for evaluation of gas sensing capabilities of the doped materials.

3.6 Sensing Materials for Formaldehyde/Bezene (F/B) Mixture Evaluation

PANI, P25DMA, P4VP, PAAc-130K, PAAc-450K were chosen as promising sensing materials for formaldehyde and benzene gas mixtures. Benzene was chosen as it represents aromatics and represents the effect of a non-polar interferent.

3.7 Sensing Materials for Formaldehyde/Acetaldehyde (F/Ac) Mixture Evaluation

PANI, PANI doped with In$_2$O$_3$, and PANI doped with NiO were evaluated for formaldehyde/acetaldehyde gas mixtures. Acetaldehyde was chosen since it is chemically very similar to formaldehyde.

3.8 Preparation of Sensing Materials

3.8.1 Low Molecular Weight PMMA

0.2 g of 15K PMMA was weighed into a 100 ml round bottom flask. 5 ml of ethanol was then added to the flask. Flask was swirled for 30 seconds to disperse the polymer and coat the flask in a way that more surface area of the polymer would be exposed to the analyte. The polymer was then dried in oven for 2 hours at 60 ℃. Then, the polymer was stored in glass vials. Prior to testing, the polymer samples were purged with nitrogen gas for more than 45 minutes before being exposed to the gas analyte to ensure any residual analyte possibly sorbed onto the polymer was released.

3.8.2 High Molecular Weight PMMA

0.2 g of 120K PMMA was weighed into a 100 ml round bottom flask. 5 ml of ethanol was added to the flask. The other steps taken are similar to the procedure discussed in section 3.8.1.

3.8.2 PMMA with Metal Oxide

These concentrations reflect the amount of metal oxide added during synthesis, with respect to the total polymer weight (i.e., 5% ZnO and 95% PMMA).

3.8.3 Low and High Molecular Weight PAAc

0.2 g PAAc (from each molecular weight) was weighed into a 100 ml round bottom flask. 5 ml of ethanol was added to the flask and the flask was swirled for 30 seconds to disperse the polymer

and coat the flask. The polymers were then dried overnight under fume hood. Prior to testing, the polymer samples were purged with nitrogen gas for more than 45 minutes before being exposed to the gas analyte.

3.8.4 P4VP

As per sections 3.8.3.

3.9 Synthesis of Sensing Materials

3.9.1 PMMA Synthesis

Poly (methyl methacrylate) (PMMA) was synthesized by bulk polymerization. MMA monomer was added to 20 ml vials. Azo-bis-iso-butyronitrile (AIBN) was added (0.3% by wt. on monomer) as initiator. The vials were heated in a water bath at 70 °C. The induction time before formation of visible polymer in the solution was 30 minutes. After 45 minutes of reaction, the first set of polymer samples was taken out from the water bath. These polymers had a weight-average molecular weight of 0.5 M. Another polymer sample was heated for 120 minutes to achieve a weight-average molecular weight of 1 M. Polymers were then crushed and dried in oven at 90°C for two days until constant weight was achieved.

3.9.2 PANI Synthesis

Polyaniline (PANI) was synthesized by mixing aniline and ammonium persulfate in deionized water. 0.4 ml of aniline provided from A.C.S. reagent, Sigma-Aldrich, Oakville, Ontario, Canada, was added to 20 ml of deionized water and then put into a sonicator for 30 minutes. Next, the monomer solution was cooled to −3 °C in a bath of a mixture of water and ethylene glycol before the addition of a solution containing 1.0 g of ammonium persulfate (A.C.S. Reagent, Sigma-Aldrich, Oakville, Ontario, Canada) in 5 ml of deionized water. The solution was shaken for one minute to ensure thorough mixing. The mixture was subsequently left to react at -3°C for 6 hours (Stewart et al., 2012). The polymer was filtered out using a funnel and Wattman #42 (2.5 µm pore size) filter paper, then washed with deionized water and ethanol until the liquid ran clear. Finally, the polymer was air dried and stored in a glass vial under atmospheric conditions.

3.9.3 P25DMA Synthesis

Poly (2,5-dimethyl aniline) (P25DMA) was synthesized as per section 3.9.2. In this synthesis, 2,5-dimethyl aniline was used as monomer (A.C.S. reagent, Sigma-Aldrich, Oakville, Ontario, Canada).

3.10 Synthesis of Sensing Materials doped with Metal Oxide

3.10.1 PMMA Doped with Metal Oxide

After no significant sorption was measured by the commercially available PMMA with metal oxide, we decided to synthesize PMMA and add metal oxide initially to the polymer in order to get a more homogeneous polymer and metal oxide incorporation.

These concentrations reflect the amount of metal oxide added during synthesis, with respect to the total polymer weight (i.e., 5% ZnO and 95% PMMA).

Zinc oxide (ZnO) particle size <100 nm, 50 wt. % in water, tin (IV) oxide (SnO_2) (stannic oxide) particle size <100 nm, and tunsgten trioxide (WO_3) particle size <100 nm were purchased from Sigma-Aldrich, Oakville, Ontario, Canada, and used as received.

Dopants in three weight ratios of 5, 10, and 20% were added to the monomer solution initially. The rest of the polymerization procedure was the same as described above for PMMA without any dopant.

3.10.2 PANI Doped with Metal Oxide

To obtain PANI doped with metal oxide, the monomer was polymerized with the dopant in the starting solution. 5% by weight dopant with respect to the monomer was added before the solution was initially cooled. This is prior to the addition of the ammonium persulfate as initiator. Other than the addition of dopants, which were nickel oxide (NiO) (particle size <50 nm, concentration of 99.8%) and indium (III) oxide (In_2O_3) (particle size <100 nm), both from Sigma-Aldrich, Oakville, Ontario, Canada, the polymerization procedure was the same as described for PANI without dopants.

3.10.3 PANI/In_2O_3/NiO Composite

Composites of tin dioxide/zinc oxide and tin dioxide/indium oxide may display enhanced sensitivity to 5 ppm ethanol when compared with the single oxide sensor (Wang et al. 2010). 0.1

g of PANI doped with 5% In_2O_3 and 0.1 g of PANI doped with 5% NiO were mixed together in a round bottom flask to achieve a PANI composite with In_2O_3 and NiO.

3.11 Evaluation of Sensing Materials

The polymer samples were exposed to gas analytes individually and the GC was used to measure the amount of gas that did not sorb (residual gas). The amount sorbed is calculated by subtracting the concentration of analyte after exposure to polymer from the concentration of analyte before exposure to the polymer sample (see Equation 3.5).

$$Analyte\ sorbed\ (ppm) =\ Analyte\ before\ exposure\ to\ polymer\ (ppm) -$$
$$Analyte\ after\ exposure\ to\ polymer\ (ppm) \qquad \text{(Equation 3.5)}$$

The typical single gas evaluation procedure is outlined below (as an example, we use testing of PMMA's ability to sorb from a 5ppm tank acetone).

First, nitrogen-containing 5 ppm acetone is introduced to the system at a rate of 200 sccm (standard cubic centimeters per minute) for 1 hour, which ensures that the entire test system contains 5 ppm acetone. Second, a blank (empty) flask is present in place of the sample flask (see Figure 3.1) so that all of the acetone coming from the tank is going directly into the gas chromatograph.

The GC measures the gas concentration under these conditions so that we have a baseline for the day. This would be close to 5 ppm but may change slightly from day to day (due to temperature and pressure fluctuations within the building). We continue to measure the gas concentration every 12 minutes until two consecutive readings are stable. This typically takes between 60 to 120 minutes and indicates that the system has reached steady state. A steady state condition is reached when the concentration of analyte sorbing onto the sensing material in the flask equals the concentration that is released back into the air. Before a steady state is reached, more analyte will sorb onto the sensing material than is released back into the air. When equilibrium is reached, the active sites on the sensing material surface cannot sorb more analyte.

At that time, the baseline for the day is established, and the flask containing the PMMA sample is purged under pure nitrogen flow at 200 sccm.

After we have established our baseline (or "blank" value) for the day, we exchange the empty flask with a flask containing the PMMA (doped or un-doped) sample. Now, the flowing acetone

gas is exposed to our sensing material. If it is an appropriate sensing material for acetone, some of the gas will be attracted to the polymer (that is, the analyte will sorb onto the sensing material). Since some (even if slight) of the acetone is sorbed by the PMMA, the GC will record a lower acetone (exit) concentration. Again, the acetone concentration is recorded every 12 minutes until the measurements become stable. Finally, we calculate the concentration of analyte sorbed by the sample using equation 3.1.

The same process is repeated for all sensing materials, both with formaldehyde, benzene, and acetaldehyde simultaneously. When benzene is present in the system, GC measurements take longer (benzene requires more time to elute from the GC). Thus, in the case of benzene evaluation, the concentration of the gas is recorded every 20 minutes.

In the gas mixture evaluation procedure (as an example, we describe the testing of PANI with respect to a formaldehyde and benzene mixture of ~2 ppm for each gas), the steps are as follows (see also Appendix A):

Initially, nitrogen-containing 5 ppm formaldehyde and 5 ppm benzene gas are introduced to the GC system both at a rate of 100 sccm. These gases are mixed in the passive mixer. The mixture then flows for 1 hour, which ensures that the entire test system contains 2 ±0.5 ppm each formaldehyde and benzene. Secondly, a blank (empty) flask is present in place of the sample flask so that all of the gas mixture coming from the tank is going directly into the gas chromatograph. The GC measures the gas concentration under these conditions so that we have a baseline for each gas for the day. This would be close to 2 ppm for each gas but may change slightly from day to day (due to temperature and pressure fluctuations within the lab). We continue to measure the gas concentration every 12 or 20 minutes (in case benzene is present) until two consecutive readings are stable. This typically takes between 60 to 200 minutes and indicates that the system has reached steady state. We are establishing the baseline for the day, while the flask containing the PANI sample is purged under pure nitrogen flow at 200 sccm. Once we have established our baselines for the day, we exchange the empty flask for a flask containing the PANI sample. Now, the flowing formaldehyde and benzene gases are exposed to the sensing material. If it is an appropriate sensing material for formaldehyde, some of the gas will be attracted to the polymer. Since some of the formaldehyde is sorbed by PANI, the GC will record lower formaldehyde and benzene

concentrations compared to the blank one. Finally, we calculate the concentrations of formaldehyde and benzene sorbed by PANI.

4. Results and Discussion (Part 1): Evaluating Sensitivity of Sensing Materials

4.1 Determining the Amount of Sorbed Analyte onto the Polymers

All potential sensing materials were evaluated based on the amount of gas analyte they sorbed from an initial analyte concentration. 0.2 g of each sensing material was placed into a 100 ml round bottom flask and used for gas sensing evaluation. During all experiments, each sensing material evaluation was independently replicated so as to establish a reliable error measure.

4.2 Comparison of Polymer Sorption Averages

4.2.1 Analysis of Variance (ANOVA)

To check if there is a significant difference between the means (μ) of two or more samples, the collected data were analyzed through analysis of variance (ANOVA). This method starts from a null hypothesis (H_0) that states there is no difference between the means.

H_0: $\mu i - \mu j = 0$ for all i, j   (Equation 4.1)

Then, the sum of squares (SS), degrees of freedom (df), and the mean square (MS) were calculated for all data. $F_{observed}$ value was then calculated from the MS and MS_{error}. If $F_{critical}$ at a given confidence level of 95%, i.e., significance level $\alpha = 0.05$, is smaller than $F_{observed}$, the null hypothesis is rejected. Otherwise, there is no sufficient evidence to reject the null hypothesis. When the null hypothesis is rejected, at least two of the sample means are significantly different. If the null hypothesis is not rejected, no significant difference exist between the means.

4.3 Comparison of Polymers for Sensitivity towards Acetone

Table 4.1 provides an overview of the materials that could be tested for this investigation. The combinations that were selected for testing are marked with a ✓. Blank cells represent potential future investigations if there is an indication of sorption. Some grid combinations were abandoned as no sorption was established. PMMA of two different molecular weights of 15 K and 120 K was deposited and tested. Also, PMMA materials doped with three metal oxides (ZnO, SnO_2, and WO_3) in three different weight ratios of 5, 10, and 20% were prepared and investigated for sensing capabilities. PMMA doped with metal oxide samples did not show a uniform texture i.e., metal oxides were agglomerated at the bottom of the sample flask, separated from PMMA. In this case very low metal oxide was exposed to target gas analyte. In order to overcome this issue, a 2-step

deposition was examined; first we deposited PMMA into a flask and after it dried, the second layer of metal oxide was deposited onto the PMMA layer. Therefore, more metal oxide was exposed to gas analyte. After not seeing measurable sorption of acetone with these polymer materials, we decided to synthesize PMMA and PMMA doped with 10% ZnO of two weight-average molecular weights of 0.5 M and 1 M. These polymers were evaluated for sensing capability toward 5 ppm, 100 ppm, and 1100 ppm acetone.

The summary of PMMA samples for different acetone concentrations tested is shown is Table 4.1.

Table 4.1 Overview of PMMA sensing materials and acetone concentrations

	Metal oxide			Acetone concentration (ppm)		
Sample	ZnO	SnO_2	WO_3	5	100	1100
15K PMMA in Toluene deposition				✔		
15K PMMA in Acetone deposition	✔	✔	✔	✔		
120K PMMA in Acetone deposition	✔	✔	✔	✔		
120K PMMA doped with WO_3 (2-step deposition)			✔	✔		
0.5M synthesized PMMA						✔
1M synthesized PMMA					✔	✔
0.5M synthesized PMMA doped with 10%ZnO	✔					✔
1M synthesized PMMA doped with 10%ZnO	✔				✔	✔

4.3.1 Sensitivity of Commercially Available PMMA Doped with ZnO, SnO_2, and WO_3

To evaluate the sorption of each analyte onto the polymeric sensing materials, nitrogen gas containing approximately 5 ppm of acetone was passed over the polymers.

Replicated data points in percentages were recorded for the acetone sorption of deposited pure PMMA, and PMMA doped with ZnO, SnO_2, and WO_3, in three weight ratios of 5, 10, and 20%

metal oxide. Note that each doped polymer will be referred to by the amount of dopant added during deposition/synthesis (e.g., PMMA doped with 10 wt. % ZnO will be referred to as PMMA 10% ZnO, and so on). Figure 4.1 shows precentage acetone sorption of doped and undoped-PMMA.
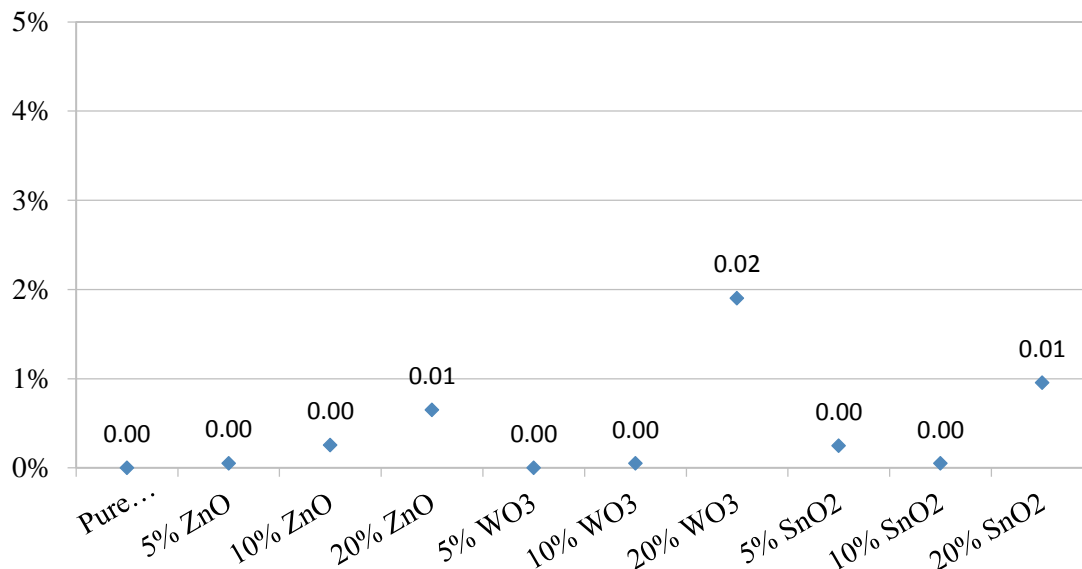
Figure 4.1 Acetone sorption of PMMA from 5ppm tank

From visual lab observations during preparation, ZnO and WO_3 did not incorporate well into PMMA as we could see ZnO particles in yellow and WO_3 particles in green in certain parts of the PMMA film. SnO_2 powder is white and therefore we could not distinguish it in the PMMA film. More details about these samples are provided in Chapter 6.

A small amount of metal oxide that seems to be incorporated in the PMMA had a negligible effect on the sorption of acetone.

4.3.2 Sensitivity of Synthesized PMMA Doped with 10% ZnO

In order to further evaluate PMMA as a sensing material, synthesized PMMA of two molecular weight of 0.5M and 1M was tested. In an attempt to improve the sensitivity of the synthesized PMMA, this polymer was doped with 10% ZnO during synthesis to achieve similar molecular weights of 0.5M and 1M.

Two samples of synthesized PMMA with weight-average molecular weights of 0.5M and 1M doped with 10% ZnO showed no sorption from 100 ppm acetone. Subsequently, these polymers

were exposed to a higher concentration of 1100 ppm acetone. Figure 4.2 represents the percent sorption of each potential sensing material. The numbers in Figure 4.2 have been rounded-off.
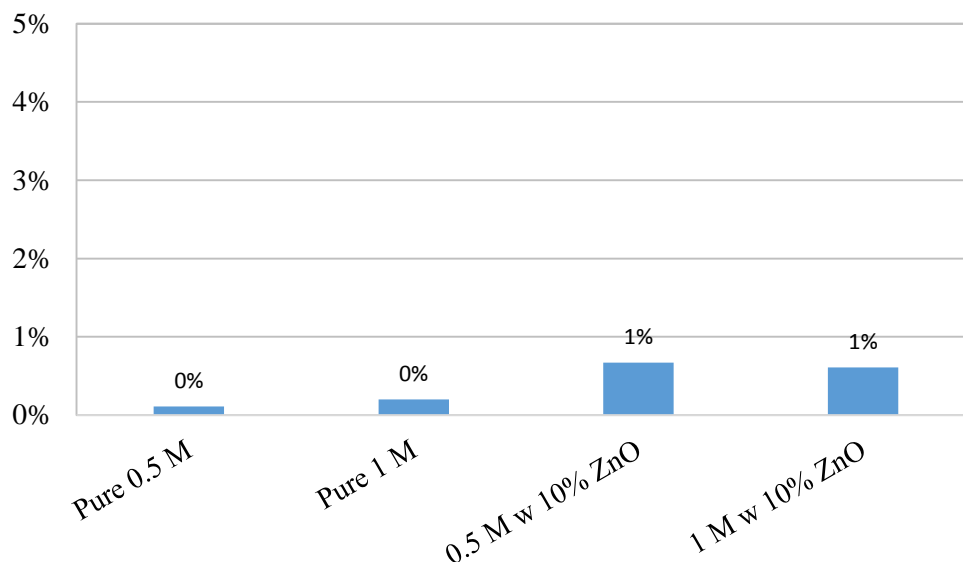
Figure 4.2 Acetone sorption of PMMA from 1100ppm tank

The addition of ZnO did not significantly change the amount of acetone that sorbed onto PMMA.

ZnO did not incorporate well into PMMA. More ZnO was accumulated in some parts of the polymer and not homogeneously throughout the whole polymer.

A summary of the sorption averages in ppm and percent for each synthesized PMMA sample is given in Table 4.2. The averages are based on 4 to 5 experimental data points for each sample.

Table 4.2 Overview of acetone sorption by synthesized PMMA

	Average sorption (ppm)		Average % sorption	
Sample	100	1100	100	1100
Pure PMMA (Mw: 0.5M)	-	1.22	-	0.11%
Pure PMMA (Mw: 1M)	0.00	2.25	0.00	0.20%
PMMA 10% ZnO (Mw: 0.5M)	2.26	7.40	2.38%	0.67%
PMMA 10% ZnO (Mw: 1M)	-	6.65	-	0.61%

4.4 Comparison of Polymers for the Sensitivity towards Formaldehyde (F), Acetaldehyde (Ac) and Benzene (B)

Table 4.3 provides an overview of the materials tested for individual gas analytes in different concentrations. Any blank cells represent potential further investigations if there is an indication of sorption. Some combinations were abandoned completely (for PAAc, for example) as no sorption capabilities were established.

Note that each doped polymer will be referred to by the amount of dopant added during synthesis (e.g., PANI doped with 5 wt. % In_2O_3 will be referred to as PANI 5% In and so on).

Table 4.3 Overview of sensing materials and gas concentrations for F, B, and Ac

	F (5ppm)	F (10ppm)	B (5ppm)	Ac (10ppm)
PANI	✓		✓	✓
P25DMA	✓		✓	
P4VP	✓		✓	
PAAc-1M	✓		✓	
PANI/In_2O_3		✓		✓
PANI/NiO		✓		✓
PANI/In_2O_3/NiO		✓		

4.4.1 Sensitivity of Polymers to 5 ppm Formaldehyde

Initially, polyaniline (PANI), poly (2,5-dimethyl aniline) (P25DMA), P4VP, and PAAc-1M were evaluated as potential sensing materials for formaldehyde (F). Each polymer sample was exposed to 5 ppm of formaldehyde and the amount of formaldehyde sorbed was measured. Here, as many independent replicates as possible were taken per sample; these ranged from 4 to 6 data points for the formaldehyde sorption of P25DMA, P4VP, PAAc with a molecular weight average of 1M, and PANI.
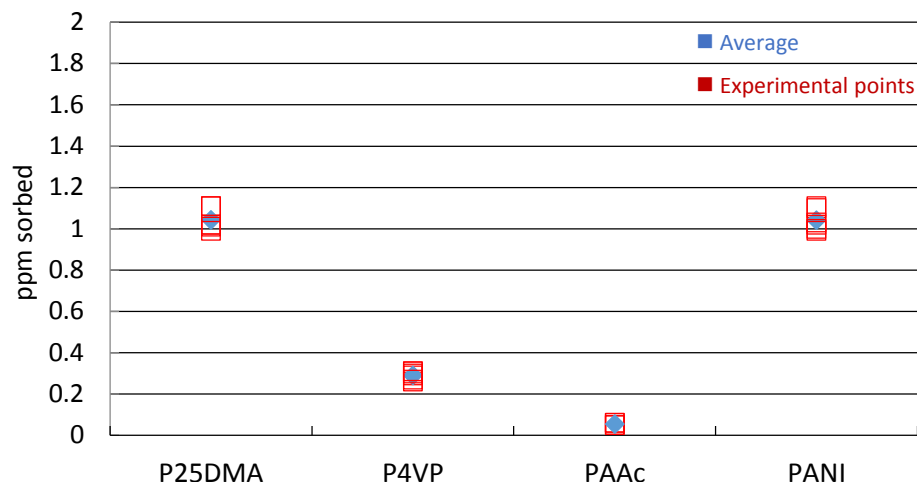
Figure 4.3 Sorption of polymeric sensing material from 5ppm formaldehyde

From Figure 4.3 it is observed that formaldehyde sorption is similar for P25DMA and PANI since comparison of means shows no statistically significant difference. Also, the P4VP average sorption is less than PANI and P25DMA. PAAc with molecular weight of 1,000,000 shows no sorption from 5 ppm formaldehyde. From now on, the 'blue' symbol represents the mean sorption in ppm.

A summary of the sorption averages in ppm and the corresponding coefficients of variation (CV) for P25DMA, P4VP, PAAc-1M, and PANI is given in Table 4.4. Blank averages (in ppm) for each sensing material are also given in Table 4.4. From now on, blank averages represent the average of daily baseline values when an empty flask was placed into the GC system. This is essentially the analyte concentration that passes through a sensing material trial. Sample sizes for each sensing material were again between 4 to 6 in this study.

Table 4.4 Sorption averages and CV of polymeric sensing material from 5ppm formaldehyde

	P25DMA	P4VP	PAAc-1M	PANI
Blank average (ppm)	4.45	4.43	4.68	4.45
Sorption average (ppm)	1.04	0.29	0.05	1.04
CV (%)	2.56	3.97	5.73	2.33

4.4.2 Sensitivity of Polymers to 10 ppm Formaldehyde

To evaluate the sorption of formaldehyde onto the polymeric sensing materials, nitrogen gas containing 10 ppm of formaldehyde was passed over the polymer samples. Replicated data points for PANI, PANI doped with 5% In, PANI doped with 5% NiO, PANI composite of 5% In and 5% NiO, and P25DMA were recorded. These results were compared to undoped PANI sorption (see Figure 4.4). Sample size was 4 to 6 in this case.
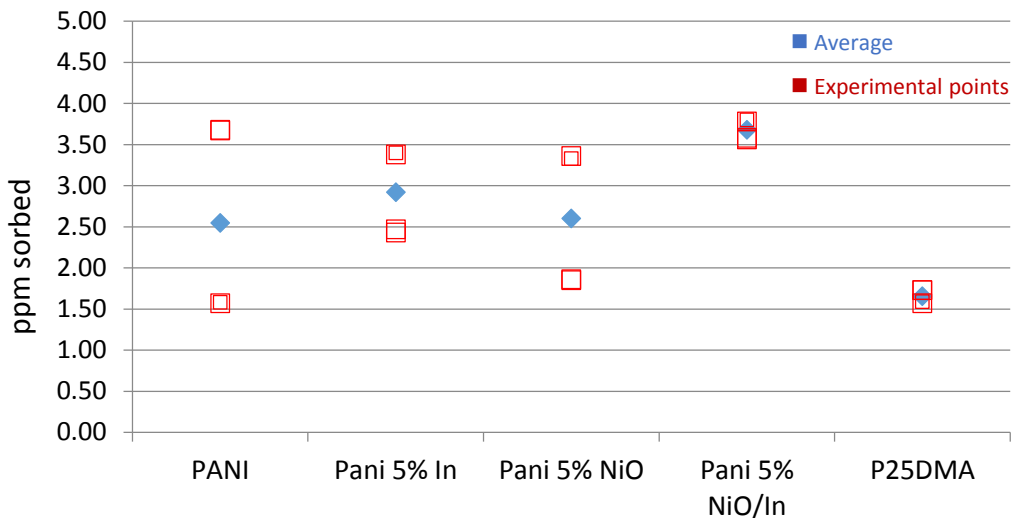

Figure 4.4 Sorption of polymeric sensing material from 10 ppm formaldehyde

The composite blend of the two doped PANI samples 5 wt. % In and PANI with 5 wt. % NiO shows an increase in sorption compared to undoped PANI, but the increase is not statistically significant. We can also normalize the sorption values (that is, consider % formaldehyde sorbed) to allow for direct comparison to earlier (5 ppm) formaldehyde studies. A comparison between formaldehyde sorption at 5 ppm and 10 ppm is provided in Table 4.5.

The PANI composite of 5% In and 5% NiO sorption amounts show smaller error/variability compared to undoped PANI, PANI doped with 5% In, and PANI doped with 5% NiO, as the experimental data points are closer to the average in this sample. This recorded variability by the sensitive GC is not only due to typical experimental error fluctuations, as expected from day to day and from trial to trial. Since the experimental trials were run at different days and times, in order to achieve independent replication to the extent possible, we observed that some days were worse than others due to ventilation changes and temperature fluctuations in the building itself. These fluctuations were not in our control. However, the overall experimental error, even with

these fluctuations superimposed, was still acceptable in order to make reliable statements about trends (and subsequent comparisons).

Table 4.5 Comparison of normalized formaldehyde sorption for PANI

	Pure PANI	PANI w 5% In_2O_3	PANI w 5% NiO	PANI 5% NiO/In
formaldehyde concentration	5 ppm	10 ppm	10 ppm	10 ppm
Sorption average (%)	24.14%	29.45%	26.84%	37.01%

The blend of the two materials has the highest normalized sorption. This suggests that combining the properties of PANI, In_2O_3 and NiO into a single material may improve the sensing performance of the polymeric material. Gas sensors based on the composite are more sensitive than the individual components due to the interface heterostructure and a synergistic effect between the two components.

A summary of the sorption averages and blank averages in ppm, and coefficient of variation (CV) for PANI, PANI doped with 5% In, PANI doped with 5% NiO, PANI composite of 5% In and 5% NiO, and P25DMA is given in Table 4.6.

Table 4.6 Sorption averages and CV of polymeric sensing materials from 10 ppm formaldehyde

	PANI	PANI 5%In	PANI 5%NiO	PANI 5%In/NiO	P25DMA
Blank average (ppm)	9.92	9.90	9.97	9.94	9.99
Sorption average (ppm)	2.55	2.92	2.60	3.68	1.66
CV (%)	12.11	7.15	11.94	2.17	1.03

4.4.3 Sensitivity of Polymers to 5 ppm Benzene

To evaluate the sorption of benzene onto the polymeric sensing materials, nitrogen gas containing approximately 5 ppm of benzene was passed over the polymers. In Figure 4.5 replicated data points are shown for the benzene sorption of P25DMA, P4VP, PAAc-1M, and PANI.

Figure 4.5 Sorption of polymeric sensing material from 5ppm benzene

There is no evidence of benzene sorption onto P4VP and PAAc-1M according to Figure 4.5. Also, both P25DMA and PANI sorb benzene, but sorption is not as high as it was for formaldehyde. Benzene sorption seems to be higher for PANI than for P25DMA, but a comparison of means shows that there is no statistically significant difference.

Sorption averages and blank averages in ppm, and coefficient of variation (CV) for P25DMA, P4VP, PAAc-1M, and PANI, are summarized in Table 4.7. Sample size for each sensing material was 4 to 8 in this study.

Table 4.7 Sorption averages and CV of polymeric sensing materials from 5 ppm benzene

	P25DMA	P4VP	PAAc-1M	PANI
Blank average (ppm)	4.79	4.85	4.58	4.79
Sorption average (ppm)	0.33	0.04	0.00	0.39
CV (%)	9.68	3.16	3.06	10.85

4.4.4 Sensitivity of Polymers to 5 ppm Acetaldehyde

To evaluate the sorption of acetaldehyde onto the polymeric sensing materials, nitrogen gas containing approximately 5 ppm of acetaldehyde was passed over the polymers. In Figure 4.6 replicated data points are shown for the benzene sorption of PANI, PANI doped with 5% In, and PANI doped with 5% NiO.
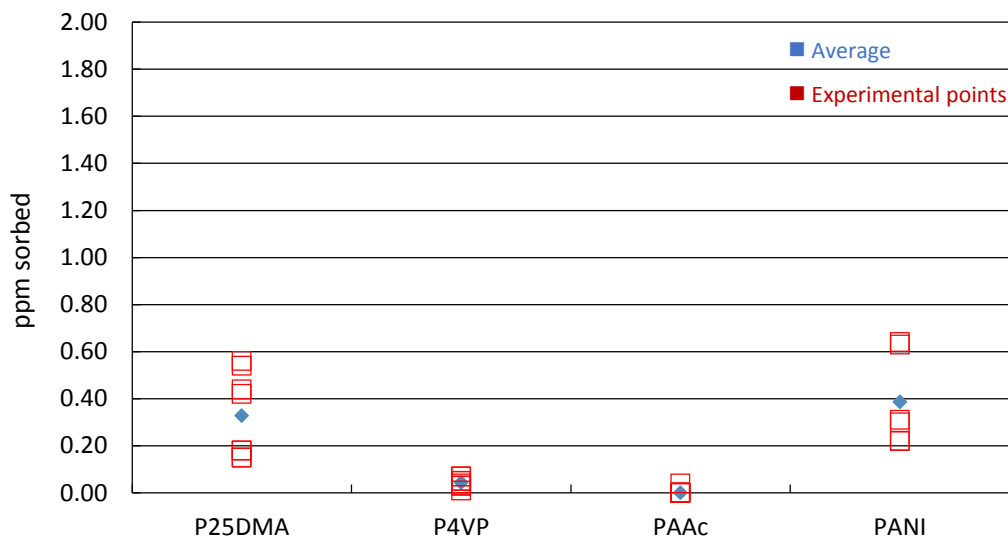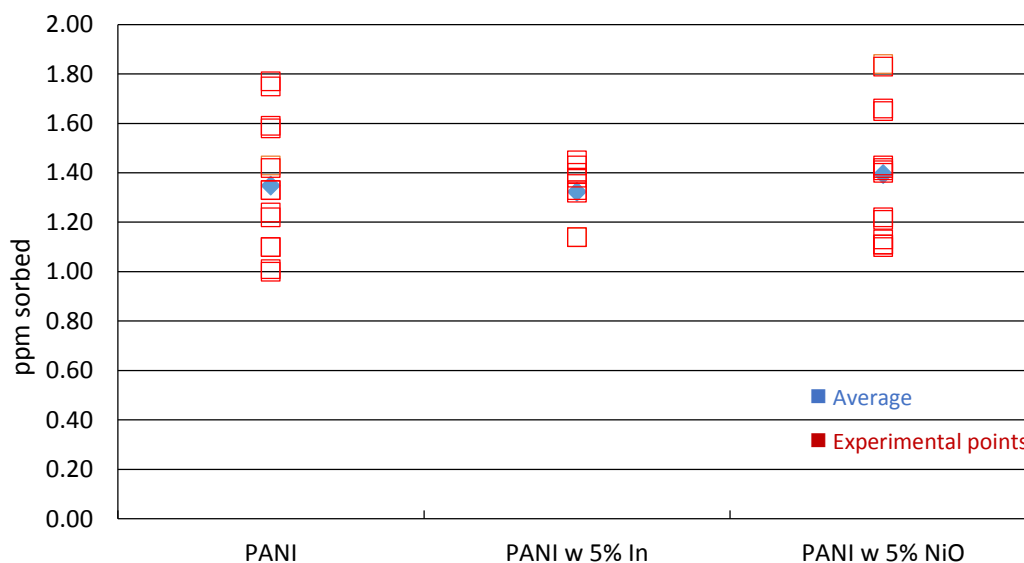

Figure 4.6 Sorption of polymeric sensing material from 5 ppm acetaldehyde

By incorporating 5% In and 5% NiO into PANI, the sensitivity to acetaldehyde has not changed significantly. Therefore, adding NiO and In to PANI during polymerization did not affect the sorption of acetaldehyde.

A summary of the sorption averages and blank averages in ppm, and coefficient of variation (CV) for of PANI, PANI doped with 5% In, and PANI doped with 5% NiO is given in Table 4.8. Sample size for each sensing material was 8 to 14 in this study.

Table 4.8 Sorption averages and CV of polymeric sensing material from 5ppm acetaldehyde

	PANI	PANI 5% In	PANI 5% NiO
Blank average (ppm)	5.09	5.10	5.07
Sorption average (%)	1.35	1.32	1.39
CV (%)	8.28	6.55	5.88

From the three polymeric materials, PANI with 5% In_2O_3 is the most repeatable, although they all center on the same average value. Also, no statistically significant differences exist among these three PANI samples.

5. Results and Discussion (Part II): Evaluating Selectivity of Sensing Materials

5.1 Comparison of Polymers for Selectivity towards Formaldehyde (F)

Based on the sorption tests shown in Chapter 4, the most promising sensing materials for formaldehyde were PANI and P25DMA. These materials were further evaluated for selectivity along with P4VP and PAAc (for completeness of the trends). Two interferent gases, benzene and acetaldehyde, were used to evaluate the selectivity of formaldehyde toward these analytes.

Evaluating gas mixtures, that is exposing a sensing material to formaldehyde and benzene simultaneously, provides information about the selectivity of the polymeric sensing material. This allows one to check if the sensing material still sorbs the target analyte, formaldehyde in this case, in the presence of other analytes as interferents (benzene (B) and acetaldehyde (Ac)).

The gas mixtures were created through static mixing of gas analytes from a 5 or 10 ppm gas tank of formaldehyde, benzene or acetaldehyde.

Since PAAc with molecular weight of 1M did not sorb individual gases, lower molecular weights of PAAc (130K and 450K) were studied for the F/B gas mixtures. In addition, the values reported for each gas, to compare selectivity, represent an average of three to eight independent replicates. Table 5.1 provides an overview of the materials tested for certain gas mixtures in different concentrations.

Table 5.1 Overview of sensing materials and gas combinations for F/B and F/Ac

	F/B mixture (~2ppm each)	F/B mixture (~6ppm each)	F/B mixture 7ppm F/ 4ppm B	F/Ac mixture (~2ppm each)
PANI	✔	✔	✔	✔
P25DMA	✔	✔	✔	
P4VP	✔	✔	✔	
PAAc-130K	✔			
PAAc-450K	✔	✔		
PANI 5% In_2O_3				✔
PANI 5% NiO				✔

5.1.1 Selectivity of Polymers in F/B Mixture of 2ppm F & 2ppm B

The 2 ±0.5 ppm mixture was created through static mixing of gas analytes from a 5 ppm formaldehyde tank and a 5 ppm benzene tank. Five polymers (P25DMA, P4VP, PANI, PAAc-130K, and PAAc-450K) were evaluated for selectivity to formaldehyde (see Figure 5.1). From now on, in all selectivity figures and for all bar graphs, the interval line)represents sorption amount ± one standard deviation (for sensing material sorption measurements when exposed to a certain concentration of analyte).
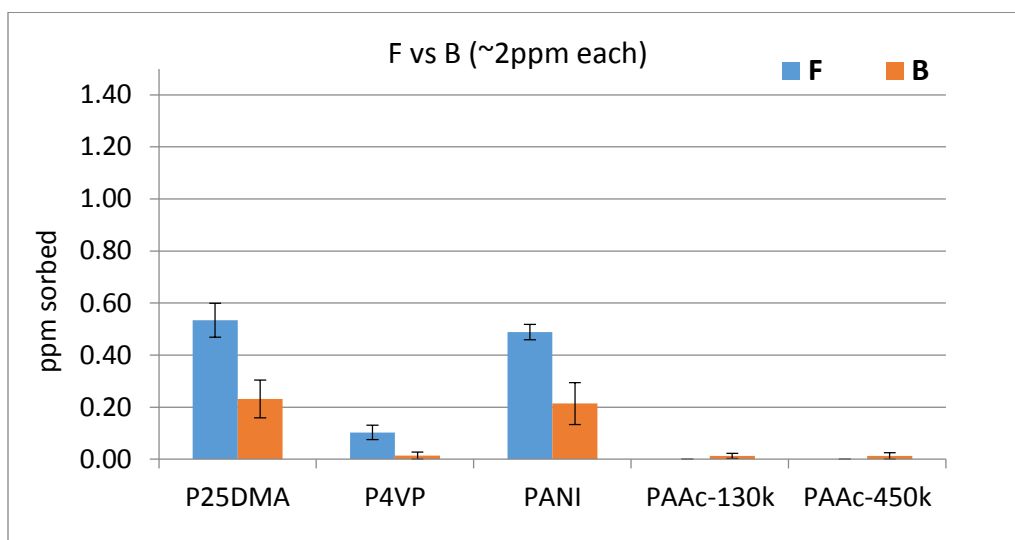

Figure 5.1 Selectivity of sensing materials towards formaldehyde in the presence of benzene F/B, ~2ppm each

The sorption behaviour of P25DMA and PANI is similar; the P25DMA looks to have a higher average sorption, but there is no statistically significant difference (notice that the average F sorption of PANI falls within the error bar for F sorption of P25DMA). Also, PANI is slightly more selective toward formaldehyde than P25DMA, meaning less of the benzene gas is sorbed by PANI in this case. From this mixture data we can observe that benzene sorption is similar for both P25DMA and PANI. This result agrees with what was observed for the single gas case with 5 ppm benzene. Regarding PAAc, even using different molecular weights, very little or negligible sorption is observed.

A summary of the sorption averages for each gas, blank averages in ppm, and coefficient of variation (CV) for P25DMA, P4VP, PAAc-130K, and PAAc-450K is given in Table 5.2. Sample size for each sensing material was 4 to 8 in this case.

Table 5.2 Sorption averages, selectivity, and CV of polymeric sensing materials from F/B, ~2ppm each

	P25DMA		P4VP		PANI		PAAc-130K		PAAc-450K	
	F	B	F	B	F	B	F	B	F	B
Blank average (ppm)	1.90	1.60	1.95	1.53	1.93	1.58	1.93	1.62	1.93	1.62
Sorption average (ppm)	0.53	0.23	0.10	0.01	0.49	0.21	0.00	0.01	0.00	0.01
CV (%)	3.24	8.07	1.37	2.66	5.27	7.70	-	-	-	-
Average selectivity	2.49		6.05		2.62		0		0	

The reported average selectivity is calculated based on all individual formaldehyde to benzene (ratio values) selectivities. According to Table 5.2, selectivity of P4VP is 6.05, which is a large number compared to the other sensing materials evaluated in this gas mixture. Note that gas sorption of P4VP is very small (=< 0.1 ppm), thus, the ratio between the two small numbers will result in a large number. Therefore, this number is not stating the true selectivity of P4VP value in a meaningful way.

5.1.2 Selectivity of Polymers in F/B Mixture of 6ppm F & 6ppm B

The 6 ±0.5 ppm mixture used a 10 ppm formaldehyde tank and a 10 ppm benzene tank to create the F/B gas mixture. Sorption of both analytes in the mixture was measured simultaneously, and the results are shown in Figure 5.2.

The amounts of formaldehyde and benzene that sorbed on P25DMA, P4VP, and PANI from the F/B mixture of 6 ±0.5 ppm each, remained roughly the same compared to the F, B mixture of 2 ±0.5 ppm. As per Figure 5.2, P4VP sorption of formaldehyde is again lower than PANI and P25DMA. Again, benzene sorption for PANI and P25DMA is similar and it agrees with single 5 ppm benzene evaluation. It is also observed that PAAc 450K shows negligible sorption of formaldehyde.
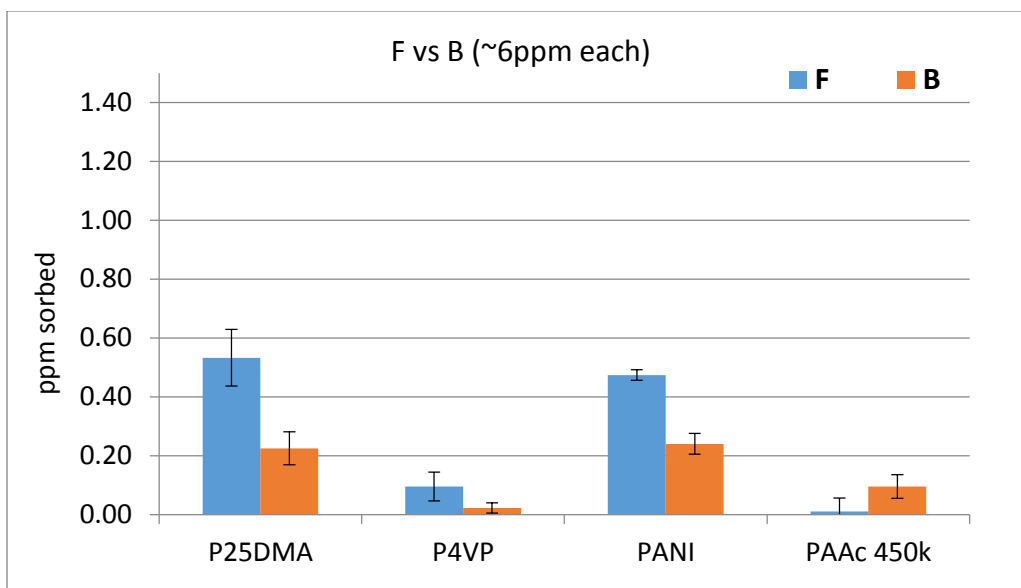
Figure 5.2 Selectivity of sensing materials towards formaldehyde in the presence of benzene F/B ~6ppm each

A summary of the sorption averages to each gas, blank averages in ppm, and coefficient of variation (CV) for of P25DMA, P4VP, PANI, and PAAC-450K is given in Table 5.3. Sample size for each sensing material was 4 to 8 in this case.

Table 5.3 Sorption averages, selectivity, and CV of polymeric sensing materials from F/B, ~6ppm each

	P25DMA		P4VP		PANI		PAAc-450K	
	F	B	F	B	F	B	F	B
Blank average (ppm)	6.26	5.91	6.25	5.91	6.19	5.97	6.27	5.92
Sorption average (ppm)	0.53	0.23	0.10	0.02	0.47	0.24	0.02	0.01
CV (%)	0.68	2.56	0.46	2.00	0.67	1.04	0.36	0.49
Average selectivity	2.43		4.24		2.01		0.19	

5.1.3 Selectivity of Polymers in F/B Mixture of 7ppm F & 4ppm B

To further investigate the selectivity of formaldehyde toward benzene as interferent, a different ratio (higher amount) of target analyte (formaldehyde) to (lower amount of) interferent (benzene)

was investigated. The target was to introduce the formaldehyde and benzene gas mixture to each potential sensing material in about 2:1 ratio. This study would be an evaluation of whether P25DMA, P4VP, and PANI are sorbing formaldehyde and to what extent in the face of benzene as interferent.

A formaldehyde to benzene mixture of 7 ±0.5 to 4 ±0.5 ppm was created through static mixing of gas analytes from a 10 ppm formaldehyde tank and a 10 ppm benzene tank.

Sorption of both analytes in the mixture were measured simultaneously, and the results are shown in Figure 5.3.
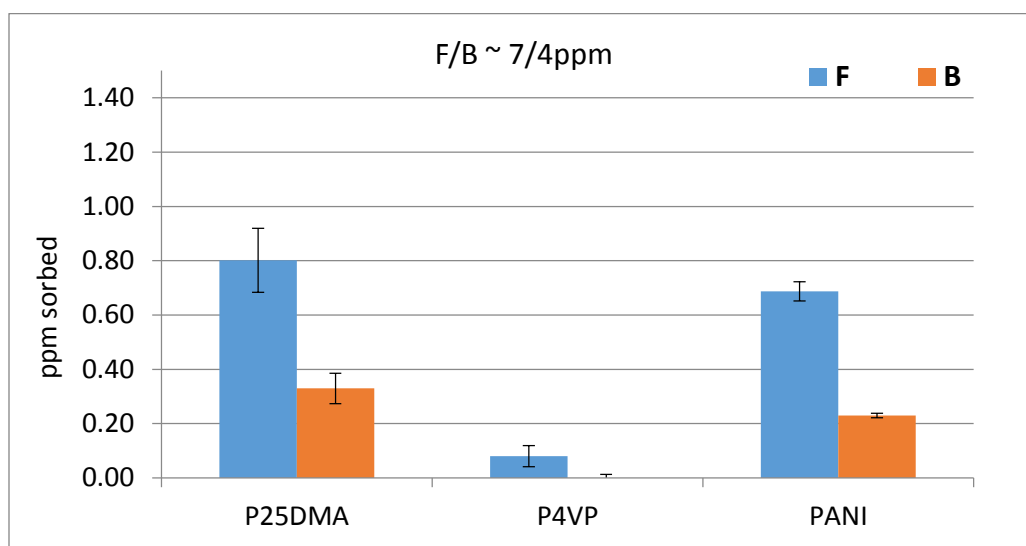

Figure 5.3 Selectivity of sensing materials towards formaldehyde in the presence of benzene F/B, ~7/4 ppm

P25DMA is slightly more selective toward formaldehyde than PANI, but there is no statistically significant difference since the average formaldehyde sorption of PANI falls within the error bar for formaldehyde sorption of P25DMA. The benzene sorption amount remained roughly similar to the 2 ±0.5 ppm and 6 ±0.5 ppm experiments.

It is very interesting that at a higher concentration of formaldehyde, more formaldehyde is sorbed by both P25DMA and PANI. In both cases, the concentration of formaldehyde sorbed increases by approximately fifty percent. In contrast, no change is observed in the P4VP formaldehyde sorption compared to previous tests. Approximately 0.1 ppm of formaldehyde is sorbed by P4VP, and benzene sorption is negligible as before.

A summary of the sorption averages to each gas, blank averages in ppm, and coefficient of variation (CV) for of P25DMA, P4VP, and PANI is given in Table 5.4. Sample size for each sensing material was 4 to 6 in this case study.

Table 5.4 Sorption averages, selectivity, and CV of polymeric sensing materials from F/B ~7/4 ppm

	P25DMA		P4VP		PANI	
	F	B	F	B	F	B
Blank average (ppm)	7.24	4.22	7.14	4.30	7.11	4.31
Sorption average (ppm)	0.80	0.33	0.08	0.01	0.69	0.23
CV (%)	1.53	4.70	1.12	1.56	0.79	2.55
Average selectivity	2.46		4		2.99	

5.1.4 Selectivity of Polymers in F/Ac Mixtures of 2ppm F & 2ppm Ac

Formaldehyde and acetaldehyde have chemical similarities. They both contain the same carbonyl group, which makes it possible to exhibit polarity, hydrogen bonding, and/or Lewis acid-base characteristics. Therefore, in mixing the two gases together, we examine an interferent analyte that has similar properties as the target analyte. To investigate sensing materials in this mixture, the 2 ±0.5 ppm F/Ac gas mixture was obtained by using a 5 ppm formaldehyde tank and a 5 ppm acetaldehyde tank.
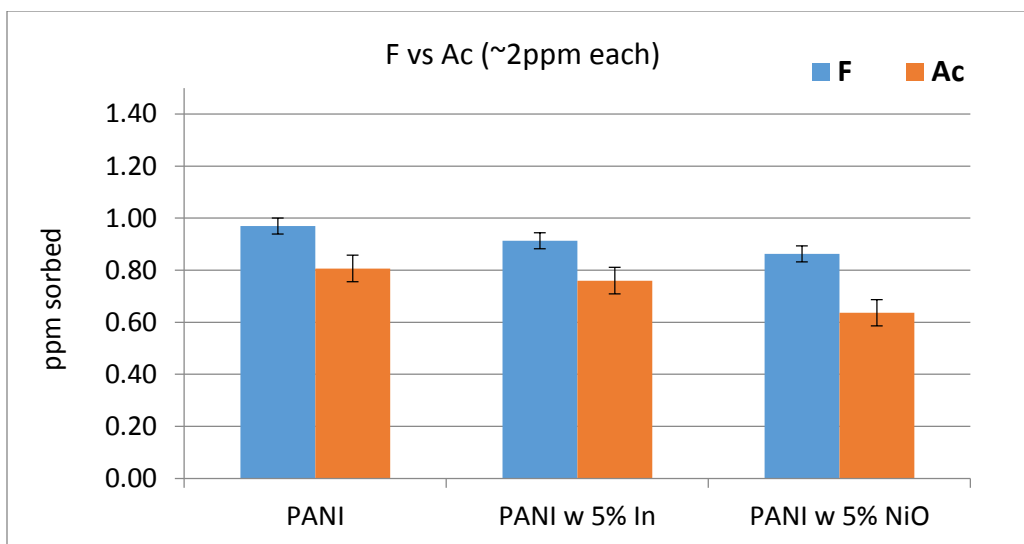
Figure 5.4 Selectivity of sensing materials towards formaldehyde (F) in the presence of acetaldehyde (Ac); F/Ac, ~ 2 ppm each

As expected, the amount of formaldehyde sorption is similar to the amount of acetaldehyde sorption. Also, given the results of Figure 5.4, the sorption performance of all three materials, whether doped or un-doped, is approximately equal. Table 5.5 gives more detailed calculations. Sample size for each sensing material was equal to 6 in this study.

Table 5.5 Sorption averages, selectivity, and CV of polymeric sensing material from F/Ac, ~2 ppm each

	PANI		PANI 5% In		PANI 5% NiO	
	F	Ac	F	Ac	F	Ac
Blank average (ppm)	2.07	2.08	2.08	2.09	2.08	2.09
Sorption average (ppm)	0.97	0.81	0.91	0.76	0.86	0.64
CV (%)	12.22	8.95	12.01	13.71	7.84	5.30
Average selectivity	1.20		1.21		1.36	

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6. Results and Discussion (Part III): Polymeric Sensing Material Analysis

6.1 Dopant Concentration (EDX) and Morphology (SEM)

Scanning electron microscopy (SEM) can provide information about the topology and the composition of the polymeric samples. The final characterization steps were to investigate the surface morphology of representative sensing materials, both metal oxide-doped and undoped materials, for comparison. Also, the degree of incorporation of the metal oxide in the sensing material was evaluated with Energy Dispersive X-Ray Analysis (EDX). EDX was used to confirm whether the amount of metal oxide added during synthesis was actually incorporated into the polymer matrix. SEM and EDX were performed on polymer samples (selectively) at the Waterloo Advanced Technology Laboratory (WATLAB) at the University of Waterloo.

6.1.1 SEM Images of PMMA Doped with 10% ZnO, SnO$_2$ and WO$_3$

The morphology of selected polymeric sensing materials including PMMA with SnO$_2$, PMMA with WO$_3$, and PMMA with ZnO were examined. Figure 6.1 provides a direct comparison at 1000x magnification. The effect of doping the sensing material can be qualitatively evaluated using SEM.
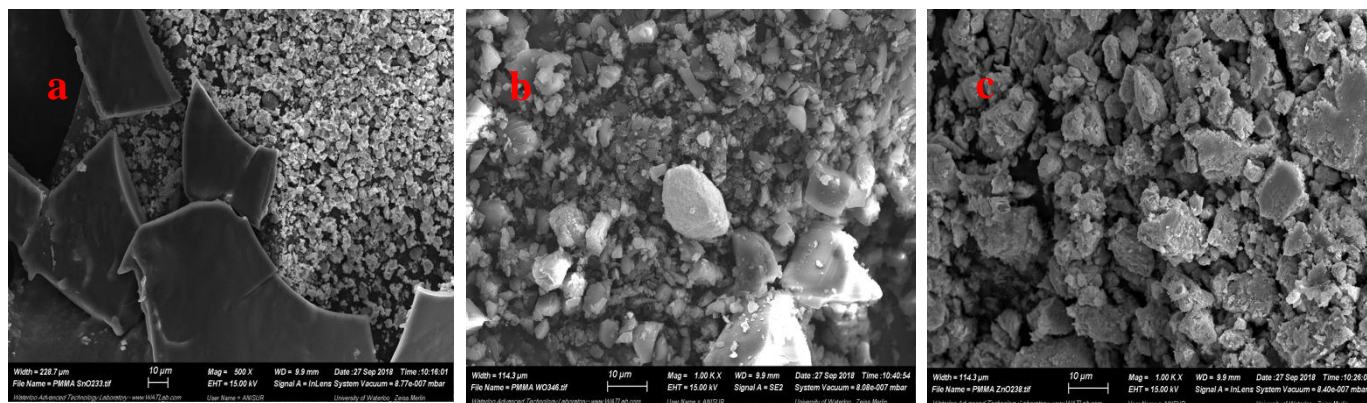

Figure 6.1 Scanning Electron Microscopy images for (a) PMMA with 10%SnO2, (b) PMMA with 10%WO3 and (c) PMMA with 10%ZnO

From Figure 6.1 (a), it is clear that SnO$_2$ has not incorporated well into PMMA, as the white smaller particles on the right side of the picture are SnO$_2$ particles and the bigger 'plate-like' surface represents PMMA (more details in Section 6.1.4). This suggests that the sorption capability of this sample is limited, as the analyte may not sorb as easily to uniformly 'smooth' material.

Figure 6.1 (b) can be directly compared with Figure 6.1 (c); these two independently prepared PMMA samples with 10% WO_3 and 10% ZnO seem to exhibit a similar acceptable dispersion and hence more consistent properties.

The morphology of synthesized pure PMMA and synthesized PMMA doped with ZnO were also examined. Figure 6.2 shows a direct comparison of these polymers at 500x magnification.
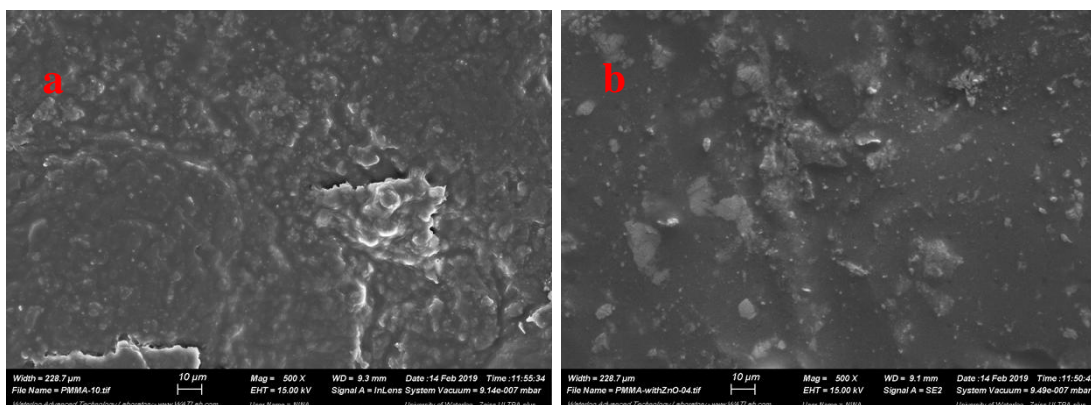

Figure 6.2 Scanning Electron Microscopy images for (a) synthesized PMMA, (b) synthesized PMMA with 10% ZnO

From the SEM images of Figure 6.2, PMMA has a rather flat surface and shows no porous structure to provide more surface area and hence available sites for gas sorption onto it. Even by adding metal oxide, the morphology has not changed.

6.1.2 SEM Images of PANI, P4VP, and P25DMA

The morphology of selected polymeric sensing materials (specifically, those materials that showed promising sorption during testing) was examined next. Figure 6.3 provides a direct comparison of P25DMA, P4VP and PANI, all at 5000x magnification.
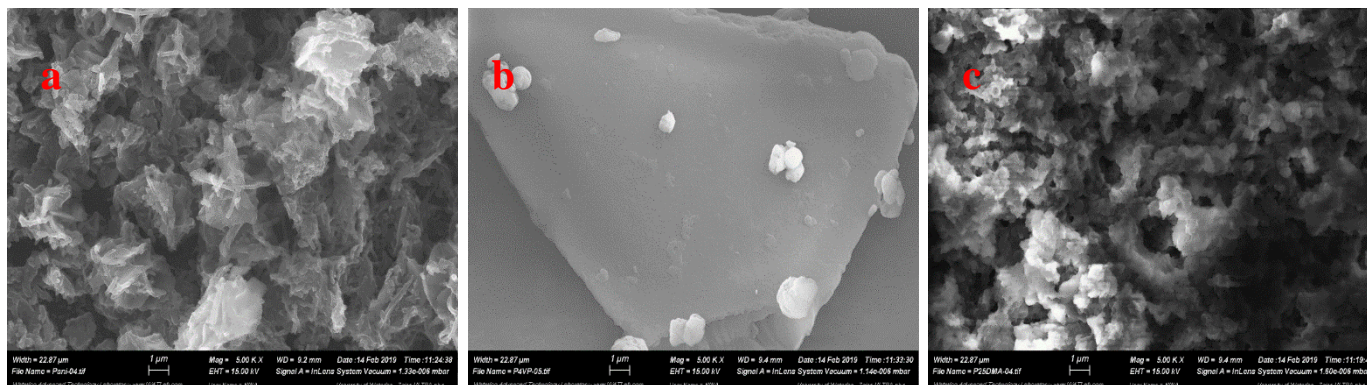

Figure 6.3 Scanning Electron Microscopy images for (a) PANI, (b) P4VP and (c) P25DMA

In figure 6.3, PANI and P25DMA both show a large surface area; more surface area is exposed to gas and more sorption "sites" are available for interactions between sensing material and analyte. P25DMA has a rounded, cauliflower-like structure, with pores throughout the sample. The PANI sample exhibits a more fibrous structure and shows many 'cavities' dispersed throughout the sample. In both cases of PANI and P25DMA, these broccoli- or cauliflower-like structures resemble what happens when a catalyst particle accommodates a reaction in it that produces new material that causes fragmentation of the (almost spherical starting) particle. This 'explosion-fragmentation' in its turn creates a large fraction of interstitial space. In other words, more surface area is exposed and thus more area is available for whatever interactions can take place between the sensing material and the analyte. Hence, there are many sorption "sites" available for an analyte (like formaldehyde) to sorb (analogous to active sites in a catalytic system that can bind with adsorbing reactant molecules to lead to surface reaction and subsequently desorption of product molecules). Therefore, it makes sense that both P25DMA and PANI showed good sorption of the target analytes.

In contrast, P4VP, is a different material compared to the other two morphologies discussed above. The SEM image reveals a rather smooth and 'plate-like' structure. This suggests that the sorption capability of this polymer is limited and the analyte may not sorb as easily to such a uniformly 'smooth' material. Thus, the SEM images further support our sorption measurements that P25DMA and PANI have more surface area available compared to P4VP, which is influencing the sorption capabilities of these sensing materials.

6.1.3 SEM Images of PANI Doped with 5% In_2O_3 and 5% NiO

In Figure 6.4, SEM images of pure PANI, PANI with 5% In_2O_3, and PANI with 5% NiO are provided, all at 1000x magnification.
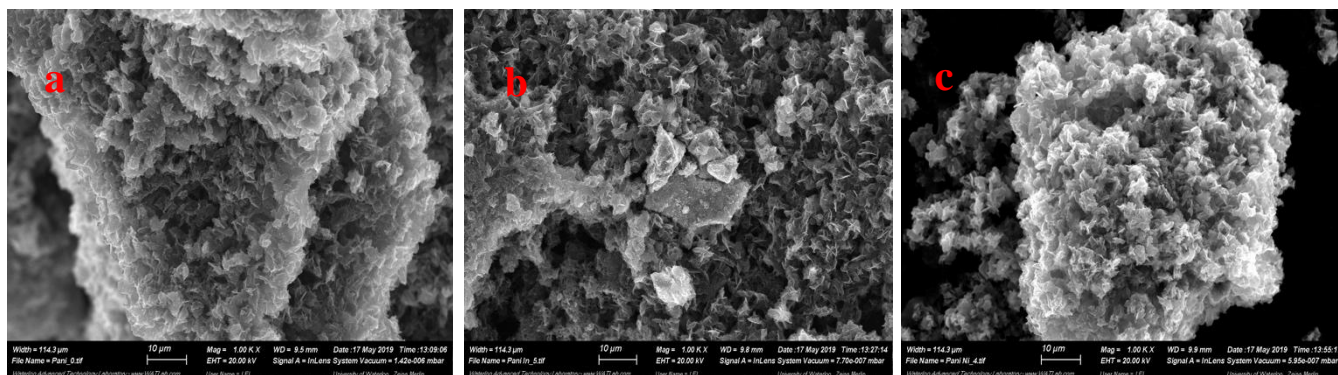
Figure 6.4 Scanning Electron Microscopy images for (a) pure PANI, (b) PANI with 5% In2O3 and (c) PANI with 5% NiO

As observed in figure 6.4, PANI again has many 'cavities'. As before, the cavities are well dispersed throughout the sample. The significant amount of surface area exposed allows for high sorption levels.

Comparison between the undoped and doped PANI also shows some interesting behavior. Figure 6.4 (a) and Figure 6.4 (c) are very similar; both exhibit the same cauliflower-like structure. Therefore, NiO addition does not seem to significantly affect the morphology of the polymer. In contrast, Figure 6.4 (b) has flat (and relatively smooth) shards in the foreground of the image (fairly central in the image), and the cauliflower-like structure is in the background of the image. The smoother portions are likely agglomerations of In_2O_3, superimposed onto (rather than incorporated into) the PANI sample.

6.1.4 EDX results for doped PMMA and doped PANI

The interpretation of SEM images was confirmed using EDX measurements. The EDX results are also aligned with the sorption measurements for these metal oxide-doped materials. Very little improvement was observed when metal oxides were added, which is likely due to the rather low levels of metal oxide incorporation. Additional steps (pretreatment of nanoparticles or a change in the synthesis procedure) may be required to improve metal oxide incorporation and (potentially) also improve sensitivity and selectivity of the polymeric sensing materials.

In Figure 6.5 (a), area 1, one can see 100% SnO_2, whereas in area 2, zero metal oxide is detected. In general, low levels of metal oxide (around 2 wt %) are determined via EDX in both the In_2O_3-doped and NiO-doped samples (Figures 6.5 (a) and (b)). The exception to those results are

localized measurements in area 1 of Figure 6.5?4 (b), which has much high levels of In. Therefore, the results are as expected: both In_2O_3 and NiO are present in the PANI samples.
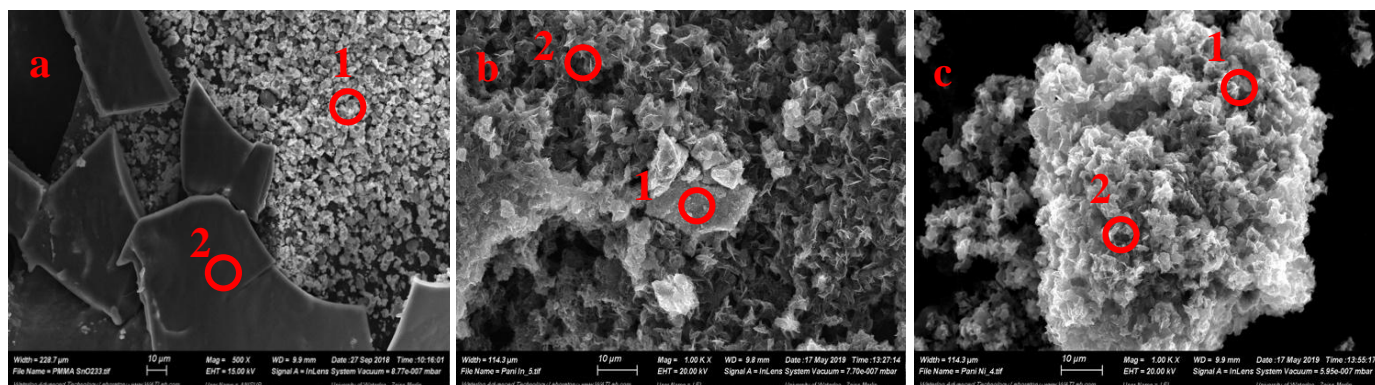

Figure 6.5 Energy Dispersive X-Ray images for (a) PMMA with 10% SnO_2, (b) PANI with 5% In_2O_3 and (c) PANI with 5% NiO

6.2 Possible Mechanistic Explanations

Possible sensing mechanisms describe the way gas analytes and sensing materials will interact. These mechanisms can be categorized as primary and secondary sensing mechanisms. Primary effects may contain polarity and hydrogen bonding, Lewis acid-base interactions, p-orbitals and π-stacking, metal coordination, Van der Waals forces, and steric hindrance. Secondary mechanisms include swelling and solvent effects.

The dominant mechanisms in our research seem to be hydrogen bonding and Lewis-acid interactions, followed by steric effects. PANI contains an amine group that makes it polar and able to hydrogen bond between the amine group and the oxygen on formaldehyde. In P25DMA, two methyl side groups result in a less closely packed structure. Therefore, this provides more available interstitial spaces for the gas sorption onto in. A Lewis acid is characterized as an electron deficient atom, such as a carbon atom. Lewis base attacks the electron deficient atom and forms a weak physical bond. Acetaldehyde is an example of this. Aromatic rings in benzene are able to π-stack with the polymeric materials. In fact, aromatic compounds are typically the only VOCs that are able to π-stack (Li et al. 2007). In addition, benzene aromatic molecules are bulkier than the other VOCs, therefore they need larger interstitial spaces to easily sorb into the polymer matrix (Shi-Zhen et al. 2009). When PANI coordinates with Ni, the aromatic ring bends into the shape of a 'boat' with two carbons bent upwards (Figure 6.5). This is called Ni coordination to the nitrogens

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in the quinoid ring. If too much metal oxide is used, polymeric chains will be too strained and may begin to break (Stewart and Penlidis, 2016).
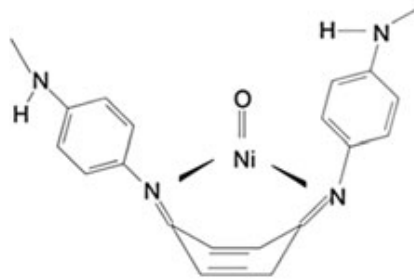

Figure 6.6 Ni coordination to the nitrogens in the ring (Han et al, 2006)

Indium oxide (see also Appendix B) is a semi-conductor material and exhibits low resistance. Therefore, when gases meet with strong oxidizability, free-electrons on the surface of metal oxide will be consumed, which makes the sensing material become of high resistance. Because of this, indium oxide has a good capability in sensing oxidizing gases (Liu et al. 2004; Francioso et al. 2006).

7. Concluding Remarks and Recommendations

7.1 Concluding Remarks

Comparison of synthesized PMMA samples and commercially available PMMA suggests that PMMA synthesis had no effect on sorbing capabilities from acetone. Even in higher concentration of acetone (1100 ppm), no significant sorption is achieved. Different methods of doping PPMA with metal oxide have been investigated. Doping PMMA with ZnO, SnO_2, and WO_3 in different weight percentages of 5%, 10%, and 15% did not seem to change the percentage of acetone sorbed onto it. In addition, PMMA doped with ZnO during synthesis provided us with similar results. Therefore, pure PMMA and PMMA doped with zinc oxide, tungsten trioxide, and tin (IV) oxide are not potential sensing materials for acetone at room temperature

In the case of formaldehyde sorption by different sensing materials, the percentage of sorbed formaldehyde did not vary much between high and low target concentrations of formaldehyde, which varied from 5 ppm to 10 ppm in single gas, and ~2 ppm and ~6 ppm for gas mixtures of formaldehyde and benzene. In other words, regardless of whether we introduce ~2 ppm of each formaldehyde or benzene or ~6 ppm of each of the gases to the sensing material, the absolute value of the sorption remains about constant. This suggests that, at least at these ppm levels, higher concentration does not lead to higher sorption for the formaldehyde and benzene mixtures.

Among the polymeric sensing materials used for formaldehyde sorption, P4VP and PAAc in three average molecular weights of 130K, 450K, and 1M are not promising sensing materials. On the other hand, PANI and P25DMA are both sensitive and selective toward formaldehyde. Furthermore, although the composite of PANI with 5% In_2O_3 and PANI with 5% NiO showed an increase in sorption of formaldehyde in 10 ppm, the increase was not statistically significant.

Doped PANI with 5% In_2O_3 and PANI with 5% NiO did not change its sensing capabilities in a ~2 ppm of each formaldehyde and acetaldehyde gas mixture compared to un-doped PANI.

From sensing material SEM images we conclude that morphology of the sensing material affects its gas sensing capabilities. The more porous the surface of the sensing material, the more active sites are available for the gas to diffuse. Also, from EDX results, it was observed that not all metal oxides can be incorporated into a polymer matrix.

7.2 Recommendations for Future Work

Among the several steps that can be performed as future work, some steps seem to be more interesting. Other metals or metal oxide dopants such as Pd and Pt can be used to evaluate a potential increase in gas sensing capabilities of polymer material. Also, more composite blends of polymers can be made and evaluated for gas sensing in future work. In addition, gas mixtures of more than two analytes can be conducted to further investigate the selectivity properties of the promising sensing materials when more than two gas analytes are present. Lower concentrations of gas analytes can also provide more information on the sensitivity of sensing materials (detection limit). The promising sensing materials can also be deposited onto a microcantilever sensor for more investigations, as currently pursued by our collaborators in Systems Design Engineering (Prof. E. Abdel-Rahman's group).

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Appendix A

Typical gas mixture calculations, corresponding to section 3.2.

F: Formaldehyde

Ac: Acetaldehyde

Mw: Molecular weight

Ideal Gas Law: $PV = nRT$

F_{Mw}: 30.03 (g/mol)

Ac_{Mw}: 44.04 (g/mol)

To get the volume needed for each gas inlet in the mixture:

F mass ~ Ac mass (achieve equal concentrations of each gas in the mixture)

Then,

$P_F V_F = n_F R T_F$, $P_{Ac} V_{Ac} = n_{Ac} R T_{Ac}$

Assume R, P, and T constant;

$$\frac{VF}{nF} = \frac{VAc}{nAc}$$

Also $V_F + V_{AC} = 230$ sccm (maximum total volume that can be measured by flow controller)

Therefore,
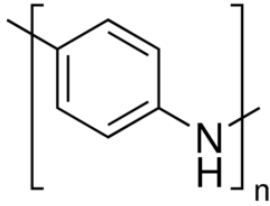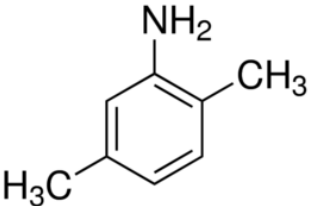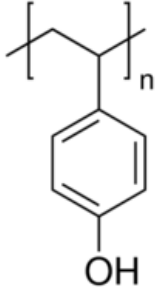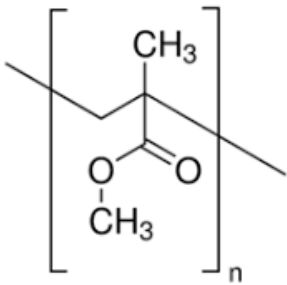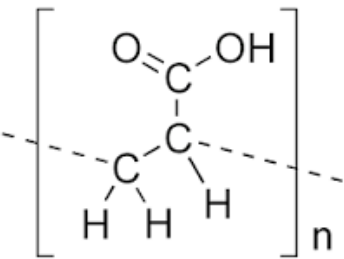
$$\frac{VF}{30.03} = \frac{VAc}{44.04}$$

$V_F = 93.26$ sccm, and $V_{Ac} = 136.74$ sccm

These numbers were used as volumes for each gas analyte entering the GC (measured by flow controller), and were slightly adjusted (fine-tuned) based on experimental observations/ experience with the set-up.

Appendix B

Chemical structure of polymers

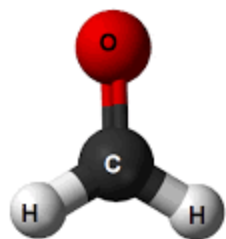|	
PANI	P25DMA
P4VP	PMMA
PAAc	

Chemical structure of gas analytes
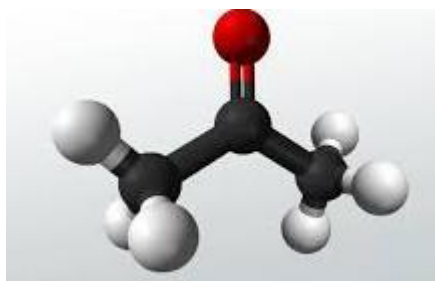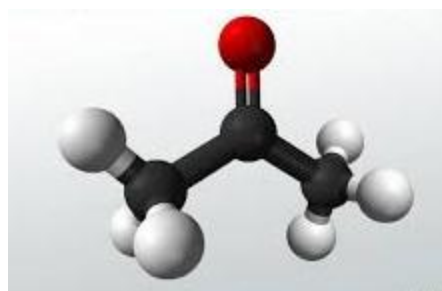
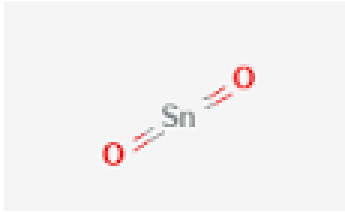|	
 Acetone	 Acetaldehyde
 Formaldehyde	 Benzene
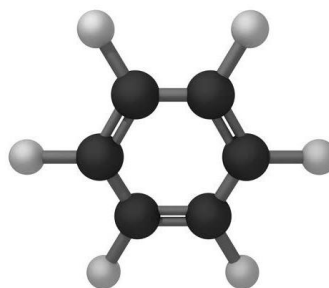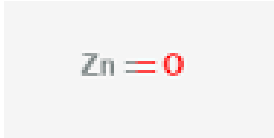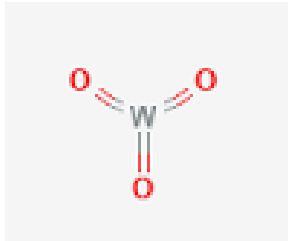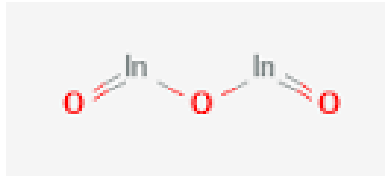
Chemical structure of metal oxides

$Zn = O$ ZnO	$O = Sn = O$ SnO$_2$
$O = W = O$ $\|\|$ O WO$_3$	$O = In - O - In = O$ In$_2$O$_3$
$Ni = O$ NiO	