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Detecting and Identifying Clandestine Drug Laboratories: Sensing Technology Assessment

March 2008

Prepared by the

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For the
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March 31, 2008

The University of British Columbia

ABSTRACT

Clandestine drug laboratories, of which the majority are producing methamphetamine, represent one of the most significant social challenges facing Canada and in particular British Columbia. Such laboratories are capable of producing large quantities of illicit drugs in production cycles that can often span less than 48 hours, making timely discovery essential. This report outlines the first phase of a larger project aiming at developing sensor technology targeted at detecting these clandestine methamphetamine laboratories. As part of this report, we provide a detailed analysis of the most common methamphetamine manufacturing processes and identify the airborne chemicals released during manufacturing. Since each of these manufacturing processes has a unique chemical and temporal signature, these signatures can be used to distinguish methamphetamine laboratories from other legitimate sources of these gases. In the context of the target gases, this report also provides a detailed assessment of available sensor technology, as well as sensor technology currently under development. The objective of this assessment is to identify the sensor technologies that would be most suitable for this application. In addition, recommendations for future steps are developed in order to further assess the feasibility of this project.

EXECUTIVE SUMMARY

The primary objective of the project is to develop detection technology that will be used by law enforcement units to uncover clandestine methamphetamine laboratories and chemical waste dumps. In the initial phase of this project, target chemicals used in the production of methamphetamine are identified through a detailed analysis of the common manufacturing processes. The results presented are essential to developing a database of chemical signatures that will be used to distinguish the clandestine laboratories and waste dumps from other legitimate sources of these gases. In addition, a detailed assessment of sensor technology was completed in order to identify technologies that are most suitable for this purpose. In summary, this research has:

1. Identified a detailed list of target gases that are released from common methamphetamine manufacturing processes (Birch Reduction method, P2P-based methods, Red Phosphorus-based methods).

2. Identified the expected temporal sequence of gases for the various methods, which will form the chemical signature of each particular manufacturing process. Where possible, the estimated concentration of those gases both inside and outside of the laboratory has been provided.

3. Identified common uses and sources of the target gases in order to reduce false identifications of clandestine laboratories.

4. Identified the potential point sensor technologies that could be used in the detection of the target gases and provided the detectable levels of those gases.

5. Developed a set of recommendations outlining a series of required experiments that will enable a project feasibility assessment. These include:

    a. Setting up a mock clandestine lab site for research and detection of harmless simulant gases in order to determine expected concentrations in and around the laboratory. This initial setup will be used to simulate the propagation of gas outside of the lab and to establish preliminary estimates of gas concentration.

    b. Performing live testing using colorimetric detection tubes mounted on patrol vehicles. This highly sensitive method will demonstrate if target gases can be detected from a moving vehicle.

    c. Setting up a model clandestine laboratory and / or waste dump in order to obtain accurate airborne target gas concentrations in the vicinity of the laboratory for the most common manufacturing methods. This data will be used to assess existing technology and determine where further research will be required.

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LIST OF ABBREVIATIONS

BAW	Bulk acoustic wave
CMOS	Complementary metal oxide semiconductor
CWA	Chemical warfare agent
DMSO	Dimethyl sulfoxide
eV	Electronvolt
Fe_2O_3	Iron oxide
FET	Field effect transistor
FOEW	Fibre optic evanescent wave
FPW	Flexural plate wave
FTIR	Fourier transform infrared
IDT	Interdigital transducer
IMS	Ion mobility spectrometry
IR	Infrared
MEMS	Microelectromechanical system
MoO_3	Molybdic oxide
MOS	Metal oxide semiconductor
MS	Mass spectrometry
NEMS	Nanoelectromechanical system
PLS	Partial least squares
Pd	Palladium
PDMS	Polydimethylsiloxane
PID	Photoionization detector
Pt	Platinum
ppb	Parts per billion
ppm	Parts per million
ppt	Parts per trillion
QCM	Quartz crystal microbalance
RIfS	Reflectometric interference spectroscopy
SAW	Surface acoustic wave

SnO_2	Tin dioxide
SWNT	Single walled nanotube
TIC	Toxic industrial chemical
TIRF	Total internal reflection fluorescence
TSM	Thickness shear mode
μTAS	Micro-total analysis system
UV	Ultraviolet
VOC	Volatile organic compound
WO_3	Tungsten oxide
ZnO	Zinc oxide

Introduction

The primary objective of the overall project is to develop technology-based sensing tools that will assist law enforcement units in uncovering clandestine methamphetamine laboratories and chemical waste dumps. The role of this report is to help assess the feasibility of such a project. The report has been broken down into three main sections: section A, which describes common methamphetamine manufacturing processes and identifies target chemicals associated with these processes, section B, which describes chemical sensing technology currently in the commercial or research stage, and section C, which assesses the sensing technology in the context of the project and provides recommendations for moving forward.

The approach taken for formulating the recommendations is as follows:

1. Identify a list of target chemicals and possible concentrations, based on:
    a. Common methamphetamine manufacturing processes, including released chemicals and sequence of release (signature).
    b. Characteristics and layout of clandestine drug labs and chemical waste dumps.
2. Analyze sensing technology to detect the target chemicals, including current and next generation commercial gas sensors, as well as gas sensors that are currently undergoing researched enhancements, using performance metrics such as lowest detection limit, response time, etc.

Part A: Determining the Chemicals involved in Clandestine Methamphetamine Production

The Needs Triangle of clandestine labs, according to forensic experts, consists of three key components: chemicals, equipment, and knowledge [1]. Within the context of this report, each of these three components plays some role in the detectability of a particular laboratory. The location, lab operator, and equipment required for clandestine methamphetamine production is the focus of Section 1, while the chemicals required for the drug synthesis are detailed in Section 2 with a focus on the most common methamphetamine manufacturing processes.

1. Characteristics of Clandestine Drug Laboratories

The characteristics of clandestine drug laboratories: location, equipment, and operator, have a direct impact on the amount of gas released during the drug production cycle. For example, small clandestine labs account for far more explosions and fires (with one major reason being more frequent accidental releases of explosive gases) because less-skilled “cooks” operate the labs using more primitive equipment and facilities [2].

Data is available in the literature on typical concentrations of chemicals inside homes/apartments used for controlled methamphetamine syntheses. However, no data exists for chemical concentrations within the vicinity of the cook site outside the building, which is more relevant to this study. This fact was confirmed by email correspondence with Dr. John Martyny, a researcher with the National Jewish Medical Center, U.S.A., who has published several reports on chemical concentrations at controlled methamphetamine “cooks”. It is expected that environmental factors such as humidity, wind speed, etc. will significantly affect the ambient concentration of chemicals. Since an actual controlled cook could not be conducted in order to measure the concentrations of the released chemicals outside the laboratory, it can only be assumed that the gas concentration outside the building will likely be at least two to three orders of magnitude lower than the average concentration present inside, using the upwind concentration at the front door of a controlled cook as a general rule of thumb. This estimation is based on experiments presented in [3].

1.1 Location

Clandestine labs producing methamphetamine, versus other synthetic drugs such as Ecstasy, accounted for the majority of lab seizures in Canada, with over 80% in 2004 [4]. Clandestine lab activity is greatest in British Columbia with 66% of Canada’s seizures in 2005, followed by Ontario, Quebec, Alberta, and Saskatchewan. Clandestine drug labs are found in very different settings including rental properties, motel rooms, even high-end hotel rooms, vehicles and motor homes, as well as in the remote rural areas [5]. In 2005, Lower Mainland police responded to over 30 discovered clandestine drug labs, 3 of which were located in Vancouver [5]. The majority of these clandestine drug labs were found in suburban or semi-rural areas. This statistic is in agreement with the local RCMP’s observation that clandestine “super-labs” have become more common than small-scale labs in recent years. A super-lab is defined as a clandestine lab that produces, on average, more than 10 pounds of methamphetamine per production cycle [1]. As mentioned earlier, most explosions (and the accidental gas releases that cause them) occur in small-scale labs. Super-labs may be more difficult to detect since they are better organized and employ additional equipment to suppress the release of gases. Super-labs are typically located in less densely populated areas to minimize the chances of detection.

1.2 Operators

According to Christian, there are three main types of clandestine lab operations: small-scale, commercial, and educated [1]. Operators of small-scale labs are typically methamphetamine users themselves. They produce methamphetamine for their own consumption and additional small amounts to sell. Operators of commercial laboratories are motivated primarily by financial gain, and run multi-site operations using optimized industrial-scale manufacturing processes. Educated operators possess formal education in chemistry or on-the-job training, and are the least-encountered type of lab operator. They may act as consultants for small-scale or commercial lab operators. Table 1 summarizes the likely characteristics of the three types of lab operators.

Table 1 - Characteristics of clandestine lab operators [1]. Local distribution means the drug is sold geographically close to the operator, and not through a distribution network.

Characteristic	Small-Scale Operator	Commercial Operator	Educated Operator
Chemical education	No	Yes	Yes
Drug user	Yes	Maybe	Maybe
For profit	No	Yes	Maybe
Legitimate chemical supply	No	Maybe	Yes
Single location operation	Yes	No	Yes
Local distribution	Yes	No	Maybe

The type of lab operator heavily influences the amount of gas released during drug production. For example, educated lab operators will be more likely to use ventilation to reduce the level of toxic and/or explosive gases inside the lab. In a study by Martyny *et al.*, the researchers found that by simply opening a window and placing a fan next to it, the concentration of a reactant gas inside the facility was drastically reduced [3]. For a gas detection scheme, this ventilation would be advantageous as the outdoor concentration of gas would be increased.

1.3 Equipment

The choice of equipment used in a clandestine drug lab operation depends highly on the manufacturing process utilized to produce the drug; the specifics of the most common production routes are explained in section 2. Scientific-grade equipment, if available, is preferred, although clandestine lab operators will occasionally use substitutes to avoid detection. Using scientific-grade equipment may result in less frequent releases of gases which makes detection more difficult, while substitute equipment may be more prone to failure. All manufacturing processes can be broken down into four distinct processes: **extraction, conversion, synthesis, and tableting** [1]. Labs can specialize in one of the processes, or perform a combination of processes. Extraction refers to the process of retaining a particular ingredient from a mixture while removing the rest. The process of transforming a specific material from one form to another is conversion; this includes changing the drug from its freebase form to salt form or vice versa. Synthesis involves chemically reacting molecules or parts of molecules to create new molecules; this is the key step in the fabrication process. The final process is tableting, where the finished product is placed into smaller, more salable units such as tablets for distribution.

The core pieces of equipment used for the production of methamphetamine are collectively referred to as “the kit” [6], which includes:

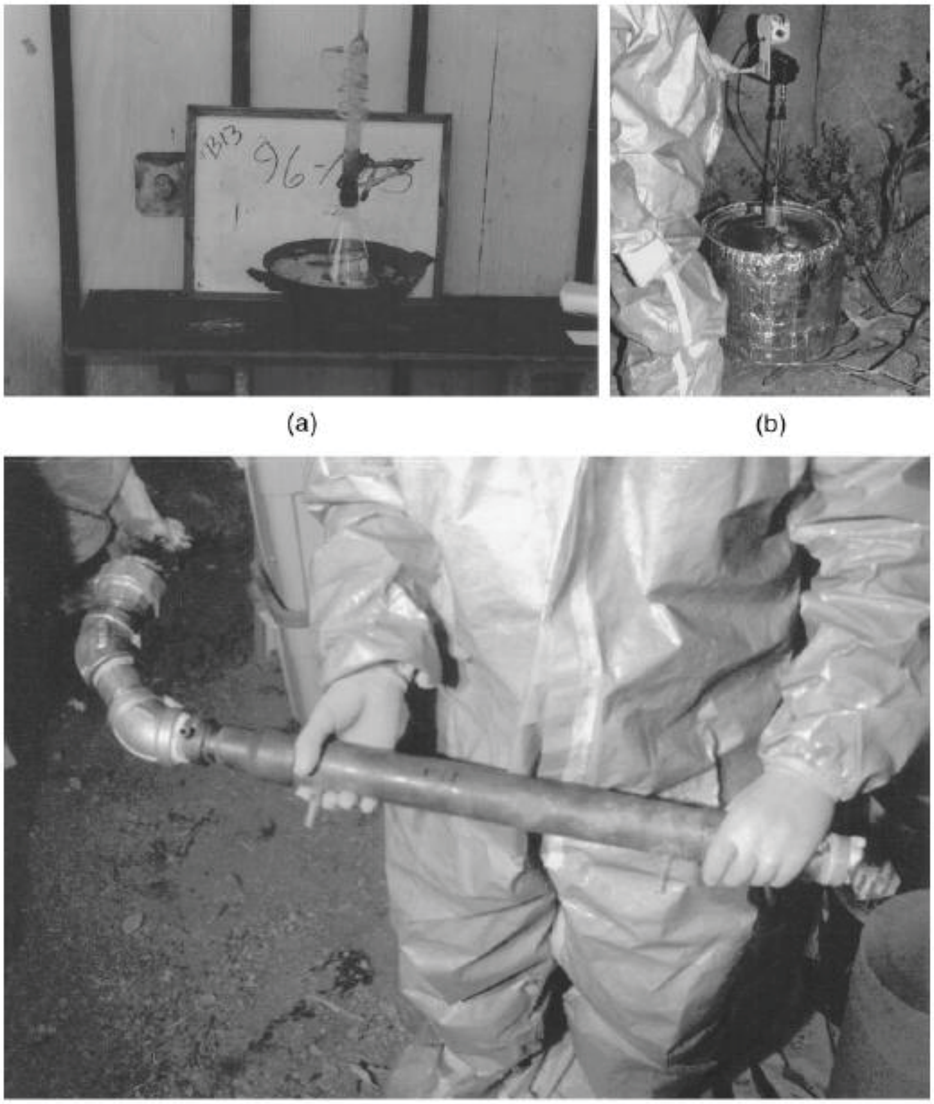
- Several round bottom flasks
- Claisen adapter
- Still head with thermometer holder, and thermometer
- Condenser

- Vacuum adapter
- Separatory funnel

The pieces all have ground glass joints, so the entire setup can be reconfigured for different processes. Usually this scientific-grade equipment is stolen or diverted from legitimate sources. Table 2 lists the scientific-grade equipment used in clandestine drug manufacture, their substitutes, and purpose.

Table 2 - Core equipment used for clandestine methamphetamine production, along with substitute equipment

Process	**Scientific-grade Equipment**	**Examples of Substitute Equipment**	**Purpose**
Refluxing	• Reaction flask • Condenser • Heating mantle with rheostat	• Glass cookware or pot, stainless-steel canister, copper reaction pot if strong, hot acids used • Pot lid, makeshift condenser from stainless-steel or PVC pipe, teflon-coated copper condenser if strong, hot acids used • Stove or hot plate, along with oil bath, counterdrop deep fryers as oil baths	• Controlled boiling process, where evaporated liquid condenses and returns to reaction mixture.
Distillation	• Reaction flask, condenser, heating mantle with rheostat • Second flask	• Similar to above • Similar to above	• Separate a liquid from a solid or other liquid, using evaporation followed by condensation. Exploits differences in boiling points.
Hydrogenation	• Hydrogenator (“the bomb”)	• Aluminum fire extinguisher, emptied, coated on inside with Teflon-based paint	• Adds hydrogen to a substance under high pressure to convert from one substance to another, useful for industrial-scale manufacture.
Extraction	• Vacuum filtration unit • Separatory funnel	• Air compressor from fridge or air conditioner used to generate vacuum, aspirator used with cold running water • Turkey baster, water bottle with squirt top	• The physical and/or chemical properties of a component are used to separate it from the whole.



(a) (b)

Figure 1 - Equipment used as substitutes for scientific-grade equipment in clandestine drug manufacture, (a) oil bath reflux (b) beer keg reaction vessel (c) copper tube condenser [1]

2. Common Clandestine Methamphetamine Manufacturing Processes

All methamphetamine manufacturing methods include a sequence of the four main process stages outlined above. The chemicals released during the different stages are specific to the respective method. There are two chemical signatures that can be associated with a particular manufacturing method. First is the signature attained from any one particular measurement of airborne chemicals; i.e., the relative concentration of the various gases in any one measured sample. The other is the temporal signature, which is attained from several measurements over an extended period of time. In this case, the release sequence of the different chemicals represents the signature of that method. A maximum level of certainty about the nature of the source can be attained if a measurement of chemical concentrations over time can be matched with the temporal signature of a production process. The production steps, as well as the associated signatures are outlined below for the different manufacturing methods.

2.1 Birch Reduction Method

2.1.1 Background

The Birch reduction method is one of several popular ephedrine/pseudoephedrine-based methamphetamine manufacturing processes. It uses ephedrine or pseudoephedrine from over the counter cold medicine, where it is found as an ingredient in various medications such as Sudafed ®. A simple representation of the process is shown in Figure 2. It uses large amounts of anhydrous ammonia and therefore, it is also known as the anhydrous ammonia method. Informally the Birch method is also known as the “Nazi” method [3]. The method produces high quality product, can be easily scaled up for industrial production using parallel processes, has a short reaction time (on the order of tens of minutes), and the reactants and catalysts are relatively easy to obtain. Various forms of this method have become widespread in rural areas within the past decade [7]. Reasons include readily accessible sources of anhydrous ammonia (stolen from or even sold by farmers), and lower chance of detection due to the remote location, since ammonia has a distinct, unpleasant odour that can be easily identified by humans.

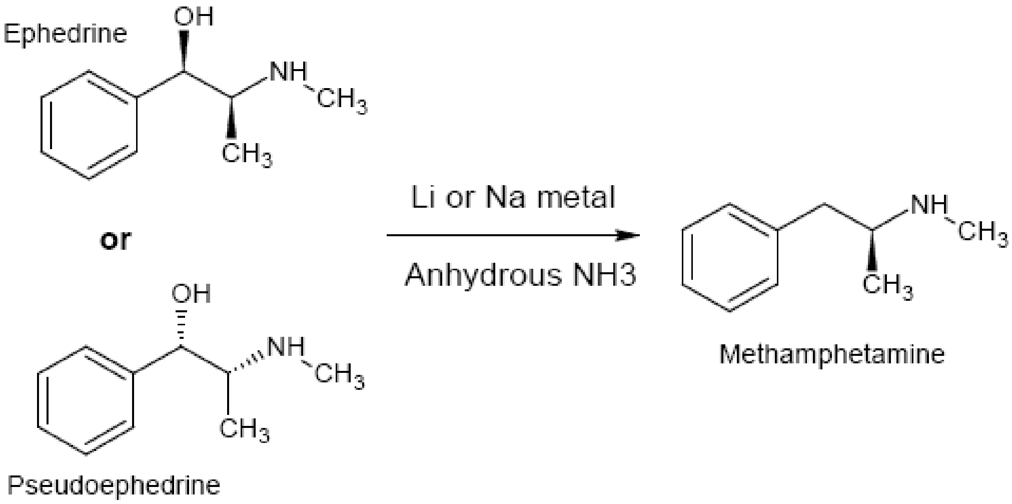


Figure 2 - Birch Reduction method

2.1.2 Reaction

The Birch method requires the use of a catalyst such as sodium or lithium metal. Clandestine manuals providing techniques for removing the lithium from batteries, or using an electrochemical cell (Down’s cell) to produce metallic sodium from lye, can be found on the Internet or in underground literature. The lithium or sodium metal is first dissolved in liquid ammonia, forming a blue solution. After the ephedrine or pseudoephedrine free base has been extracted from the tablets, it is dissolved in tetrahydrofuran (THF) or ether. The dissolved ephedrine/pseudoephedrine solution is added to the ammonia solution over a span of 10 minutes. The reaction is allowed to proceed for 10-20 minutes, after which it is quenched by adding water. During this process the ammonia evaporates, and more water is added to dissolve the salts of lithium. After this process has completed, the water layer is separated off from the ether layer. The ether layer is dried using anhydrous sodium sulfate, and the hydrochloride salt of methamphetamine is obtained by bubbling hydrogen chloride gas through the solution. The hydrochloride salt crystals are filtered and dried. Table 3 summarizes the reactants, solvents, catalysts, and by-products associated with this method of methamphetamine synthesis.

Table 3 - Summary of reactants, solvents, catalysts, and by-products associated with the Birch reduction method

Type of Chemical	Reactants	Solvents	Catalysts	By-products
• Inorganic	• Ammonia	• Hydrogen chloride	• Lithium/Sodium • Sodium sulphate	• N/A
• Organic	• Ephedrine/ Pseudoephedrine	• Toluene • Camper fuel (hexane, heptane, cyclohexane) • THF • Ether	• N/A	• N/A

2.1.3 Temporal Chemical Signature and Typical Concentrations

A simulated controlled cook using the anhydrous ammonia method was investigated by Martyny *et al.*, who recorded concentrations of ammonia and hydrogen chloride throughout the manufacturing cycle [3]. High organic solvent levels were not observed in prior testing, so the investigators did not sample for volatile organic compounds (VOC's). Three cooks were conducted, cook #1 was conducted with all windows and doors in the cook area closed, cook #2 had a small fan placed near an open window, and cook #3 had a relatively well ventilated cook area but used no fans.

As cook #1 was initiated, the ammonia gas monitor in the cook area exceeded its upper detection limit (200 ppm) within 5 minutes, and all other ammonia monitors within the building exceeded their upper detection limits within 16 minutes. The highest recorded level of ammonia was 3348 ppm using Drager colorimetric tubes, and the average measured concentration of ammonia during the first 3 hours exceeded 410 ppm. During cook #2, real-time ammonia concentrations collected in the air stream of the fan ranged between 50-100 ppm. Less than 66 ppm of ammonia was measured across the room, meaning that an open window and simple fan are effective at reducing interior ammonia concentrations. At cook #3, average ammonia levels ranged between 500 ppm to 2000 ppm, 500 ppm was measured if the solution was not agitated. Average measured concentration at the cook area was 338 ppm during the first 101 minutes of the cook, and 141 ppm during the 46 minutes of the acidification phase. Ammonia concentrations were measured at 50 ppm outside the window near the cook area, and at 4 ppm upwind by the front door (outside).

As for hydrogen chloride, the researchers noted that the measured concentrations may be lower than expected because the gas monitors were overloaded due to high anhydrous ammonia levels, and hypothesized that in addition the anhydrous ammonia was reacting with hydrogen chloride to produce ammonium chloride which was not detected by the available equipment. At cook #1, >0.2 ppm was measured at the cook area. The cook area of cook #2 had >0.02 ppm of hydrogen chloride, and >0.6 ppm of hydrogen chloride was measured at the cook area of cook #3.

2.1.4 Summary of Target Chemicals for Birch Reduction Method

Of the list of organic and inorganic chemicals listed in Table 3, ammonia and hydrogen chloride are in gaseous form, and the organic solvents are volatile liquids at room temperature. The list of potential targets for this process consists of:

- Ammonia
- Hydrogen chloride
- Camper fuel (hexane, heptane, cyclohexane)
- Tetrahydrofuran

2.2 P2P-based Methods

2.2.1 Background

Prior to the 1990's, the most popular clandestine methamphetamine synthesis process was the P2P method, which uses the precursor, phenyl-2-propanone (also known as phenylacetone or P2P) and is structurally very similar to methamphetamine. The motorcycle gangs in California used this manufacturing process extensively. The popularity of the process diminished as precursor chemicals became more difficult to obtain after P2P was placed onto the controlled substances list in the United States in 1988; Canada followed suit by classifying P2P as a Schedule VI Class A regulated precursor chemical [8]. Compared to modern processes, P2P-based methods also produce a lower quality product with less addictive properties [9]. One P2P-based method, the Leuckardt-Wallach reaction, can be used to produce up to ½ pound batches [6]. A simple representation of the process is shown in Figure 3.

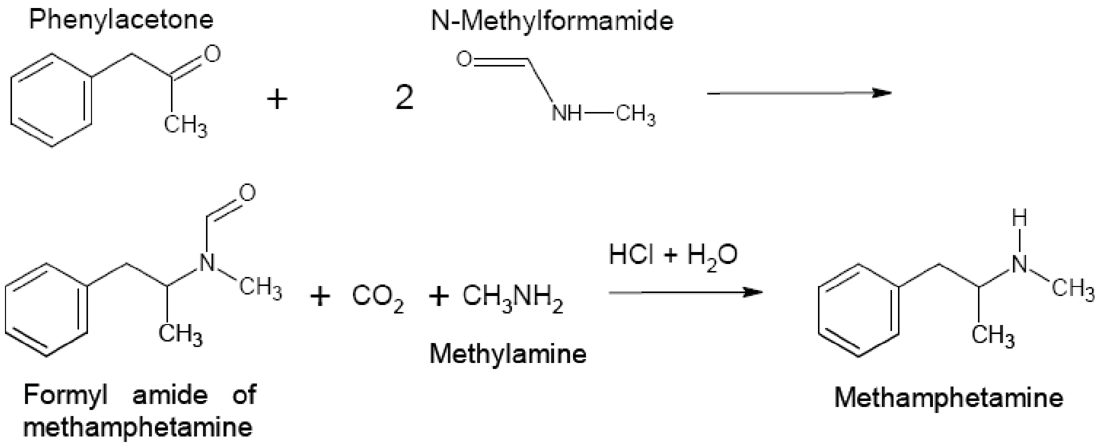


Figure 3 - P2P Leuckardt-Wallach method

2.2.2 Reaction

The key reaction for methamphetamine production through the P2P method is the P2P Leuckardt-Wallach reaction. It is assumed that the operator will already have the two primary precursors: phenylacetone and N-methylformamide. Otherwise, P2P can be synthesized from phenylacetic acid and acetic anhydride, and N-methylformamide can be synthesized from methylamine and formic acid. A mixture of P2P and N-methylformamide is prepared, using 4 to 6 moles of N-methylformamide for every mole of phenylacetone. The mixture is carefully heated to between 105 ºC and 110 ºC, which is the temperature at which the reaction starts to occur. The mixture begins to bubble, and the temperature is kept as low as possible while still maintaining the reaction. The reaction mixture takes on an amber colour. The temperature is moderately increased after 1-2 hours to keep the reaction going, which is monitored through the amount of gas formation. The bubbles being formed are carbon dioxide, a by-product, and the amount of generated carbon dioxide is used as an indicator of how well the reaction is progressing. Over a total period of 24 to 36 hours, the temperature is incrementally increased to 145 ºC.

Once the reaction stops, the mixture is allowed to cool, at which point the solution should still have an amber colour. A reddish tint means the reaction was unsuccessful. At this point the cook may recover some of the unused N-methylformamide by reacting it with sodium hydroxide to form methylamine gas, which is piped into formic acid to regenerate N-methylformamide for the next batch. After the N-methylformamide recovery process, the red methamphetamine formyl amide solution is mixed with hydrochloric acid and gently heated. The mixture turns black as methamphetamine formyl amide reacts with hydrochloric acid to produce methamphetamine hydrochloride and formic acid. The black reaction mixture is slowly added to a solution of sodium hydroxide in order to neutralize the excess acid and convert methamphetamine hydrochloride into free base, resulting in a brown methamphetamine free base layer that will separate above the sodium hydroxide solution. Toluene is then added to extract the free base, and the methamphetamine-toluene layer is separated from the rest of the mixture and distilled, yielding a small volume of clear to pale yellow methamphetamine. The free base methamphetamine is converted into crystalline methamphetamine hydrochloride using hydrogen chloride gas. The crystals are filtered and dried. Table 4 summarizes the reactants, solvents, catalysts, and by-products associated with this method of methamphetamine production.

Table 4 - Summary of reactants, solvents, catalysts, and by-products associated with P2P Leuckardt-Wallach method

	Reactants	**Solvents**	**Catalysts**	**By-products**
• Inorganic	• Sodium hydroxide • Hydrogen chloride	• N/A	• N/A	• Carbon dioxide
• Organic	• Phenylacetone • N-Methylformamide For making precursors • Phenylacetic acid • Acetic anhydride • Methylamine • Formic acid	• Toluene • Ethyl ether • Camper fuel (hexane, heptane, cyclohexane)	• N/A	• Formic acid

2.2.3 Temporal Chemical Signature and Typical Concentrations

Data on experimentally determined chemical concentrations during various phases of the P2P Leuckardt-Wallach method is not available in the scientific literature. One reason may be that the popularity of the P2P process diminished quickly after the 1990's. However, based on the cooking method a qualitative temporal chemical concentration signature can be assumed as described below.

It is expected that vapours of the reactants, phenylacetone and N-methylformamide, will be present during the first reaction phase, particularly since the reaction mixture is at an elevated temperature of up to 145 ºC. At 150 ºC, N-methylformamide is quite volatile with a vapour pressure of 22.6 kPa, which is a fifth of atmospheric pressure. The reaction vessel cannot be sealed, as the reaction produces carbon dioxide gas. Although the temperatures used during this phase are fairly high, they are below the boiling points of the reactants (boiling point of phenylacetone: 216.5 ºC, boiling point of N-methylformamide: 199.5 ºC). After the initial reaction, the clandestine operator may recover the unused N-methylformamide, a process that will produce methylamine gas. Although the methylamine is piped into another flask holding another reactant, gas leaks may occur resulting in low but detectable concentrations of methylamine. After the recovery of N-methylformamide is performed, the second reaction phase involves the use of hydrochloric acid and as a result, hydrogen chloride gas will become detectable at this point. An organic solvent such as toluene is used in the following stage to extract the liquid methamphetamine free base, and as a result, organic solvent vapours may be detectable at this point. Finally, the crystallization phase involves bubbling hydrogen chloride gas through an organic solvent such as ethyl ether, toluene, or mineral spirits (i.e. Coleman camper fuel), so vapours of hydrogen chloride and the organic solvent may be detectable. The organic solvent vapours may still be detectable after the crystallization process since the crystals will usually be left out to dry.

2.2.4 Summary of Target Chemicals for P2P Method

Of the list of organic and inorganic chemicals listed in Table 4, hydrogen chloride is in gaseous form at room temperature, toluene and all of the organic reactants are volatile liquids (with varying degrees of volatility) at room temperature. The list of potential targets for this process consists of:

- Hydrogen chloride
- Acetic anhydride
- Formic acid
- Methylamine
- N-Methylformamide
- Phenylacetone
- Phenylacetic acid
- Toluene

2.3 Red Phosphorus-based Methods

2.3.1 Background

Ephedrine/pseudoephedrine-based methamphetamine synthesis methods became popular shortly after regulations on P2P were introduced. The most popular of these methods was the Red Phosphorus (Red P) method and its derivatives, particularly from the 1980's until the mid 1990's. The process is also known in the United States as the "Red, White, and Blue Process", since it involves red phosphorus, white ephedrine/pseudoephedrine, and blue iodine [10]. A simplified version of the Red P synthesis route is depicted in Figure 4. Several variants of this method have been used, for example iodine crystals can be substituted for hydroiodic acid. Red phosphorus can be obtained from the strike pads on matchboxes (40% red phosphorus) [6]. Starting in the mid-1990's, the "Hypo" method, substituting hypophosphorous acid for red phosphorus, has become popular [11]. Another variation, involving the substitution of phosphorous flakes for red phosphorus has also gained popularity. Phosphorous flakes are readily accessible from agricultural fertilizers [11]. Clandestine operators prefer the Red P method because it is relatively simple to perform, but precautions such as using pure ephedrine must be followed or else the product will be useless. Pharmaceutical companies add additional fillers to their products to interfere with the extraction of ephedrine. For the Red P-Hydroiodic acid method, the majority of the product can be obtained in 10 hours, 75% is complete within 16 hours, and the process is entirely complete within 24 hours [6].

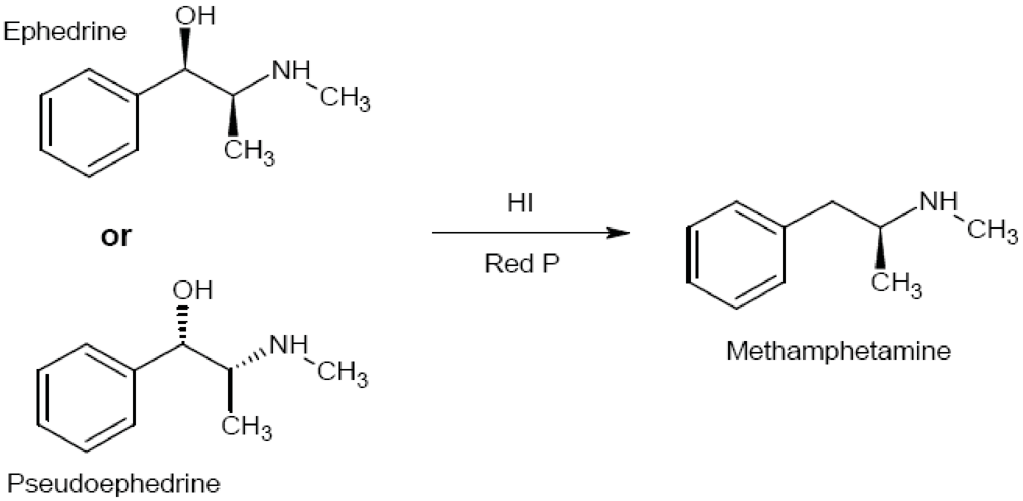


Figure 4 - Red P method

2.3.2 Reaction

To start, ephedrine hydrochloride, red phosphorus, and hydroiodic acid are added to a flask. Hydroiodic acid can be made by adding iodine crystals to red phosphorus suspended in water. A by-product from *in situ* hydroiodic acid production is phosphine, a toxic gas. The mixture is boiled under reflux for one day, and the progress of the reaction can be monitored by observing the consumption of red phosphorus. After the mixture is cooled and diluted with water, red phosphorus is filtered out using conventional coffee filters or equivalent. The filtered solution should be golden in color. If the solution is reddish in color, there may be residual iodine in the solution, which can be reduced to iodide by adding sodium bisulfite or sodium thiosulfate. Next, the solution is made strongly alkaline by adding lye or sodium hydroxide. A layer of free base methamphetamine forms, and will separate to the top of the aqueous solution. To extract the free base methamphetamine, toluene is added and the methamphetamine-toluene solution is separated from the rest of the mixture. Hydrogen chloride is bubbled through the methamphetamine-toluene solution to crystallize the free base methamphetamine into the hydrochloride form of methamphetamine. Table 5 summarizes the reactants, solvents, catalysts, and by-products associated with this method of methamphetamine synthesis.

Table 5 - Summary of reactants, solvents, catalysts, and by-products associated with Red P method

	Reactants	Solvents	Catalysts	By-products
• Inorganic	• Hydroiodic acid • Iodine • Red phosphorus • Sodium bisulfite • Sodium thiosulfate • Sodium hydroxide	• Hydrogen chloride	• N/A	• Phosphine
• Organic	• Ephedrine/Pseudoephedrine	• Toluene	• N/A	• N/A

2.3.3 Temporal Chemical Signature and Typical Concentrations

A study conducted by Martyny *et al.* examined airborne concentrations of methamphetamine, VOC's, iodine, and hydrochloric acid [12]. The Red P and iodine method was used to produce methamphetamine. During the controlled cook, the highest measured concentration for hydrogen chloride was 0.42 ppm in the cook area. Prior experiments by the DEA and National Jewish Medical Center have reported up to 150 ppm peak during the salting out (crystallization) phase. The average concentration of iodine measured during the cook was 0.12 ppm, although it is likely that peak concentrations will be higher. The extraction solvent used consisted of hexane, heptane, and cyclohexane, and the maximum average concentration reached a peak of 280 ppb for each VOC.

Another study by Martyny *et al.* focused on two cooks: cook #1 used hypophosphorous acid in the ephedrine/pseudoephedrine reduction method, and cook #2 used phosphorous flakes. Maximum phosphine levels were detected during the salting out phase and not the cooking phase, and were 13 ppm for cook #1 and 0.6 ppm for cook #2. Airborne iodine levels were not detected in cook #2, but for cook #1 the iodine concentration was 0.005 ppm during the cooking phase and 0.004 ppm during the salting out phase. The measured concentrations of hydrogen chloride were significantly higher during the salting out phase as compared to the cooking phase. For example, in cook #2 the average concentration during salting out was 3.1 ppm, and an average concentration of 0.13 ppm was measured during the cooking phase. Similar results were measured during cook #1.

2.3.4 Summary of Target Chemicals for Red P Method

Of the list of organic and inorganic chemicals listed in Table 5, hydrogen chloride, hydrogen iodide, and phosphine are in gaseous form at room temperature, and toluene is a volatile liquid at room temperature. Iodine sublimes slowly at room temperature. The list of potential targets for this process consists of:

- Hydrogen chloride
- Hydrogen iodide
- Iodine

- Phosphine
- Toluene

2.4 Other Methods

Many other manufacturing methods exist to produce methamphetamine, although the three methods outlined here (Birch, P2P, Red P) are the most common. The other manufacturing methods will be simply mentioned here for reference, but since they are uncommon, a list of target chemicals for these methods will not be created. With ephedrine/pseudoephedrine as precursors, there are two main ways to obtain methamphetamine: direct reduction and indirect reduction. The Birch reduction and Red P methods are direct reduction techniques for instance. Direct reduction methods are essentially one step processes. Other direct reduction methods include the Wolff-Kishner method, which uses hydrazine hydrate as the reducing agent, and the Zinc reduction method, which involves the use of zinc metal and formic acid.

Indirect reduction uses a two-step process whereby the hydroxyl group on the ephedrine/pseudoephedrine molecule is first replaced by a chlorine or bromine atom. The chlorine/bromine atom is subsequently replaced by a hydrogen atom to yield methamphetamine [6]. Compounds such as thionyl chloride ($SOCl_2$), phosphorus pentachloride (PCl_5), phosphorus trichloride (PCl_3), phosphorus pentabromide (PBr_5), and phosphorus tribromide (PBr_3) can all be used to accomplish the first step. The second step, replacing the chlorine/bromine with hydrogen, can be accomplished via several routes, such as the use of lithium aluminum hydride or via catalytic hydrogenation (the catalyst can be Raney nickel, platinum, palladium, etc.). The Emde method is an example of indirect reduction; ephedrine/pseudoephedrine is first converted into chloroephedrine using thionyl chloride, then into methamphetamine via catalytic hydrogenation.

3. Illegal Chemical Waste Dumps

Methamphetamine labs typically produce 5 units of toxic waste for every unit of methamphetamine produced [7]. Chemical and equipment wastes are often haphazardly disposed of in public spaces, ranging from parks to waterways, posing a danger to both people and the environment. Documentation of these illegal waste dumps is rare in the literature, and we were not able to visit such waste dumps. The information contained within this section is derived from a presentation by the Surrey Fire Department, whose Hazardous Materials (HazMat) team handles waste dump clean-up [13]. Unfortunately, data on chemical concentrations present at waste dumps was not included in the presentation.

3.1 Location

Common waste dump sites include:

- Ditches by the side of the road
- Vacant lots
- New housing developments

- Fields
- Parks
- Waterways

Figure 5 - Methamphetamine production waste dump, 4 barrels and bags containing garbage. Ditch in the 18500-block of 28th Avenue, Surrey, BC, Canada [13]

Clandestine lab operators are fairly indiscriminate about where the wastes are dumped, as long as the location is isolated yet accessible with a vehicle.

Figure 6 - Example of a portable container dump site [13]

3.2 Characteristics

There are several strong indicators that identify a collection of garbage as a clandestine drug lab waste dump. For instance:

- Industrial chemical containers (plastic or metal) are present
- Chemical name, WHMIS, or HazMat labels are visible
- Labels appear to be intentionally removed or painted over
- Chemicals come from an industrial or chemical supplier, or home hardware store
- Abnormal tubes/hoses protrude from containers
- Objects are heavily stained
- Lab equipment or glassware is present

Containers of the following chemicals, many of them available at the local hardware store, may indicate the presence of a clandestine lab waste dump:

- Acetone
- Toluene
- Paint thinner
- Camp fuel
- Ether (starting fluid)
- Denatured alcohol

- Muriatic acid
- Iodine tincture
- Drain cleaner
- Rubbing alcohol

Likewise, the presence of the following items may indicate that a waste dump is present:

- Stained coffee filters
- Glassware
- Mason jars
- Buckets

Characteristics of waste dumps vary tremendously. As mentioned by Deputy Fire Chief Jim Bond of the Surrey Fire Service, some waste dumps will feature liquid and solid wastes fully sealed in industrial drum containers, while other dumps will consist of garbage bags containing coffee filters, broken glassware, etc. Other factors that affect the characteristics of waste dump sites include the manufacturing process used (even for the same process different chemicals may be substituted), the indifference of the lab operators, and even the current availability of containers.

4. Summary of Target Chemicals

Based on the list of detectable gases and volatile liquids given at the end of each methamphetamine manufacturing process in this section, below is a table containing the target list of chemicals, classified by methamphetamine manufacturing process (Table 6).

Table 6 - List of target chemicals, classified by methamphetamine manufacturing process

	Birch Reduction	**P2P**	**Red P**
Ammonia	**X**		
Hydrogen Chloride	**X**	**X**	**X**
Hydrogen Iodide			**X**
Phosphine			**X**
Iodine			**X**
Acetic Anhydride		**X**	
Formic Acid		**X**	
Hexane	**X**		
Heptane	**X**		
Cyclohexane	**X**		
Methylamine		**X**	
N-methylformamide		**X**	
Phenylacetone		**X**	
Phenylacetic acid		**X**	
Tetrahydrofuran	**X**		
Toluene	**X**	**X**	**X**

5. General Information on Legitimate Uses of Target Chemicals

Most of the chemicals used in methamphetamine production are, or can be extracted from common household chemicals. A summary of legitimate uses of these chemicals is provided in a clandestine methamphetamine cookbook, which also includes a section on strategies to acquire these chemicals in large quantities and evade police [6]. Below is a series of tables detailing the legitimate uses of the target chemicals, organized by methamphetamine synthesis method.

5.1 Common Chemicals for all Methods

Table 7 - Summary of legitimate uses of chemicals used in nearly all methamphetamine manufacturing processes

Chemical	**Legitimate Use**
Hydrogen Chloride	Household • Toilet bowl cleaner Industrial • Chemical intermediate in many chemical reactions • Wool-cotton separation
Toluene	Household • Paint thinner • Solvent for adhesives, silicone sealants, etc. • Octane booster in gasoline fuels Industrial • Metal degreaser • Manufacture of insecticides

5.2 Birch Reduction Method

Table 8 - Summary of legitimate uses of chemicals specific to the Birch manufacturing process

Chemical	**Legitimate Use**
Ammonia	Household • Water disinfectant (added with chlorine) Industrial • Production of nitric acid for fertilizers and explosives • Alternative fuel
Hexane	Household • Camper fuel • Constituent of gasoline Industrial • General purpose non-polar solvent • Constituent of glues used for shoes, leather products, roofing
Heptane	Household • Camper fuel • Rubber cement solvent Industrial

	• General purpose non-polar solvent
Cyclohexane	Household • Camper fuel Industrial • General non-polar solvent • Used in production of intermediates used in nylon production
Tetrahydrofuran	Industrial • General moderately polar solvent used to dissolve wide range of nonpolar/polar compounds • Used in polymer science • Metal degreaser

5.3 P2P-based Methods

Table 9 - Summary of legitimate uses of chemicals specific to P2P-based manufacturing processes

Chemical	**Legitimate Use**
Acetic anhydride	Industrial • Manufacture of photographic film • Dehydrating agent
Formic acid	Industrial • Preservative and antibacterial agent in livestock feed
Methylamine	Industrial • Production of insecticides, explosives
N-methylformamide	Industrial • Used in drug, dye, flavour, plating and electrolysis industries
Phenylacetone	• No major legitimate use
Phenylacetic acid	Industrial • Manufacture of perfumes, herbicides, penicillin, flavouring agents

5.4 Red Phosphorus-based Methods

Table 10 - Summary of legitimate uses of chemicals specific to Red P-based manufacturing processes

Chemical	Legitimate Use
Hydrogen Iodide	Industrial • Disinfectant • Chemical reagent
Iodine	Industrial • Manufacture of iodine compounds and antiseptics
Phosphine	Industrial • Fumigant • Dopant in semiconductor industry

Part B: Chemical Sensing Technologies

The following sections focus on analyzing sensing technologies that are currently commercially available and/or are described in research literature. The objective of the following section is to provide detailed descriptions of the most important chemical sensing technologies and the performance of those technologies with respect to the target analytes and the proposed application. Each sensing technology will be treated individually. The focus will be on sensors capable of detecting the target analytes. Commercially available sensor technologies and published research devices will be investigated with respect to detection limits, sensitivity, response time, selectivity, size, and cost. The section will be concluded with a summary of the performance of the sensing technologies for all target analytes.

Sensor Arrays

Simultaneous detection of several chemical compounds can be performed with either individual highly selective sensors or arrays of cross-sensitive sensors where the individual sensors are sensitive to multiple analytes in a distinct manner. Sensor arrays can be constructed using homogenous or heterogeneous sensing technologies. If sensor arrays are used, then chemometric data processing, based on statistical pattern recognition techniques, is used to identify the unique signature in the joint response of all sensors in the array [14].

1. Electrochemical Sensors

1.1 Principles of Operation of Electrochemical Gas Sensors

Electrochemical sensors are based on the chemical reactions and electronic charge transfer that occur at the interface of an electron conductor (typically a metallic electrode) and an ionic conductor (a liquid or solid electrolyte) [15]. Electrochemical cells can be divided into two basic groups: those that produce current as a result of the conversion of chemical to electrical energy (galvanic cells) and those that require an external current to produce chemical changes, thus converting electrical to chemical energy (electrolysis cells). Electrochemical sensors may belong to either category.

Electrochemical sensors can also be classified into the following three categories: potentiometric (change in voltage), amperometric (change in current), and impedance/admittance (change in resistance) based devices [16]. Most commercial electrochemical sensors are amperometric, and a typical gas sensor will consist of the sensing/working electrode where the reaction of interest is taking place, a liquid electrolyte solution, and a counter electrode to complete the electrical circuit, as shown in Figure 7. Figure 8 shows a picture of a typical commercial electrochemical sensor. Electrochemical gas sensors typically include a small capillary-type opening for the analyte gas to diffuse through, as well as a hydrophobic membrane; this design is used to prevent the liquid electrolyte from leaking out of the sensor [17]. The gas that diffuses through the membrane reacts at the surface of the sensing electrode, and is catalyzed by the electrode material, which is specifically designed for this purpose [17]. An external driving voltage is applied to the cell, and the resulting electrical current is proportional to the concentration of analyte gas. A third electrode, the reference electrode, is located in proximity to the sensing electrode. It has a fixed absolute electric potential and enables the sensor to maintain a stable potential at the sensing electrode, by maintaining a constant voltage between the sensing and reference electrodes.

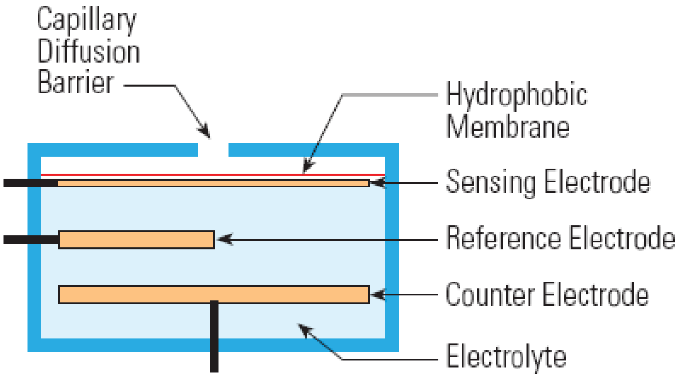


Figure 7 - Schematic of a typical electrochemical gas sensor [17]

Figure 8 - Commercial electrochemical sensor (DrägerSensor). The diameter of the sensor body is approximately 50 mm.

1.2 Commercial Electrochemical Gas Sensors

The first electrochemical sensors dates back to the 1950's and were used for oxygen monitoring [18]. Through several decades of research and development, electrochemical sensors have been proven as a mature and successfully commercialized technology. Amperometric electrochemical gas sensors are often used to detect toxic industrial chemicals (TIC's) due to their small size, low power requirements, and good performance/cost trade-off [16]. Ammonia, hydrogen chloride, and phosphine are among the toxic gases that are detectable using electrochemical sensors. Commercial companies offering electrochemical sensor products are listed in Table 11.

Table 11 - Companies selling electrochemical gas sensors

Company	Product(s)
• Airsense Analytics	• GDA 2
• BW Technologies (Honeywell International)	• GasAlert Extreme • GasAlert Micro 5
• City Technology Ltd.	• Sensoric
• Crowcon (Halma plc)	• TXgard-IS+ • Xgard
• Drägerwerk AG	• DrägerSensors
• ENMET	• SDS-97D • Target • TX-2000
• Manning Systems (Honeywell International)	• EC-F9-NH3 • EC
• Mine Safety Appliances	• ALTAIR Pro • SAFESITE Sentry
• RAE Systems	• AreaRAE
• Sensidyne (Siegel-Robert Inc.)	• SensAlert Plus • SensAlert
• Tyco Scott Instruments	• Freedom 5000 • Mini SA • Sentinel II

1.3 Recent Research on Electrochemical Gas Sensors

Although electrochemical sensors are a commercially mature technology, research innovations are still taking place. Nakano and Ogawa used thin gold-film electrodes to improve the sensitivity of an electrochemical gas sensor for detecting phosphine; the reported detection limit was 0.01 ppm [19]. Nagashima and Suzuki created a sensor with silver and platinum mesh electrodes and a silver iodide disk acting as a solid electrolyte [20]. The electrochemical sensor was able to detect iodine vapour down to 0.1 ppb with a response time of 3 minutes.

Various researchers in the field have investigated miniaturization of gas sensors in order to further reduce the weight, volume, and energy consumption of sensors. The sensor can be assembled onto a small chip or be integrated into a complete mini analytical instrument using microfabrication techniques to forma micro total-analysis system (μTAS). Lauque *et al.* fabricated electrochemical microsensors by sputtering thin films of CuBr on inter-digitated copper electrodes [21]. The detection limit for this technology was stated to be below 10 ppm for ammonia [22].

Researchers have also explored array-based electrochemical sensing, in an attempt to build sensors that are capable of detecting a larger range of chemicals. For example, Stetter *et al.* have used an array of four different electrochemical sensors that can be operated in four different modes depending on their respective heater filament (platinum or rhodium) and its operating temperature, for detecting hazardous gases such as ammonia, benzene, acetone, pyridine, etc. [23]. Reported detection limits ranged from 20-300 ppm for all of the organic vapours.

1.4 Properties of Electrochemical Sensors

Electrochemical sensors are mildly prone to cross-interference from other gases and are generally specific for a particular gas or vapour. In addition, they do not get poisoned, and can monitor at or below ppm levels [24]. However, electrochemical sensors are typically available only for toxic gases and oxygen, and not organic compounds. As well, the membrane protecting the inside of the sensor is prone to degradation over time [24].

2. Gravimetric Sensors (Surface Acoustic Wave, Bulk Acoustic Wave, and Flexural Plate Wave Devices)

2.1 Principles of Operation of Gravimetric Gas Sensors

Acoustic waves are strain waves that propagate at the speed of sound in solids. Due to the high quality factor of the propagation medium, the waves travel with very little energy loss. One of the two most common configurations applied to sensing is the thickness-shear mode (TSM) resonators, or bulk acoustic wave (BAW) as used in the quartz crystal microbalance (QCM), where the wave propagates through the bulk of the material. The second most common principle is the surface acoustic wave (SAW) resonator, where the acoustic wave travels only along the surface, down to a depth of about one acoustic wavelength into the crystal [25]. Figure 9 shows the operation principle of a SAW sensor. A third and less common type of acoustic sensor uses flexural plate waves (FPW). FPW devices rely on Lamb wave propagation in a thin membrane [26].

In many cases, especially for SAW sensors, the acoustic wave device is essentially used to form a stable oscillating circuit which consist of three key sections: electrical to mechanical wave conversion, mechanical transmission line, and mechanical to electrical conversion. At the transmission line, energy is transmitted exclusively as acoustic waves. In most cases, the confined acoustic wave is generated using the piezoelectric effect, requiring a piezoelectric substrate. Magnetostrictive materials can also be used, although they are far less common when compared to piezoelectric devices and therefore will not be described in this report. Piezoelectric crystals and ceramics are materials that generate an electric charge in response to applied mechanical stress. The effect can be reversed; an external applied voltage will result in mechanical deformation of the piezoelectric material. Utilizing this effect, an input transducer, often in form of an interdigital transducer (IDT), will convert an electrical signal (at a frequency near the resonant frequency of the mechanical system) into a mechanical, acoustic wave, which propagates over/through the substrate to the output transducer. At the output transducer, the mechanical wave is converted back into an electrical signal.

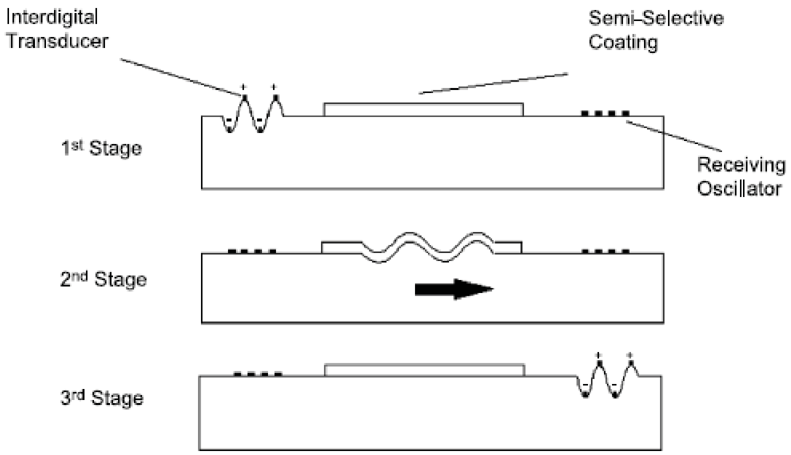


Figure 9 - Operation principle of a SAW sensor [27]

A SAW chemical sensor can be formed by coating the substrate between the transducers with a layer that is sensitive to the desired analyte(s). For example, if the sensing layer contains material that absorbs organic molecules from the gas phase, the mass of the absorbed molecules will be added to the surface of the device. This added mass will produce a measurable change in the resonant frequency of the sensor. The selectivity of the sensor is highly dependant on the selectivity of the sensing layer. However, the sensitivity of the SAW sensor is very high since frequency measurements can be made with very high precision using lock-in techniques. The challenge with these sensors is the choice of the appropriate chemistry for the sensing layer in order to achieve the required selectivity. A top-down view of a SAW sensor is shown in Figure 10.

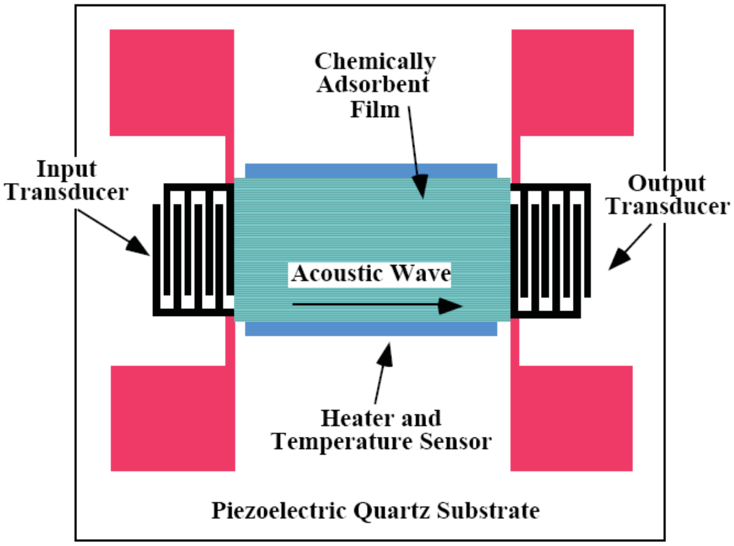


Figure 10 - Top-down view of a SAW chemical sensor, piezoelectric substrate is typically quartz but can be other materials [24]

2.2 Commercial Gravimetric Gas Sensors

At the present, only two companies offer commercial SAW-based gas sensing units, as shown in Table 12.

Table 12 - Companies selling gravimetric gas sensors

Company	**Product(s)**
Electronic Sensor Technology	• Model 4200 Znose • Model 7100
Microsensor Systems Inc. (Mine Safety Appliances)	• HAZMATCAD • SAW MiniCAD mkII

2.3 Recent Research on Gravimetric Gas Sensors

Shen *et al.* fabricated YX-$LiNbO_3$ SAW chemical sensors with L-glutamic acid hydrochloride sensing films; the lowest detection limit for ammonia is reported to be 0.56 ppm [28]. The challenge with this sensor is associated with the long-term stability, as the measured values drift at a rate of -0.01 ppm per day at room temperature. Penza *et al.* used carbon nanotube coated SAW sensors to detect ethanol, ethylacetate, and toluene [29]. Ethanol and toluene were detected at levels as low as 1 ppm. The researchers also found that the selectivity to volatile organic compounds (VOC's) can be tuned by the choice of organic solvent used to disperse the carbon nanotubes onto the SAW sensors. Li *et al.* applied cyclodextrin thin films to SAW sensors using self-assembled monolayers and sol-gel techniques, this technique permitted the detection of acetone vapours at concentrations of 0.2 ppm [30]. Kim and Choi fabricated an activated carbon-coated quartz crystal sensor that is capable of detecting n-heptane at concentrations below 21 ppm [31].

2.4 Properties of Gravimetric Technology based Sensors

SAW sensors possess several key advantages, including low power requirements, low detection limits, and good sensitivity. However, the sensing ability of SAW sensors is highly dependent on the selectivity of the sensing layer, so discrimination among unknown mixtures of chemicals may be poor. Arrays of SAW sensors with coatings of different selectivity can be used to partially resolve this issue. In addition, if the sensing layer is polymer-based, there may be issues with sensor drift since the polymer layer might degrade over time. These sensors possess significant potential in the application of methamphetamine laboratory detection but will require additional research to determine the optimal sensing layer geometry and chemistry.

3. Chemical Sensing using Infrared Spectroscopy

3.1 Principles of Operation of Infrared Spectrometry

Infrared (IR) spectrometry is a branch of spectroscopy that uses infrared light as the radiative source. IR spectrometry belongs under the category of optical sensing, but it was separated into a distinct section because the technique has been heavily investigated, and it is arguably the most popular optical technique used for remote sensing. The analyte is excited by a range of IR wavelengths and the unique absorption spectrum of the analyte is used to identify the sample constituents. The chemical functional groups present in the sample each have a unique IR absorption spectrum. IR is a non-contact and non-destructive measurement technique, and can be used in both point and remote sensing applications. Compounds that do not absorb IR wavelengths are homonuclear diatomic molecules such as nitrogen, oxygen, and hydrogen. However, organic compounds, which make up the bulk of the target chemical list, can be readily identified.

Early infrared spectrometers were of the dispersive type, and emerged in the 1940’s. A dispersive infrared spectrometer can only measure one wavelength at a time. The versatility of infrared spectroscopy was greatly enhanced with the introduction of Fourier transform infrared (FTIR) spectrometers in the 1960’s. An FTIR spectrometer first obtains an interferogram of a sample signal using an interferometer. A Fourier Transform is then applied to the data forming the interferogram to yield the IR spectrum. The spectrum represents the percentage intensity (0-100%) of light that passes through the sample for each IR wavelength, as depicted in Figure 11. The spectrum of the sample is then compared with a reference spectrum, in the absence of the sample. A qualitative analysis of the result is straight forward for single component compounds. However, for more complex compounds or mixtures containing many components, statistical analysis techniques are used such as Partial Least Squares (PLS), artificial neural networks, or a self-organizing map for automatic compound identification; a review of both, qualitative and quantitative techniques is given in [32].

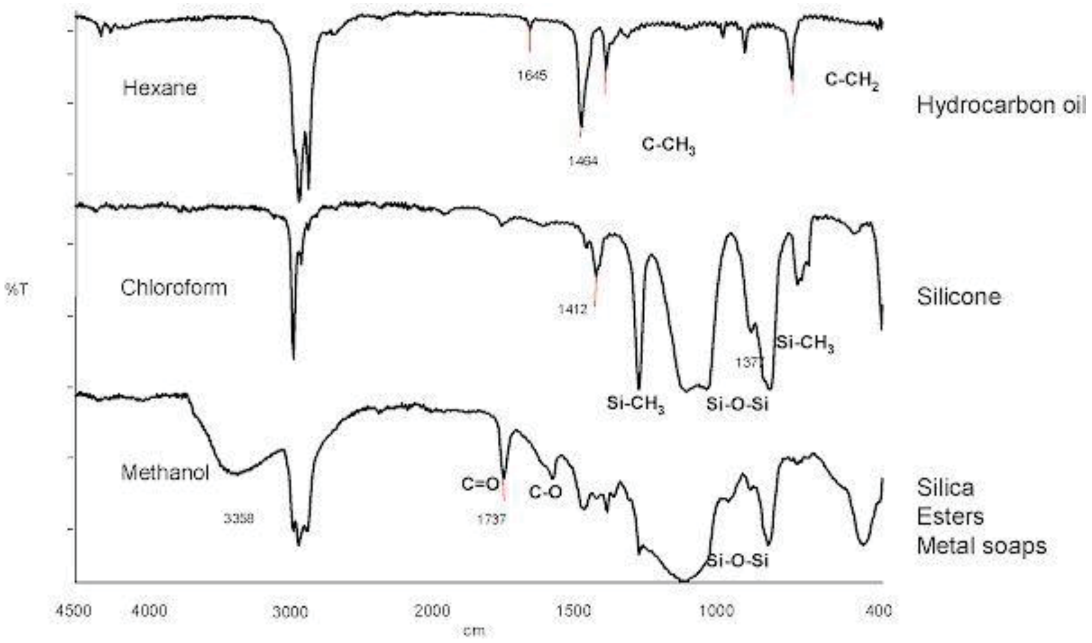


Figure 11 - Example of IR spectra of 3 different organic compounds. The graphs show the normalized transmittance (%T) as a function of wavelength in cm. Different bonds (i.e. C-CH_3, C=O, etc.) within these compounds are excited by different IR wavelengths, at which they absorb the IR radiation. [33]

3.2 Commercial IR Gas Sensors

Companies that offer FTIR-based gas sensing equipment are listed in Table 13, and companies that offer dispersive IR-based gas sensing equipment are listed in Table 14. FTIR spectrometers are available in a variety of configurations. FTIR equipment is becoming increasingly portable; an example is the Environics Oy ID100, which packs the spectrometer, sample cell and signal processing electronics into an 11.5 kg backpack (Figure 12).

Figure 12 - Environics Oy ID100 portable FTIR gas analyzer [34]

Table 13 - Companies offering FTIR gas sensors

Company	Product(s)
• ABB Bomen	• FTLA2000 series
• Bruker-Daltonics Inc.	• RAPID
• Environics Oy	• ID100
• Smiths Detection	• GasID • HazMatID

Table 14 - Companies offering dispersive IR sensors

Company	Product(s)
• Crowcon (Halma plc)	• Triple Plus+ IR • Detective+
• Delphian Corporation	• Determinator
• ENMET	• IR-6000
• e2V technologies Ltd.	• IR1xxx Series 1
• LaserGas	• LaserGAS II • LaserGAS I
• Mine Safety Appliances	• Orion Plus IR
• Sensidyne (Siegel-Robert Inc.)	• SensAlert Plus

3.3 Recent Research on IR Gas Sensors

By exploiting the change in absorbance of polyaniline exposed to ammonia, Christie *et al.* were able to detect ammonia at levels as low as 6 ppm using standard telecom 1300 nm IR wavelengths [35]. In a recent review paper on near-infrared diode laser spectroscopy, Martin summarizes the detection limits for several gas species as concentration x path length (ppm.m). The detection limits for hydrogen chloride, hydrogen iodide, and ammonia are 0.008 ppm.m, 0.2 ppm.m, and 0.203 ppm.m respectively [36].

3.4 Properties of IR Spectrometry based Sensors

The greatest advantage offered by IR spectrometers is the ability to sense gases remotely; the sensor itself does not need to be exposed to corrosive or reactive gases [37]. In addition, IR spectrometers can be used to detect many types of organic and inorganic compounds. Disadvantages of IR sensing equipment include susceptibility to temperature fluctuations since an IR detector is essentially a temperature sensor, and the ability to remotely detect low concentrations of gas depends to a large degree on the background. In addition, IR devices can only monitor gases that have non-linear molecules, and due to the high complexity of the units they also tend to be relatively high in cost.

4. Ion Mobility Spectrometry

4.1 Principles of Operation of Ion Mobility Spectrometry

Ion Mobility Spectrometry (IMS) is a highly sensitive technique that can be used to analyze the composition of gas mixtures. Once a gaseous sample has been introduced into the detection chamber, it is ionized with a radiation source, and the ions are exposed to a uniform electric field that accelerates the ions towards the detector. Ions with different mass and charge configuration require a different electric field in order to reach the detector. When the ion arrives at the detector, a charge transfer takes place from the ion to the detector and results in a measurable current. As the electric field intensity is varied over time, different sets of ions will be able to reach the detector as a function of time, depending on their mass and charge. As a result, gases of different composition produce a unique amperometric signature. The IMS operating principle is depicted in Figure 13. An example measurement result is shown in Figure 14, where ammonia, the compound of interest is detected along with a contaminant. IMS is distinct from mass spectrometry (MS) because it operates under atmospheric conditions and does not require large and expensive vacuum pumps. This feature enables IMS technology to be easily miniaturized [24]. IMS response times are quite short, typically on the order of a few seconds.

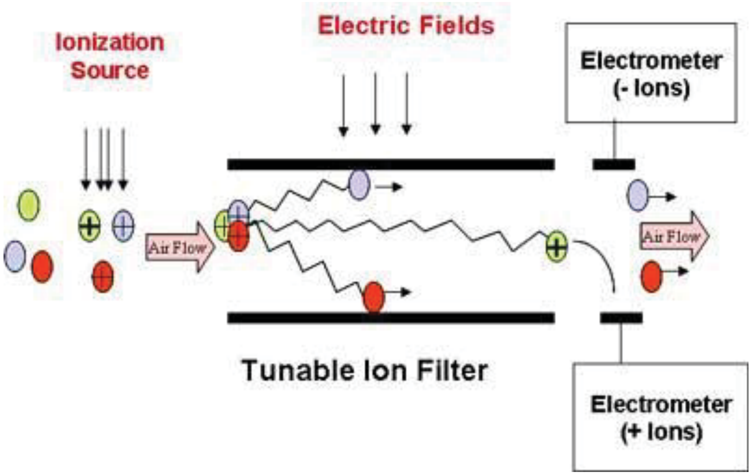


Figure 13 - Schematic showing the IMS principle of operation. The collected electric charges from the ions on the detectors are measured using electrometers [38]

IMS is capable of detecting and identifying many types of compounds such as narcotics, explosives, and chemical warfare agents. The selectivity of IMS response can be tuned via the choice of ionization source and polarity (positive or negative) of product ion to monitor [39]. Ionization sources can be radioactive or non-radioactive (i.e. photoionization, corona discharge ionization, etc.). As for the choice of ion polarity, electronegative compounds (i.e. explosives) are best detected as negative ions, while electropositive compounds (i.e. drugs and other amines) are best detected as positive ions [39].

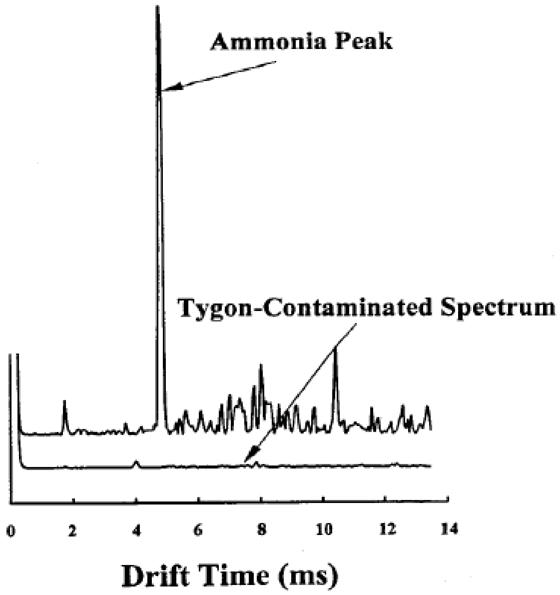


Figure 14 - Typical charge measurement from IMS, the drift time on the x-axis corresponds to electric drift field [39]

4.2 Commercial IMS Gas Sensors

IMS was first developed nearly 40 years ago by Karasek and Cohen, and as a result, the technology is quite mature. IMS detection units are readily available on the market. In particular, there has been high demand for adoption of IMS for detecting explosives, and it is currently the most widely used technology for the detection of trace levels of nitro-organic explosives on handbags and carry-on luggage in airports [40]. Commercial IMS units are available in a range of sizes, and can be miniaturized for integration into handheld units.

Table 15 lists IMS vendors with products designed to detect several of the target analytes. Sandia National Laboratories' IMS unit, MicroHound, has been included here even though it is not yet available on the market, however, development of the unit has progressed to the point where it can be readily commercialized.

Table 15 - Vendors of IMS gas sensors

Company	Product(s)
• Airsense Analytics	• GDA 2
• Bruker-Daltonics Inc.	• RAID-M Series • RAID-1
• Sandia National Laboratories	• MicroHound
• Smiths Detection	• Centurion • Sabre 4000 • HGVI • IONSCAN 500DT

4.3 Recent Research on IMS Gas Sensors

IMS continues to be an actively researched sensor technology. Miller *et al.* fabricated and tested a miniaturized, microelectromechanical system (MEMS) radio-frequency IMS (rf-IMS) [41]. Radio-frequency IMS is a recently developed technique, and unlike conventional IMS which uses a low strength electric field, rf-IMS makes use of both high and low strength electric fields. Ion species are identified based on the difference in their mobility in a high versus low strength electric field. Using a radioactive ionization source, the limit of detection for toluene was estimated to be approximately 10 ppb, for acetone the limit is around 10 ppb, and for isopropanol it is approximately 60 ppb. A review paper by Stach and Baumbach summarizes the detection limits for various compounds detected by means of IMS using radioactive β-ionization [42]. The detection limits of iodine, hydrogen chloride, hydrogen iodide, ammonia, and aliphatic amines (i.e. methylamine) are 5 ppb, 100 ppb, 100 ppb, 100 ppb, and 5 ppb respectively.

4.4 Properties of IMS Technology

Advantages of IMS include very low detection limits (ppb levels), rapid response, low power consumption, and applicability to a wide number of compounds [39]. However, the major limitations of IMS are competitive ion/molecule reactions with matrix molecules, dependence of dimerization reactions of some compounds on concentration, susceptibility to contamination, and problems with low temperature operation [39]. The matrix is essentially a clean and inert gas which causes the ions to drift, and keeps the drift tube of the spectrometer clean. The competitive ion/molecule reactions will mask the response of the analyte. As for the dimerization reactions, compounds will form different product ions depending on their concentrations. Dimethyl sulfoxide (DMSO) for example, a common solvent, forms primarily the $(DMSO)H^+$ ion at the 20-ppt (parts per trillion) level, but at the 2-ppb level there are two product ions, $(DMSO)H^+$ and $(DMSO)_2H^+$. IMS units are susceptible to contamination; some contaminants with low vapour pressure may remain inside the detector for minutes, even hours or days. Low temperature operation allows neutral water molecules in the sample and drift gas to attach to analyte ions to form multimolecular ion clusters, thus altering the mobility of the analyte ion and introducing errors into the reading. Since trace amounts of water are near impossible to eliminate from the spectrometer, it is common practice to add water at a concentration of 10 ppm to ensure reproducible responses [39].

5. Metal Oxide Semiconductor (MOS) Chemical Sensors

5.1 Principles of Operation of Metal Oxide Semiconductor Gas Sensors

Metal oxide gas sensors, initially based on tin dioxide (SnO_2), have been available since the early 1960's [25]; a diagram of a commercially available sensor is shown in Figure 15. Metal oxides such as SnO_2, zinc oxide (ZnO), iron oxide (Fe_2O_3), and tungsten oxide (WO_3) are n-type semiconductors. The metal oxide is typically heated to temperatures ranging from 200-500 ºC. This reduces the chemisorption of water at the surface and oxygen atoms from the atmosphere adsorb onto the surface of the metal oxide semiconductor (MOS) sensor thus trapping some of the electron carriers within the material and reducing the conductivity of the MOS sensor. If the MOS sensor is exposed to a reducing gas (i.e. hydrogen, methane, etc.)[43], catalytic combustion occurs and the surface density of negatively charged oxygen decreases, causing the resistance of the sensor to decrease [24]. The sensors response is taken to be the difference between the baseline resistance (absence of analyte) and the decreased resistance (presence of analyte). By varying the operating temperature of the sensor and the composition of the metal oxide, different responses to various combustible gases can be obtained.

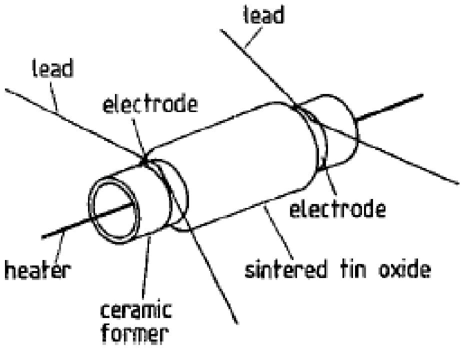


Figure 15 - Diagram of commercially available tin oxide gas sensor [25]. Leads are electrical leads.

5.2 Commercial MOS Gas Sensors

The first commercially available MOS gas sensors were introduced by Taguchi. Commercial Taguchi sensors consist of a ceramic cylinder (9.5 mm in length, radius 3 mm approximately) containing a heating coil. The outer surface of the pellet is coated with a metal oxide, usually SnO_2 doped with a small amount of palladium (Pd) or platinum (Pt) catalyst, although many other oxides (i.e. ZnO, WO_3, and TiO2) have been applied [27]. Table 16 lists the companies who are currently involved in the design and production of MOS chemical gas sensors.

Table 16 - Companies producing MOS gas sensors

Company	**Product(s)**
Airsense Analytics	GDA 2
Alpha MOS	Prometheus
Delphian Corporation	SBG-200
ENMET	EX-5150 MOS
Environics Oy	ChemPro 100i
Figaro Gas Sensors	TGS826 TGS2444 TGS2620
Microsensor Systems Inc. (Mine Safety Appliances)	VaporLab 700
RST Rostock	SamDetect GFD1

5.3 Recent Research on MOS Gas Sensors

A detection limit of 1 ppm was achieved with a WO_3 ammonia sensor with gold and molybdic oxide (MoO_3) additives [44]. Toda *et al.* detected phosphine down to 0.2 ppm with a diode-type gas sensor featuring gold film deposited on titanium oxide [45]. Su *et al.* fabricated miniaturized tin oxide semiconductor sensors using dip-pen nanopatterning [46]. The sensors showed a response time of 5 seconds and a recovery time of 20 seconds, and were able to detect acetic acid at concentrations below 330 ppm. Kim *et al.* drop-coated highly crystalline tungsten oxide nanorods onto a silicon substrate to form porous tungsten oxide films; the resulting metal oxide sensors responded to heptane at concentrations less than 5 ppm [47], Hitch and Honeybourne used tetragonal pseudo-pyrochlore, an n-type semiconductor, as the active sensing material in thick-film sensors [48]. Toluene was detected down to 10 ppm.

5.4 Properties of MOS Chemical Sensors

MOS sensors have high sensitivity to combustible gases, are compact and durable, and are relatively inexpensive to produce [24]. However, MOS sensors have a fair amount of sensitivity to humidity, and they are not selective to one particular gas, which is a major drawback. The selectivity issue can be partially addressed by carefully choosing the base semiconductor and additive(s) used to dope the semiconducting metal oxide. For example, SnO_2 is commonly used as the base semiconductor, but Timmer *et al.* selected WO_3 with gold and MoO_3 additives to optimize the sensor for detecting ammonia [44]

6. Microcantilever Gas Sensors

6.1 Principles of Operation of Microcantilever Gas Sensors

Microcantilevers are essentially very small cantilever beams with dimensions typically on the order of a few micrometers. To produce a microcantilever sensor with chemical specificity, one side of the cantilever is coated with a selective layer (such as a polymer composite for example) that demonstrates high affinity to the targeted analyte [49]. Microcantilever sensors can operate in one of two modes: static deflection mode where binding on one side of a cantilever causes unbalanced surface stress and deflects the cantilever up or down, or the dynamic, resonant mode, where binding on the cantilever increases the mass of the system and modifies the resonant frequency [50]. In vacuum, nanoelectromechanical system (NEMS) cantilevers have been operated in the dynamic mode to measure mass changes on the order of attograms or less [50].

The response of the microcantilever is detected using one of the following principles: optical, piezoresistive, piezoelectric, capacitance, or electron tunnelling [49]. In the optical method, a laser beam is focused at the uncoated side of the cantilever. The beam is reflected onto a position sensitive photodetector. The piezoresistive method makes use of microcantilevers fabricated from materials whose electrical resistance changes with applied mechanical stress (i.e. doped single crystal silicon). The piezoelectric readout technique requires a layer of piezoelectric material (i.e. ZnO) to be deposited onto the cantilever. When the cantilever is deformed, transient charges will be induced in the piezoelectric layer, generating an electric potential that can be measured. For capacitance readout, two conductors, one mounted to the cantilever and the other mounted to the stationary substrate, are used. Cantilever deformations will result in a change in capacitance between the cantilever and the substrate. In the electron tunnelling method, a bias voltage is applied between a conducting tip and the cantilever (which are separated by an extremely small gap); the magnitude of tunnelling current is related to positional changes in the tip of the cantilever.

6.2 Commercial Microcantilever Gas Sensors

Commercial gas sensors based on microcantilevers are not yet available. However, patents for microcantilevers-based sensors have been filed. Two examples are:

- “Uncoated microcantilevers as chemical sensors” – USPTO patent 6212939, issued Apr 10, 2001
- “Microcantilever sensor” – USPTO patent 6523392, issued Feb 25, 2003

6.3 Recent Research on Microcantilever Gas Sensors

Microcantilever sensors have been used to detect many types of gas phase and liquid phase analytes, ranging from chemical vapours to viruses. Here we will focus on microcantilever gas phase chemical sensors. Static bending mode was used in the majority of studies [49].

Baller *et al.* produced a microcantilever array, each cantilever was coated with a different polymer, forming a sensor array [51]. Using the sensor array, a homologous series of primary alcohols from methanol to heptanol, as well as polar and nonpolar solvents such as acetone and toluene could be identified. The researchers estimate detection levels to be below 1 ppm. Hierlemann *et al.* used polyetherurethane-coated silicon microcantilevers to detect toluene down to 10 ppm [52]. Betts *et al.* investigated silicon microcantilevers with thin films of polymeric gas chromatographic stationary phases, and found that this treatment increased the responses of coated microcantilevers to organic compounds such as pentane, toluene, and ethanol noticeably [53]. However, no detection levels were mentioned. Datskos *et al.* found that microcantilevers with adsorbed analytes will undergo photoinduced bending that is dependant on the number of adsorbed molecules on the surface [54]. Calculated limits of detection for 1,8-dimethylnaphthalene, 2,7-dimethylnaphthalene, trichloroethylene, and tetrachloroethylene were determined to be 5.3 ppb, 2.7 ppb, 5.2 ppm, and 17.5 ppm. Li and Li used a SiO_2 microcantilever sensor to detect ammonia with a reported detection limit of 0.1 ppm [55].

6.4 Properties of Microcantilever Gas Sensors

Microcantilever gas sensors are still primarily research-based devices. However, published limits of detection are promising, with detection at ppb to ppt (parts per trillion) levels demonstrated [56]. A significant advantage of microcantilever sensors is that they can operate in vacuum, in gases, and in liquids [49]. The weakness of microcantilever sensors lies in their sensing layer. The selectivity of a microcantilever sensor is determined by the coating, which could be gold for detecting mercury vapour or a polymer for detecting VOC's. As a result, the lifetime of the sensor is primarily determined by the lifetime of the coating, which, if it is a polymer, may be quite limited due to polymer degradation in the presence of light, heat, and other chemicals.

7. Nanomaterials

7.1 Principles of Operation of Nanomaterials-based Gas Sensors

The term "nanotechnology" has become much more prominent in recent years, as more and more researchers devote their efforts towards exploring nanostructures and their applications. Nanotechnology can be defined as an interdisciplinary field (engineering, physics, chemistry, biology) that focuses on the study and manipulation of materials at the nanoscale. The term "nanomaterials" is very broad, encompassing a wide range of nanostructures ranging from nanotubes to nanobelts. Nanostructures have at least one dimension that is on the order of a few nanometres (10^{-9}m). Nanomaterials possess several key advantages over their bulk counterparts. For example, due to their very high surface to volume ratio, minor changes at the surface of a nanostructure can result in large changes in the electrical, mechanical and/or optical properties of the structure, allowing very sensitive sensing devices to be constructed. The following section describes sensors based on nanotubes, nanorods, nanobelts, nanowires, and nanofibers.

Of all of the nanostructures mentioned above, carbon nanotubes are one of the most well known as they were discovered the earliest. Nanotubes can also be formed out of metal oxides such as Co_3O_4, Fe_2O_3, SnO_2 and TiO_2, and metals such as platinum [57]. Gas exposure is detected by a change in the resistance of the individual, as well as networks of nanotubes. Analyte adsorption on the surface of the nanotubes modulates the carrier concentration, which results in an increase or decrease in the conductance of the nanotube. Selectivity is attained by appropriate functionalization with affinity to the desired analyte. Sensors capable of detecting changes in capacitance have also been constructed out of nanotubes [58].

Like nanotube-based sensors, nanowire, nanobelts, and nanofiber sensors typically detect the presence of analyte via conductance changes. Nanowire sensors differ significantly in the material used to construct them. Research has been conducted on metallic (copper, palladium, silver, etc.), silicon (and doped variants), metal oxide (In_2O_3, SnO_2, ZnO, etc.) and polymer nanowires. Nanorods can be considered as shortened nanowires; nanowire lengths range from 10's to 100's of microns whereas nanorods are typically 10's of microns in length [57]. For nanorods, researchers have focused most of their efforts on zinc oxide.

Nanobelts are single-crystalline, quasi-one-dimensional nanomaterials that can form helical nanostructures and nanorings when rolled up [59]. The key difference between nanobelts and nanowires is the additional control over growth direction: the side surfaces of nanobelts are better defined and the cross-section is more uniform [59]. Like nanorods, zinc oxide nanobelts are the most extensively studied structure although nanobelts of $Cu(OH)_2$, MoO_3, MgO, and CuO have also been successfully synthesized.

7.2 Commercial Nanomaterials Gas Sensors

Currently there are no commercially available gas sensors with a gas sensing element that is built exclusively of nanomaterials. Select companies are using nanomaterials embedded into a bulk material such as a polymer to form nanostructure/polymer composite chemically sensitive layers; these are described in the polymer section. However, it is clear from the available research literature that these materials hold significant promise for commercialization and it is expected that such devices will begin to appear on the market in the near future.

7.3 Recent Research on Nanomaterials Gas Sensors

Research into improved sensors based on the unique properties of nanomaterials is very active. The research-based sensors described briefly below represent a small subset of the total amount of work conducted in this field. The field of gas sensing using nanomaterials is rapidly evolving; a recent review article [57] covers developments within the last five years and contains 117 references.

Someya *et al.* have fabricated sensors based on single-walled carbon nanotube (SWNT) field-effect transistors (FET's), which are sensitive to various kinds of organic alcohols such as methanol and ethanol [60]. The FET consists essentially of two gold electrodes, the source and drain, connected together by a SWNT. Different types of alcohols were identified by the magnitude of drain current reduction for a given pair of voltage biases (source-drain, gate). Methanol at a partial pressure of 59 mmHg (0.79 kPa) results in a device current reduction of 57% as compared to the unexposed baseline current, and ethanol at a partial pressure of 126 mmHg (1.68 kPa) results in a current reduction of 70%. The response is rapid and occurs within 5-15 seconds.. Chemicapacitive SWNT sensors were investigated by Snow *et al.*, who fabricated sensors capable of detecting various VOC's such as benzene, hexane, heptane, toluene, acetone, etc. via changes in the baseline capacitance of the sensor [58]. The minimum detectable level was estimated to be 0.5 ppm for acetone based on a signal-to-noise ratio of 3:1. The response time was estimated to be less than 40 seconds (t_{90}).

Zhang *et al.* used In_2O_3 nanowire sensors to detect ammonia gas [61]. The oxygen doping concentration of the In_2O_3 nanowires was varied and resulted in variations in the magnitude of sensor response. Exposure to 1% ammonia in argon resulted in a -18.5%

reduction in device current accompanied by a +42.5% change in threshold voltage.. Zhou *et al.* used HF-etched silicon nanowires to detect ammonia [62]. The HF removed the amorphous silicon oxide sheath thus improving the chemical sensitivity of the nanowires. The researchers used 1000 ppm ammonia for testing, and did not quantify the detection limits of the devices.

Conductive polymer (PEDOT) nanorods were fabricated by Jang *et al.* and used to detect vapour concentrations down to 10 ppm of NH_3 and 5 ppm of HCl [63]. Jang and Bae have created polypyrrole-coated carbon nanofiber devices sensitive to ammonia and hydrogen chloride [64]. The sensors were able to detect vapours down to 10 ppm using changes in resistance. Vanadium pentoxide nanofibers were deposited onto lithographically defined interdigitated gold electrodes to form gas sensors sensitive to organic amines; Raible *et al.* determined the lower detection limit of the sensors to 1-butylamine to be below 30 ppb [65].

7.4 Properties of Nanomaterials based Chemical Sensors

Nanomaterials-based chemical sensors are a relatively new field of research. Nanostructured materials possess higher surface area to volume ratios than their bulk counterparts, and their use as sensing elements is expected to yield higher sensitivities and lower detection limits than conventional bulk sensing films. Nanostructures such as carbon nanotubes conduct electronic currents entirely on the surface of the tubes making the structure very sensitive to surface modification. To date, however, detection limits achieved with nanomaterials-based sensors have been relatively high (low ppm levels vs. low ppb levels attained with IMS). The primary reason for this is associated with the lack of highly controllable fabrication processes for these new materials, as a result there is a great deal of room for improving the performance as fabrication and processing techniques mature [57].

8. Optical Gas Sensors

8.1 Principles of Operation of Optical Gas Sensors

Optical sensing is a very broad field, and in general refers to any method by which variations in some property of light is converted into an electrical signal. Infrared spectroscopy is an optical sensing technique, but it was separated into a distinct section because the technique has been heavily investigated, and it is arguably the most popular optical technique used for remote sensing. Information on both intensity and wavelength can be collected simultaneously, making optical sensing a versatile measurement technique that encompasses a range of possible measurements such as absorbance, reflectance, fluorescence, refractive index, and colorimetry [27]. Fluorescence is a luminescence phenomenon that occurs when a sample is excited by a high-energy source and then re-emits light with a lower energy; light emission ceases once the exciting source is removed. Fluorescence can be turned on or off through the presence of an analyte, either by conformation changes in the fluorophore that shift the absorption wavelength away from the wavelength of the available excitation source or via optical quenching. Absorption techniques measure changes in light intensity transmitted through a sample and colorimetric techniques operate based on colour changes in a sample caused by the presence of the analyte of interest.

Fluorescence-based optical sensing can be performed with optical fibres. Fibres are used to direct light to the sensing element, which could be integrated onto the fibre or be located on a separate substrate [27]. Alternatively, total internal reflection fluorescence (TIRF) and fibre optic evanescent wave (FOEW) sensors have been investigated. The sensors in both cases are unclad optic fibres which have an analyte-sensitive coating. Interaction of the sensing layer with an analyte will change the optical properties of the sensing layer, which modulates the light propagating through the fibre, and is detected at the fibre termination using an optical detector. The first cross-reactive optical sensor array (1996) used dye molecules immobilized by polymer on the tips of the optic fibre [66]. The dye molecules gave different fluorescent response patterns on exposure to organic vapours, and a neural network was trained for vapour recognition using video images of the responses of the multi-fibre tip.

Absorption is the main non-fluorescence technique used for optical sensing. One example of absorption-based optical sensing uses thin films sensitive to certain VOC's, whose absorption spectra change after interacting with the analytes [67]. Another non-fluorescence optical technique is reflectometric interference spectroscopy (RIfS), which is a non-destructive technique that does not require any optical labels. In RIfS, white light is used to illuminate the sample, producing a characteristic interference pattern. A thickness change in a polymer sensing layer, which swells upon exposure to volatile organic compounds, is detected via changes in the interference pattern.

8.2 Commercial Optical Gas Sensors

Although fibre optic chemical sensors are still undergoing significant research, optical sensors based on techniques such as colorimetry have been successfully commercialized. For example, Honeywell Analytics' Chemcassette technology uses a chemically-sensitive paper tape to collect and analyze target gases. The Chemcassette changes color in direct proportion to the concentration of gas present, and the monitoring equipment relates the colour intensity changes to the gas concentration by comparison to known gas responses. The technique is extremely sensitive and is able to achieve sub-ppm detection limits [68].

Table 17 - Companies selling optical sensors

Company	Product(s)
• Dräger	• Dräger-Tubes
• Honeywell Analytics	• Chemcassette and associated MDA scientific monitors

8.3 Recent Research on Optical Gas Sensors

The most sensitive and selective detectors for ambient ammonia operate based on optical absorption spectroscopy; systems with detection limits of 1 ppb and response times on the order of a second have been reported [44]. Nakagawa *et al.* investigated the spectral changes of composite films of tetraphenylporphyrin/polymer when exposed to hydrogen chloride gas, and discovered the reversible absorbance of tetraphenylporphyrin and detection to sub-ppm levels of gas [69]. By concentrating iodine onto a membrane disk and then determining the amount of analyte extracted on the disk surface using diffuse reflectance spectroscopy, Arena *et al.* were able to measure iodine levels down to 0.1

ppm. Researchers have also investigated a variety of techniques for sensing organic analytes such as acetic anhydride, hexane, heptane, methylamine, tetrahydrofuran and toluene [75,71-73,70,74].

8.4 Properties of Optical Chemical Sensors

Optical gas sensing is a diverse field consisting of many different techniques, each technique with its unique advantages and disadvantages. As mentioned previously for IR spectrometers, the single greatest advantage of all optical chemical sensors is their ability to sense gases remotely; the sensor itself does not need to be exposed to corrosive or reactive gases. Fibre optic sensors consume little power, have no moving parts and possess low detection limits [24]. Advantages of colorimetric sensors include ease of use, visual evidence of the gas detection event, and resistance to interferences [24]. However, disadvantages include the degradation of chemically sensitive coatings, if used

9. Photoionization Detectors

9.1 Principles of Operation of Photoionization Detector Gas Sensors

Photoionization Detectors (PID) for gas detection have been available since the 1960's [76] and are commonly used for the detection of VOC's. Like IMS, PID utilizes a high energy source to ionize the analyte(s). However, PID uses an ultraviolet (UV) light source, which emits radiation of sufficient energy to ionize gas molecules that have an ionization potential below the radiation energy. The positively charged ions are attracted to the negative electrode and are detected as an electrical current. The magnitude of electrical current is proportional to the concentration of ionized molecules. A schematic of a typical PID configuration is shown in Figure 16. Actual PID sensors as the ones shown in Figure 17 are not large. PID sensors are susceptible to ambient humidity quenching as a result of the scattering of UV radiation from the water.

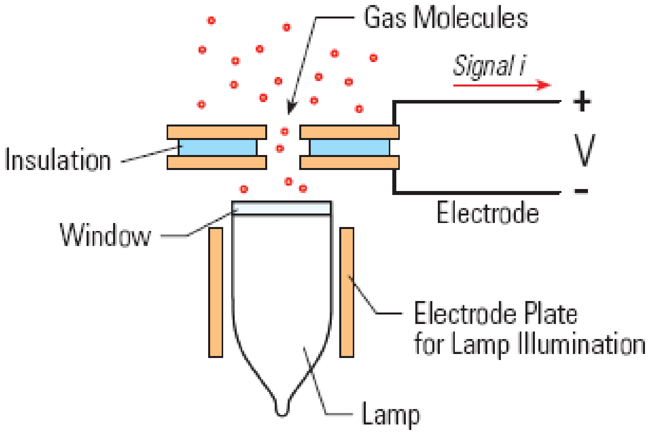


Figure 16 - Typical PID configuration [18]

The UV source is a lamp which contains a low-pressure inert gas such as argon, krypton, or xenon. When excited, the gas will emit light of constant energy with energy measured in electronvolts (eV). Xenon gas emits light at 8.4 eV and 9.6 eV, krypton emits at 10.0 eV and 10.6 eV, and argon emits light at 11.7 eV. The krypton lamp, at 10.6 eV, is the most commonly used lamp since it can ionize most organic compounds [18]. VOC gases detectable using 9.6 eV lamps include benzene, aromatic compounds, iodine, and amines. Gases detected between 9.6 eV and 10.6 eV include ammonia, ethanol and acetone, and gases such as acetylene and methanol are detected between 10.6 and 11.7 eV. Molecules which have higher ionization potentials will not be ionized, and thus will not be detected, this is an advantage since nitrogen (15.5 eV) and oxygen (12.0 eV) gas, which are abundant in the atmosphere are not detected and do not overwhelm the signal. Multiple ionization sources can be used to separate groups of gasses by comparing the respective signals, but do not provide a method of identifying individual analytes. Selectivity can be attained through design of membranes that permit only the diffusion of target gases.

Figure 17 - Commercial PID sensor, diameter is approximately 20 mm

9.2 Commercial PID Gas Sensors

Commercial companies that offer PID sensing units are shown in Table 18.

Table 18 - Companies offering PID gas sensors

Company	**Product(s)**
• Airsense Analytics	• GDA 2
• Baseline-Mocon	• piD-TECH Plus
• Mine Safety Appliances	• Sirius Multigas
• RAE Systems	• AreaRAE • EntryRAE • MiniRAE 3000 • MiniRAE 2000 • ppbRAE 3000 • ppbRAE Plus • IAQRAE • RAEGuard PID
• Smiths Detection	• HGVI

9.3 Recent Research on PID Gas Sensors

Sielemann *et al.* developed an ion mobility spectrometer that is equipped with a 10.6 eV gas-discharge lamp typically used in photoionization detectors. Detection limits for benzene, toluene, and m-xylene are 60 ppb, 80 ppb, and 70 ppb respectively.

9.4 Properties of PID Technology based Chemical Sensors

PID is a mature and commercially successful technology, and at the present, PID is the preferred choice for monitoring VOC's in general [18]. Its advantages include extremely low detection limits and fast response. However, PID suffers from poor selectivity since a single excitation source will ionize any gas with ionization potential below the source energy.

10. Polymer-based Chemical Sensors (Chemiresistors, Chemicapacitors, ChemFET's)

10.1 Principles of Operation of Polymer Gas Sensors

Traditional materials used in chemical sensors include semiconducting metal oxides, solid electrolytes, and ionic membranes. However, intrinsically conducting and insulating polymers have been attracting much more attention in recent years due to their widely tuneable chemical and physical properties, ease of deposition, and low cost. A polymer is a substance that consists of repeating structural units, or monomers, connected together via covalent chemical bonds [77]. Both synthetic and natural polymers are very common; biological polymers include DNA, proteins and cellulose, and synthetic polymers include plastics and rubber. Synthetic polymers also come in two forms: intrinsically conducting, and intrinsically non-conducting. Electrical conductivities approaching those of metals at room temperature have been achieved in intrinsically conducting polymers by doping them through careful addition of selected atoms to the polymer matrix. Intrinsically non-conducting polymers can also be made electrically conductive by creating a composite, which is a mixture of polymer and electrically conductive particles embedded within the polymer matrix.

Polymers used in sensor devices either participate in the sensing mechanisms, or stabilize the sensing components [78]. In this section, several types of polymer-based chemical sensors will be described that undergo a bulk response when exposed to a target chemical: chemiresistors, chemicapacitors, and chemFET's. One can also argue that several other types of chemical sensors: microcantilever, nanosensor, and SAW, should be placed under the polymer-based category, since they rely on polymer sensing layers for detecting analytes.

A chemiresistor is a sensor whose resistance changes according to the concentration of analyte present. A typical chemiresistor will consist of interdigitated electrodes and a thin, non-conducting polymer sensing film which has been infused with conductive particles. In its unexposed state, the sensor has a specific baseline resistance. Upon gas exposure, the polymer swells, reducing the electrical conductivity of the sensor due to the increased separation between the conducting particles. The change in resistance is used to determine which analytes are present. A chemicapacitive sensor consists of one or more capacitors (i.e. parallel plates, interdigitated capacitors, etc.) with a chemically-sensitive material acting as the dielectric between the plates [79]. Both the dielectric constant and the separation between the capacitor plates of the polymer-filled chemicapacitors is modulated by the adsorbed or desorbed analytes and can be detected either via a measurement of the time-constant of a charge or discharge operation of the capacitor or via resonant frequency in an electric resonance circuit. A FET can be used as a gas sensor provided that the analyte, upon binding, is capable of altering the field enhancement of the FET. The combination of ultra low-power Complementary Metal Oxide Semiconductor (CMOS) transistor technology and a conducting polymer gate has resulted in a transistor called a chemFET, whose conductance is a function of gas concentration [80].

10.2 Commercial Polymer Gas Sensors

Polymer-based sensors are currently in the early stages of commercialization, with two companies offering chemical sensing units listed in Table 19. Bloodhound Sensors Ltd. (acquired by Scensive Technologies) has developed a product called the Bloodhound ST214. The sensing unit features an array of 14 chemiresistor sensors; the manufacturer claims lowest detection limits of ppb's to ppm's and sampling times ranging between twenty to sixty seconds. Cyrano Science Inc. (acquired by Smiths Detection) manufactures and sells the Cyranose 320, whose sensing unit consists of 32 polymer nanocomposite sensors on a 1 inch square chip. The manufacturer claims lowest detection limits in the ppb's, and response times which are less than a minute.

Table 19 - Commercial polymer-based gas sensor companies

Company	Product(s)
• Bloodhound Sensors Ltd. (Scensive Technologies)	• Bloodhound ST214
• Cyrano Science Inc. (Smiths Detection)	• Cyranose 320

10.3 Recent Research on Polymer Gas Sensors

Chemiresistors

The chemiresistor sensors fabricated by Sutar *et al.* were able to detect ammonia levels as low as 0.5 ppm [81]. The sensing film consisted of intrinsic conducting polyaniline nanofibers arranged in a crystalline nanofibrous structure. Xie *et al.* utilized polymer-carbon black composite chemiresistors and pattern recognition analysis to recognize acetone, ethanol, toluene, methanol, and tetrahydrofuran at concentrations between 200 and 2000 ppm [82]. Individual sensors within the array used either PVPH, PEO, or PCL as the polymer sensing film. Kim *et al.* developed a portable sensing system based on a PDA; the sensor itself consists of 16 sensing elements integrated on the same silicon substrate [83]. The limit of detection for acetone was estimated to be less than 7 ppm, and between 1-20 ppm for other VOC's such as ethanol, toluene, and acetic acid. Ho *et al.* developed microchemical sensors and systems for unattended real-time monitoring of VOC's in soil and groundwater [84]. The theoretical limits of detection for PECH, PNVP, PIB, and PEVA based polymer chemiresistors to TCE is 63.8 ppm, 386.0 ppm, 22.3 ppm, and 67.0 ppm. Chemiresistor sensors respond fairly quickly to analytes, the sensors fabricated by Man *et al.* had a response time of 2-3 sec [85].

Chemicapacitors

Mlsna *et al.* of Seacoast Science Inc. used microfabrication techniques to produce chemicapacitive sensors, with 10 interdigitated capacitors on a single chip [79]. The detection limit for various chemical warfare agents (CWA's) and toxic industrial compounds (TIC's) were investigated; the only analyte relevant to this survey is ammonia, with a detection limit of 110 ppm. Patel *et al.* developed a micromachined parallel-plate chemicapacitor, which consists of a bottom layer of metal, a layer of polymer in the middle, and a porous layer of metal on top of the polymer [86]. The researchers estimate the limit of detection for acetone, benzene, ethanol, methanol, octane, and toluene to be 2 ppm, 85 ppm, 16 ppm, 7 ppm, 29 ppm, and 55 ppm respectively.

ChemFET's

Domansky *et al.* developed and tested a sensor array consisting of four chemFET's [87]. A combination of catalytic (palladium) and non-catalytic (polyaniline) thin layers were used on the chemFET's to detect hydrogen and ammonia gas. With a signal-to-noise ratio of 10, the researchers estimated the best individual sensors in the array to have detection limits of 5 ppm for hydrogen and 3 ppm for ammonia, with relative humidity ranging from 0 to 70%. Covington *et al.* characterized the response of conducting polymer gate chemFET's to ethanol and toluene vapour, and determined the detection limit for toluene and ethanol to be below 1 ppm [80].

10.4 Properties of Polymer-based Chemical Sensors

Polymers are attractive for use as the sensing layer in chemical sensors due to their ease of processing and fabrication (which leads to low cost), tuneable structure for analyte specificity, and resilience to poisoning by compounds that normally inactivate some inorganic semiconductor-type sensors. In addition, polymer science is very advanced and the ability of chemists to design very specific polymers, which target particular gases, is a significant advantage to making sensors based on these materials. However, polymers degrade over time under the influence of environmental factors such as heat, light, or chemicals, and their properties (tensile strength, shape, etc.) can change. This means the polymer-based sensing layer has a finite lifetime, and the sensor may experience drift over time. The polymer drift can be handled with the appropriate electronics or compensation.

11. Thermal Chemical Sensors

11.1 Principles of Operation of Thermal Gas Sensors

Many of the target chemicals are volatile, organic, and combustible. Thermal gas sensors such as the catalytic bead sensor detect the presence of combustible volatile organic compounds by combusting the gas in a reaction chamber. Catalysts reduce the required combustion temperature of the analyte by lowering the activation potential. When the analyte oxidizes on the surface of the sensor, the heat of combustion will cause the temperature of the sensor to rise, therefore changing the electrical resistance of a sensing wire. Each gas has a unique heat of combustion and corresponding change in electrical resistance, which can be detected using an electrical circuit consisting of the sensor and a reference device that is similar to the sensor but is non-reactive. However, a distinction between type of gas and concentration from the sensor signal is not possible.

Figure 18 - Commercial catalytic gas sensor, with sensing bead and reference bead [88]

Catalytic combustible gas sensors have been in use for more than 50 years, and in its simplest form, the sensor is a single platinum wire [88]. A modern, commercial sensor is shown in Figure 18. Platinum, palladium, and thoria compounds are all good catalysts for combustion. Platinum is preferred due to its sensitivity to temperature, high physical strength, resistance to corrosion, and ability to withstand elevated temperatures for a long period of time. However, the bare platinum wire needs to be heated to between 900 ºC and 1000 ºC in order to catalyze the combustion of hydrocarbon gases. At such temperatures, the platinum wire degrades quickly. The stability and usability of the sensor is enhanced by coating the wire with catalytically-treated metal oxide, forming a catalytic bead sensor [88]. In addition to the increased robustness, the catalytic coating reduces the temperature of operation to between 400 ºC to 600 ºC.

11.2 Commercial Thermal Gas Sensors

Commercial companies that offer thermal sensing units are shown in Table 20.

Table 20 - Companies offering thermal gas sensors

Company	Product(s)
• BW Technologies (Honeywell International)	• GasAlert Microclip • GasAlert Micro • GasAlert Micro 5
• Crowcon (Halma plc)	• Detective+ • Xgard
• ENMET	• EX-5100 • OMNI-4000
• e2V technologies Ltd.	• VQ41TSB • VQ547TS
• Mine Safety Appliances	• Titan • Ultima X Series • Toxgard
• Nemoto & Company	• NAP-100 series
• Tyco Scott Instruments	• 4888A-NIC II LEL

11.3 Recent Research on Thermal Gas Sensors

Catalytic gas sensors are a mature technology, but some research is still being conducted in this area with device miniaturization being a key trend. Recently, Sasahara *et al.* fabricated a microscale combustion-type sensor using a mixture of palladium and Al_2O_3 as the sensing material [89]. The sensor detected toluene at a concentration as low as 10 ppb, and the response was mostly independent of ambient temperature and humidity. Schreiter *et al.* fabricated and tested a calorimetric gas sensor based on integrated pyroelectric detector arrays. A polydimethylsiloxane (PDMS) polymer coating enabled the detection of heptane down to 10 ppm.

11.4 Properties of Thermal Gas Sensors

Thermal gas sensors have been in use for more than 50 years, mainly to detect combustible gases such as hexane and toluene [88]. A major advantage of thermal gas sensors lies in their simple fabrication. Disadvantages include susceptibility to catalyst poisoning (i.e. silicon compounds, sulphur compounds, etc.), susceptibility to sensor inhibitors (i.e. halogen compounds), and sensor cracking under high heat and/or gas concentrations. In addition, thermal gas sensors are non-selective and cannot be used to detect a mixture of gases; a sensor is calibrated for specific individual combustible gases by applying a correction factor to the reading.

12. Summary of Sensor Specifications

The specifications of the research-stage and commercial devices discussed in the sections above have been summarized into two tables, one listing the detection limits (Table 22 and Table 23) and the other describing specifications such as sensitivity, response time, power consumption, cost, and size (Table 21). The specifications were acquired through literature searches, general Internet searches, and manufacturers' data sheets.

Table 21 - Sensor performance specifications for all sensing technologies reviewed

Sensing Tech.		**Sensitivity**	**Response Time**	**Power Consumption**	**Cost**	**Size**
Electrochemical	Research					
	Commercial	90 nA/ppm ± 40 nA/ppm	10 sec	0.8 W (entire unit)	$400	82 g (entire unit incl. sensor)
Gravimetric	Research	15.88 ppm/ppm	20 sec			
	Commercial		10 sec	50 W (entire unit)		2.6 kg (entire unit)
IMS	Research					
	Commercial		< 20 sec		$10-12K (entire unit)	
MOS	Research					
	Commercial		< 1 min	230 mW (sensor only)		
Microcantilevers	Research	30 ppm per micron deflect				
	Commercial					
Nanomaterials	Research					
	Commercial					
Optical	Research					
	Commercial					
PID	Research					
	Commercial		3 sec	64 mW		8 g (sensor only)
Polymer-based	Research					
	Commercial		20 sec			32 oz. (entire unit)
Thermal	Research					
	Commercial	20 mV/ % vol gas	10 sec	250 mW		250 g (entire unit)

Table 22 - Sensor detection limits for all sensing technologies reviewed, inorganic analytes

Sensing Technology		Inorganic				
		NH3	HCl	HI	PH3	Iodine
Electrochemical	Research	10 ppm	1 vpm	3.5e-6 M	0.01 ppm	0.1 ppb
	Commercial	1 ppm	0.3 ppm	0.1 ppm	0.02 ppm	
Gravimetric (SAW)	Research	0.56 ppm	0.5 ppm			
	Commercial	0.5 ppm			0.5 ppm	
IMS	Research	25 ppb	0.5 ppb	100 ppb		5 ppb
	Commercial	0.1 ppb	5 ppm	< 1 ppm	< 0.5 ppm	low ppb's
MOS	Research	1 ppm			< 0.2 ppm	
	Commercial	1 ppm				
Microcantilevers	Research	0.1 ppm				
Nanomaterials	Research	10 ppm	5 ppm			
Optical	Research	1 ppb	< 1 ppm			0.1 ppm
	Commercial	0.8 ppb	0.83 ppb	0.1 ppm	6.2 ppb	3 ppm
PID	Research					
	Commercial	1 ppm		< 10 ppb	< 10 ppb	5 ppb
Polymer-based	Research	1 ppm	20 ppm			
	Commercial	ppm-ppb's				
Thermal	Research					
	Commercial	600 ppm			26% of CH4 LEL	

Table 23 - Sensor detection limits for all sensing technologies reviewed, organic analytes

Sensing Technology		Organic										
		acetic anh.	formic	hexane	heptane	cyclohexane	methylamine	N-methylfor	P2P	phenylacetic	THF	toluene
Electrochemical	Research	10 ppb	< 1 mg/m^3									
	Commercial		< 5 ppm									
Gravimetric (SAW)	Research		7.2 mg/m^3	0.7 ppm	< 21 ppm	0.1 mg/ml	5e-7 mol/l				< 6 ppt (thou	1 ppm
	Commercial											
IMS	Research	50 ppb		170 ppm	low ppm's		5 ppb		10 ppb		2-3 ppb	10 ppb
	Commercial	< 100 ppb	< low ppm's	ppb's	< low ppm's		< 0.1 ppb		~ 10 ppb			
MOS	Research	< 330 ppm			< 5 ppm							10 ppm
	Commercial			20 ppm	20 ppm	20 ppm						10 ppm
Microcantilevers	Research	2.1% acetic		1 ppm	1 ppm							10 ppm
Nanomaterials	Research	3.6 ppm	< 30 ppm			< 200 ppm						
Optical	Research	4 mmol/l		5%	0.02%		< 10 ppm				40 ppm	290 ppb
	Commercial											
PID	Research											80 ppb
	Commercial	ppb's	ppb's	ppb's	ppb's	ppb's	ppb's	ppb's	ppb's	ppb's	ppb's	ppb's
Polymer-based	Research	50 ppm			< 50 ppm	< 200 ppm	< 1 ppm				400 ppm	8 ppm
	Commercial	ppm-ppb's	ppm-ppb's	ppm-ppb's	ppm-ppb's	ppm-ppb's	ppm-ppb's	ppm-ppb's	ppm-ppb's	ppm-ppb's	ppm-ppb's	ppm-ppb's
Thermal	Research				10 ppm							10 ppb
	Commercial	1% LEL		110 ppm	105 ppm	1% LEL	3% range					120 ppm

13. Technology Assessment

The results of the performance assessment of available commercial and research sensor units/devices are summarized and presented in Table 22 and Table 23 (detection limits) and in Table 21 (other specifications such as sensitivity, response time, etc.). It is clear that not all target chemicals can be detected by any one of the sensing technologies, although most inorganic and organic compounds can be detected by more than one sensing technology. The information presented in the tables was acquired from research literature, the Internet, and company data sheets. However, not all companies and researchers disclose performance specifications of their sensor devices; as a result, performance specifications for some sensors could not be obtained.

In nearly all cases, ion mobility spectrometers and photoionization detectors provide the best detection limits for both inorganic and organic target gases. Electrochemical sensors currently dominate the market for toxic industrial chemical monitoring (most of the inorganic compounds except for iodine are toxic inorganic compounds), but cannot match the low detection limits offered by IMS (low ppb) and PID (low ppb). However, IMS units are extremely susceptible to contamination and humidity, and can be costly, and PID sensors suffer from poor selectivity since they detect all gases with ionization potentials below the energy level of the excitation source. If the detection strategy requires that the detection units be mounted onto patrol vehicles, IMS technology may not be practical due to its susceptibility to contamination and humidity. Some contaminants may take anywhere from minutes to days to exit the detection chamber. As for humidity, IMS operates best in the absence of water but if water was present, the concentration should be at a constant level so that readings are reproducible; this condition cannot be guaranteed in the external environment. PID technology may also prove to have far too low a selectivity to provide a sufficient level of certainty about the compound being detected. Emerging sensing technologies such as nanomaterials-based, SAW, and polymer-based sensors cannot yet achieve the low detection limits offered by IMS and PID, although they have the potential to be far more selective than PID and lower cost than IMS technology.

It is expected that the most effective and low cost detection unit will require a hybrid technology approach, consisting of both PID and other more selective sensors such as those based on nanostructured materials. In this approach, the PID system would provide the first level of detection at a high spatial resolution and low specificity, while a second level of inexpensive and highly selective sensors would perform the signature identification. In order to overcome the high detection limit of this second layer, a pre-concentrator stage could be used to increase the effective gas concentration.

Part C: Recommendations

The identification of target gases and an assessment of sensing technology have led to important preliminary conclusions regarding a possible technological approach to detecting clandestine methamphetamine laboratories. However, these investigations have also demonstrated that some critical information is missing or inaccessible, such as outdoor target gas concentrations, which would be necessary to compile detailed sensor specifications. As a result of the limitations of the available information, recommendations for experimental investigations are proposed to assess the feasibility of the project.

1. Limitations of Available Information

The most significant challenge encountered while preparing this report was associated with the acquisition of information on the most commonly used methamphetamine manufacturing methods and the characteristics of the most commonly encountered methamphetamine laboratories. Information on methamphetamine synthesis processes can be found in scientific and popular literature, as well as the Internet; however, information on the most widely applied methods in British Columbia is not publicly available. The combination of methamphetamine manufacturing processes and the physical characteristics of clandestine drug laboratories and/or chemical waste dumps determine the exact target chemicals and their concentrations.

Only limited information on airborne chemical concentrations present during methamphetamine manufacturing is currently available. A research group at the National Jewish Medical Center, U.S.A., lead by Dr. Martyny, has published studies on chemical concentrations inside staged methamphetamine laboratories. However, no simulated methamphetamine manufacturing for studying outdoor gas concentrations has been conducted by this group. In recent correspondence with Dr. Martyny, it was determined that his group has no intention of conducting an outdoor study nor does he know of anybody who is conducting such a study. As a result, the present study could not identify a definite set of required sensor specifications such as detection limits for the target gases.

Additionally, many of the sensors available commercially are already integrated and sensor specifications are provided for the entire unit and not the sensor itself, so that cost and power consumption for the sensor can only be estimated. Also, the types of specifications provided by the manufacturers for the sensors assessed in this study are not uniform, which makes a fair comparison between technologies challenging. For example, some companies listed the detection limit of their sensors, while others listed only the alarm levels of the unit. Further information on sensors used in commercially available units could not be obtained because many manufacturers were reluctant to disclose the detailed specifications of their products.

2. Outstanding Questions

The following list of outstanding questions requires access to sensitive information on discovered methamphetamine laboratories that could not be acquired while preparing this report. However, this information is necessary to formulate a more specific technology assessment and implementation suitable for detecting methamphetamine manufacturing in British Columbia.

Question 1: What are the most common methamphetamine synthesis methods used in clandestine laboratories in British Columbia?

Different methamphetamine manufacturing processes are associated with a unique signature of released airborne chemicals. Therefore, the manufacturing method used has a significant impact on the type and specifications of sensing technology required. For example, phenylacetone, which is only used in the P2P process (and its derivatives), is easier to smuggle into Canada (Vancouver in particular) than into the United States [90]. As a result, methamphetamine laboratories in British Columbia may use phenylacetone-based processes more often whereas laboratories in Washington State may use pseudoephedrine-based processes more often.

Question 2: What is the typical layout and sophistication of a small/medium/large-scale clandestine lab? Is any special equipment installed, such as ventilation equipment?

The typical layout and installed equipment in a clandestine methamphetamine laboratory will determine the concentrations of chemicals released into the surrounding air and will determine whether or not airborne detection of chemicals is feasible. It can be assumed that most small-scale laboratories do not use sophisticated environmental management equipment as this could seem suspicious during installation and purchase.

Question 3: What is the typical external environment of a clandestine laboratory in British Columbia?

The external environment of the building in which a clandestine laboratory is located will have an influence on the concentration of manufacturing-related gases present in the vicinity of the building. The exposure of the building will affect the gas dispersion by wind. The distance of the laboratory from public streets will have an impact on the gas concentration levels present on public grounds; this impact will be significant for laboratories located in semi-rural areas far away from public streets.

Question 4: What are the exact temporal signatures of gases released during the different production processes used in British Columbia? How long are typical production cycles for the different methods? Do cycles overlap?

Methamphetamine manufacturing involves different stages (synthesis, conversion, extraction, etc.), and concentrations of released airborne chemicals vary during the different stages. This means that every manufacturing process has a unique temporal signature, which includes the sequence of gas concentrations as well as the duration of the different stages. Identifying a temporal signature will facilitate the identification of the laboratories with greater confidence through the proposed detection scheme. The duration of one production cycle together with the sequence of gas concentrations dictates the required sampling frequency to make an assessment of lab activity with a higher level of confidence. In the event that production cycles in the same laboratory overlap, gases from different stages may be released simultaneously, which the proposed detection scheme needs to take into account.

Question 5: Do clandestine lab operators typically dump all of their waste products at one location, or separate them into solid and liquid wastes for example and dump them at different locations?

Methamphetamine waste dumps can be differentiated from normal industrial waste dumps (legal or illegal) by the types of chemicals present. Each methamphetamine manufacturing process has a unique set of associated waste materials. If lab operators do separate production wastes it will make detection more difficult. In addition, it would be useful to know the level of care that is typically taken to dispose of these chemicals – whether they are well contained in appropriate containers or whether they are poured into the environment will lead to different detectable chemical concentrations.

3. General Recommendations

This research report has provided substantial information regarding the various common methamphetamine manufacturing methods that were identified in the literature, the potential target gases released, and the performance of available sensing technology in the context of those gases. Direct information regarding the exact methods used in British Columbian clandestine laboratories was not obtained for this report due to the sensitivity of this information. The lack of this detailed information has prevented this research from identifying a specific detection technology for targeting British Columbian clandestine laboratories. Although the problem of clandestine drug labs and chemical waste dumps is not specific to British Columbia, there are unique factors present that will have a significant effect on the choice of sensing technology to use for a specific geographic area. These factors include precursor material availability, which is heavily influenced by federal chemical import restrictions and port/border security, as well as the legal framework.

The majority of data gathered on chemical concentrations present at staged clandestine laboratories was obtained from reports by Dr. John Martyny of the National Jewish Medical Center. Unfortunately, only indoor airborne chemical concentrations were obtained in the reported studies, and outdoor concentrations were not measured. However, based on the available measurements, it is expected that outdoor concentrations will occur at low ppb levels for the target gases. Without outdoor concentration measurements it is challenging to provide exact sensor performance requirements.

Based on available information, further study is needed before a conclusive feasibility assessment can be developed and recommendations can be made on the most suitable clandestine laboratory detection technology and implementation. Here we offer preliminary recommendations for experimental investigations in collaboration with the

Canadian Police Research Centre and municipal Fire Departments. The objectives of these investigations will be twofold: 1. to acquire the remaining information on performance requirements for sensing technology; 2. to perform a preliminary technology assessment through experiments. The recommendations are developed such that the results from each step can be used to assess whether or not it is feasible to continue with the project. As well, each step represents less investment than the subsequent steps and therefore, the recommendations provide a bootstrapping method for building up the project.

Recommendation 1: Set up a mock clandestine lab setting for the release and detection of harmless sample gases.

A typical clandestine laboratory setting should be used to release harmless simulant gases (to be determined) from inside a building at concentrations similar to those reported in the literature for controlled methamphetamine manufacturing processes. These gases should have similar properties to the target gases, such as density and mass diffusivity. The concentration of these gases should be measured outside of the building with a highly sensitive detector, as well as with colorimetric gas detection tubes. The reference detector will give an accurate measurement of gas concentration, while the test tubes will be evaluated on their capability to accumulate gas samples at low concentration levels. In addition, the sensors, especially the colorimetric tubes, should be mounted to a vehicle to verify whether or not the target gases can be detected with a mobile detection unit.

Recommendation 2: Perform long-term testing in a city environment using colorimetric test tubes mounted to vehicles.

If the experimental results from Recommendation 1 indicate that the gas levels at the exterior of the test site are sufficiently high for detection using colorimetric detection tubes, then a device containing similar detection tubes, which are sensitive to a selection of the target gases, should be mounted onto several patrol vehicles. The device containing these tubes will be equipped with air pumps that provide continuous sampling air to the tubes. After an appropriate amount of time, the detection tubes will be analyzed for the sample gases using highly sensitive detection methods in a research laboratory (i.e. gas chromatograph-mass spectrometer) to verify if the detection tubes have been exposed to any of the target chemicals. This investigation should be performed over a span of several weeks. Although these detections tubes are not suitable for permanent application due to the required post processing and frequent replacements, they provide a low-cost check of the feasibility of this project. However, it is possible that none of the patrol vehicles will be exposed to the vapours emitted from an operational methamphetamine laboratory. Therefore, in the event that none of the chemicals are detected, a decision can be made as to whether to extend the experiment or proceed to Recommendation 3.

Recommendation 3: Set up a model clandestine lab and/or waste dump in order to obtain airborne target gas concentrations in the vicinity of the laboratory for the most common manufacturing methods.

It is recommended that a controlled experiment including a model clandestine laboratory be constructed in order to acquire outdoor airborne gas concentrations. For this study, the use of several fixed location gas collection devices, such as gas collection tubes, as well as other point and remote sensing technology is recommended. The tubes will be analyzed using highly sensitive equipment such as a gas chromatograph-mass spectrometer. Using this experiment, both gas levels and a temporal signature will be acquired. In addition, this would provide the appropriate test site for the ABB FTIR system to determine if it is possible to pinpoint the laboratory location using this technology. The exact specifications of required sensing technology will be determined using the results of this study. In addition, the results will determine where further sensing technology research and development are required.

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