

Table of Contents:

- I) Introduction
- II) Atoms Molecules and The Periodic Table
- III) Two Basic Classes of Chemicals
- IV) Basic Principles of Organic Chemistry Relevant to This Matter
- V) Classes of Organic Chemicals: (See Exhibits E, G)
- VI) Small Molecules
- VII) Vapor Pressure and Odor: (See Exhibits B, D)
- VIII) Chemical Reactivity and Odor.

Index of Exhibits: (A - J)

- A) Periodic Table: A Systematic Table of the Chemical Elements organized into vertical columns that represent chemical similarity among elements.
- B) CRC Handbook of Chemistry and Physics, from Section 6, Table of Vapor Pressures associated with various chemicals.
- C) Merck Index entries for compounds discussed herein. The Merck Index is a comprehensive dictionary of many chemicals, with references to much published material known for the various chemicals named herein.
- D) Vapor Pressure plots of various compounds associated with contraband.
- E) Sample chemical "Functional Groups" associated with contraband described herein.
- F) Chart of Terpenes associated with Cannabis, Gertsch et al, PNAS-0803601105, p.5
- G) Table of common odiferous compounds.
- H) Atomic Orbital Diagrams of Carbon.
- I) Chirality depicted visually.
- J) Technical Support Document: Toxicology. Clandestine Drug Labs: Methamphetamine. California Office of Environmental Health Hazard Assessment. Sept. 24, 2003, pp. 2-3, describing the vapor pressure and odor of Methamphetamine.

D) Introduction:

Chemistry, and its sub-entity, organic Chemistry are vastly complex subjects, not fully understood by Man, but nonetheless applied regularly, and repeatably through the application of more-complex-than-ordinary mathematics. Not all of Chemistry is directly relevant to this matter, and that which is relevant is described by the phenomena of Organic Chemistry, and of the Organic Chemistry that is relevant, it is mostly the chemistry of "odor" and "smell" that are relevant. That subset of Organic Chemistry phenomena are described here in a simplified manner appropriate to non-chemists. It is not necessary to know the more complicated mathematics and physics that underlies chemistry to understand the concepts presented herein, and apply them to a legal decision. And they are presented as such.

II). Atoms, Molecules, The Periodic Table.

"All things are composed of atoms", Lucretius opens his tome "*De Rerum Natura*", written more than 2000 years ago, and since then at least, Man has conceived of the world as such, and to a noteworthy extent proved it to be such. (A reasonable proof of Chemistry is that a person of minimal education, and inexact technique can repeatably manufacture Methamphetamine in their garage, and actually end up with Methamphetamine as opposed to some other chemical.) Repeatability is at the core of scientific proof, and chemists can predictively create chemicals with given physical and chemical properties, using established recipes, and by applying Chemistry.

A) Atoms:

Atoms are held to be comprised of three stable atomic particles:

Neutron -- No electrical charge. Inside the "Nucleus", or center of an atom.

Proton -- Inside the "Nucleus" or center of an atom. Has a "Positive" electrical charge.

Electron -- Orbits The "Nucleus". Has a "Negative" electrical charge. Electron orbits

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can be spherical with the Nucleus at the center, or complex in shape, like multiple figure-eight patterns, or lobes, arranged around a central nucleus.

Science claims to be able to further split these atomic particles into subatomic particles, but these lesser particles are not stable across time, unless grouped together into the stable atomic particles, and practical chemistry does not require consideration of the atom in this way to be applied. In fact, chemistry as a whole almost exclusively involves the electrons in the outer orbits of an atom. Phenomena involving the center of an atom are typically referred to as Nuclear Reactions, or Nuclear Physics.

Atoms can to some extent be thought of as having a core-and-shell type arrangement where the nucleus is at the core, and the electron "Orbits" are the shell. It is not sufficient, however to think of an atom as being only spherical, but rather they may have also have shapes with lobes, that extend to the points of a flat triangle in some cases, a pyramid in others, or like an axle with four spokes in still other cases.

It is the complexity of electron "orbitals" that gives rise to a multitude of molecular shapes, some which can lay flat like sheets of paper, others that form complex 3-dimensional arrangements like branches in a tree, when Atoms combine to form Molecules. (See Exhibit H, Atomic Orbitals of Carbon).

Life itself, and likewise smell depends on the chemical composition of molecules, but also their shape and size.

Typically a single atom will connect with between one and six other atoms. Carbon is capable of forming up to four distinct bonds. By definition interatomic bonds are shared Electron pairs between atoms where their orbitals merge. When atoms combine in this way they form Molecules.

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B) Molecules:

Molecules are combinations of two or more atoms. There appears to be no upper limit to the size and complexity of Molecules, and the Molecules associated with life, like Hemoglobin and DNA, can have multiple tens, or even thousands of atoms bound to each other.

C) The Periodic Table (See Exhibit A)

The periodic table is a systematic descriptor of all the naturally occurring chemical elements. (There are 92 of them). Most elements are metal, and are to be found as one scans from left to right across the table. (In Exhibit A, these are the light-yellow colored regions). Then there are nonmetals that are positioned on the right hand side of the table. (The red colored region on the table). Between the two are "metalloids" or "semi-metals". (The blue colored region on Exhibit A). A notable example of a "Metalloid" is Silicon. (Element 14, in column 14 on the Periodic Table). Pure silicon has a dark-grey, shiny, mirror-like appearance. However it shatters like glass when dropped. (It looks like a metal, but does not bend and deform, as metals typically do. Instead, it crumbles apart like Graphite, pure Carbon). The single rightmost column of the Periodic Table (column 18), are the Inert or "Noble" Gasses. They do not ever react with other chemical elements under natural conditions, and rarely ever, under any conditions. Each vertical column of the Periodic Table represents a group of chemically similar elements that can often be substituted for each other in chemical reactions. (They will produce wholly different products, but the elements form similar bond arrangements, and as such they are considered "chemically similar" because ultimately the configuration of their electron orbitals are alike). So, for example, the elements in Column 16 which include Oxygen, Sulphur, Selenium and Tellurium, all react with Hydrogen to produce a Di-Hydride. (H_2O , H_2S , H_2Se , H_2Te). H_2O is water, but the other compounds are gasses that stink of rotten eggs, horseradish, and garlic, and are among the most offensive-smelling and toxic chemicals on Earth. Another example is Silicon and Carbon. Silicon Rubber is made by substituting Silicon atoms for Carbon atoms in a molecule that if made with Carbon, would be somewhat waxy, or like

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common packaging plastics. If a lump of each is placed in an ordinary fire, the Carbon compound will burn and produce Carbon Dioxide. The Silicon compound will burn, and produce Silicon Dioxide, which is glass. Both compounds produce a Di-Oxide when burned, but the final products are distinct.

III.) Two Basic Classes of Chemicals

Chemistry that Humans are exposed to in the natural world as well as with products produced by Man, falls into Two broad areas, Mineral and Organic.

A) Mineral

Mineral chemistry typically involves Metals, and "Metalloids". Mineral chemistry manifests itself on earth as most rocks, and ores, as well as ceramics. Mineral chemistry is not directly relevant to the capacity of drug dogs to smell, and is not addressed here.

B) Organic

Organic chemistry is the chemistry of compounds composed primarily of Carbon. Organic chemicals also commonly contain Hydrogen, Oxygen, and Nitrogen, and less commonly Sulphur, Phosphorous, and Metals. Both odor and smell, as relevant to this matter, are explained by Organic Chemistry. (For this brief, "Odor", a noun, means the actual smell of something as perceived by the smeller, and is a product of a substances' particular chemistry. "Smell" will be used as a verb, and means to detect and perceive an Odor.) Whether a compound will have an odor or not can be determined in part by examining its chemical properties. In particular, its molecular structure, chemical composition (which of the chemical elements are combined to produce it), and its overall size. The actual odor of a chemical to a living being is a product of organic chemistry at the olfactory interface, and along the pathway to consciousness.

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Examples of Organic Chemistry at work:

Drugs

Petroleum

Artificial Colors and Flavors,

Fragrances

Plastics

All Living Things.

IV). Basic Principles of Organic Chemistry Relevant to This Matter:

A). Functional Groups (See Exhibit E)

"Organic compounds are thought of as consisting of a relatively unreactive backbone, for example a chain of sp^3 hybridized carbon atoms, and one or several functional groups. The functional group is an atom, or a group of atoms that has similar chemical properties whenever it occurs in different compounds. It defines the characteristic physical and chemical properties of families of organic compounds. " IUPAC (*Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994)*) on page 1116. (" sp^3 " is the three-dimensional bond arrangement for Carbon where the axes of its electron orbitals point outward to the vertices of a pyramid, and take a "tetrahedral" shape). See Exhibit H.

B). Depicting Chemical Structures (See Exhibits C, E, G,H)

This is typically done with stick-figure diagrams that represent the chemical bonds of a Molecule. (Chemical bonds are created by overlapping or merging of electron orbitals). With some practice a person can use these diagrams to imagine how a molecule will react with other molecules, and to some extent what they will look like in three-dimensional space. Typically these diagrams are abbreviated, omitting the labeling of Carbon atoms, and Hydrogen atoms attached to Carbon, to make the diagrams easier to view, but also because these are typically the least reactive sites on the organic molecules and typically not where organic molecules will react with other organic molecules, rather, that occurs by and through

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various functional groups. The three-dimensional bond arrangements of Carbon in its "tetrahedral" or sp^3 configuration is represented by using a dashed line to represent an orbital that points away from the viewer, and a foreshortened widened line to represent orbitals that point toward the viewer. Orbitals that are perpendicular to the viewers' perspective are drawn with narrow lines. Molecules have to be perceived in at least three dimensions to understand Chirality. (Described in part D, below). This information is necessary to understand the molecular diagrams that are contained in the entries from the *Merck Index* for the chemicals relevant to this matter.

C) Organic Chemical Naming Conventions:

There is a standardized naming convention promulgated by the International Union of Pure and Applied Chemistry (IUPAC), whereby a single Carbon atom in a molecule is chosen, and labeled as the first Carbon atom, and the chemical structure is named relative to that Carbon atom. In addition, organic chemicals may have common names that arose before this naming convention was decided, or that may simply have been ascribed by the discoverer. Trade Mark names may be ascribed as well. (See Exhibit G). For example, the chemicals shown on the Vapor Pressure chart as "TriMethylPentane" are all components of Gasoline. (Octane). Octane is an alkane - a linear hydrocarbon, with eight Carbon atoms. 2,2,3-TriMethylPentane is a five-carbon alkane, (Pentane), with two single-carbon methyl groups attached to the second Carbon atom in the chain, and a third on the third Carbon atom in the chain. (Positions 2, 2, and 3, hence the name). Each methyl group has a single Carbon atom, and Pentane has five Carbon atoms. The total is eight, so "Tri-Methyl-Pentane" is a type of "Octane". In this example, 2,2,3- TriMethylPentane is the IUPAC Name, while Gasoline is the common name. The IUPAC convention is systematically descriptive, and accurate, but can be ungainly. As molecular size and complexity grows, IUPAC names can reach several hundred characters quite quickly. For this reason common names and trade names are often used. This information is necessary to understand some of the information contained in the entries from the *Merck Index* for the chemicals relevant to this matter, and is also provided

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for reference. It gives an indication of the level of detail and complexity associated with Organic Chemistry.

D). Chirality (See Exhibit I)

Because Atoms combine in complex three-dimensional shapes called molecules, some of these arrangements are complex enough that no matter how they are flipped over or rotated they cannot fit in the shape of their mirror-image. As a result, such Molecules will typically exist as, and can be produced in, both of the mirror-image arrangements. (Chirality comes from the Greek word "chiros" for "hand", and people experience Chirality by not being able to fit a Right hand into a Left-Hand glove, or by trying to shake a person's left hand with their right). The two separate mirror-image forms of a chiral molecule are referred to as "enantiomers" or "stereo-isomers", and while they are chemically identical, they are symmetrically opposite. And in the natural world, they have some distinct properties from each other. One such property is that when polarized light is shone through a sample of each enantiomer, each will rotate the plane of polarization by the same amount, but in opposite directions. Because life itself is made up of many chiral Molecules, (like DNA, and almost certainly any protein or enzyme), for certain molecules, one enantiomer will be bio-active in a particular way, while the other is not at all, or will be so in a different way. Two very notable examples of this are Thalidomide, and Accutane. Both of these cause birth defects, but only one enantiomer of each does so, not the other. Chirality is also experienced with the sense of smell. Mint and Fennel-Seed smell different, but the odor comes from enantiomers of the same Terpene: 2-Methyl-5-(1-methylethenyl)-2-cyclohexenone, also commonly called "Carvone". Perhaps most notably, however, is that one enantiomer of

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Methamphetamine has been sold over-the-counter for decades as a common nasal decongestant, while the other is a Schedule I Controlled Substance in all States' and Federal Law. In and of themselves, the two are chemically identical. Physically, they exist in three-dimensional space as mirror-images of each other. Biologically, however, they are profoundly different. The relevance to this matter is that an examination of Chirality attacks

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the reliability of any claims of canines' sense of smell. In the industries of producing odorant and flavorant compounds, as well as drugs and cosmetics, it is standard practice to determine Chirality, and separately determine the properties of both enantiomers of a given compound. The class of compounds that give Cannabis its odor, Terpenes, are mostly Chiral. Humans experience this as differences in odor or flavor as described above, but also also in some cases that one enantiomer will have an odor while the other will not. Some persons have genetic differences that preclude them from smelling certain compounds at all, or a specific enantiomer thereof, similar in principle to color-blindness. Any person claiming to be an expert on smell (whether that of a human or canine), must understand these concepts, and certify that a drug-detecting mechanism is capable of distinguishing one enantiomer from another, otherwise such a mechanism cannot truly be considered to have a sense of "Smell" at all, much less one that is analogous to humans. No competent, realistic, nor acceptable claim of anything based in Organic Chemistry can exist without an examination of Chirality, and Thalidomide and Accutane stand as examples of what happens when chemists fail to do so.

V) Classes of Organic Chemicals: (See Exhibits E, G)

Organic chemicals are classified by their composition, structure, and functional groups. Classifying organic chemicals is a practice of art, and brightline distinctions separating classes is not the practice. A chemical may have properties in more than one class. Two short lists are given below for the purposes demonstrating some general relations between chemistry and odor, relevant to the chemistry of Contraband, and as an example of some of the names used and what establishes the class. Some diagrams of particular molecules that may be of one or more classes, and may be associated with contraband, are shown in Exhibits C, and G.

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Some Chemical Classes Based on Structure :

| Class | Description | Examples |
|------------------------------|---|--|
| Alkanes | Straight-Chain, or Branched Hydrocarbons | Gasoline, Diesel Fuel, Kerosene, Paraffin wax. |
| Aromatics | Cyclic Hydrocarbons | Benzene, Naptha |
| Terpenes | Contains Isoprene Unit | Limone, Pinene |
| Amines | Contains Amino Group | Chemicals associated with dead or decaying matter. Certain Drugs, and Industrial Chemicals |
| Alcohols | Contains Hydroxy Group | Ethanol |
| Acetates, Aldehydes, Ketones | Various Arrangements of a Carboxyl group. | Fruit flavors and scents, solvents and cleaning agents. |
| Polymers | Combinations of repeating "Monomers" into larger molecules. | DNA, Silicon Rubber, most plastics. |

Some Chemical Classes based on Composition:

| Class | Description | Examples |
|------------------|---|--|
| Amines | Contains NH ₂ Functional Group | Certain Drugs, and Industrial Chemicals, and as described above. |
| Hydrocarbons | Contain Exclusively Carbon and Hydrogen. Includes Alkanes, and Aromatics mentioned above. | Gasoline, Diesel, Benzene |
| FluoroCarbons | Hydrocarbons With some Hydrogen atoms replaced by Flourine | Dry Cleaning Fluid, Refrigerants. |
| PerFluoroCarbons | Hydrocarbons With All Hydrogen atoms replaced by Flourine | Non-Stick Cookware Coating. |
| Proteins | Amino Acid Polymers. | Living Things. |

As relevant to this matter, Terpenes are a class of organic chemicals, and have a particular arrangement of atoms called an Isoprene Unit. (See Exhibit G, parts 2 and 3). The odor from C. Sativa, all Citrus, most herbs and spices, all Conifers, and many plants at large, is due to Terpene compounds.

There is a class of organic compounds referred to as "Aromatic". This is a legacy misnomer, from the early days of organic chemistry. "Aromatic" specifically refers to the presence of a

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"Graphene unit", (also called a Benzene, or "phenyl" ring), of Carbon atoms. In organic Chemistry, "Aromaticity" has come to refer to unique properties of the Graphene unit as they apply to Organic Chemistry. The misnomer arose because early organic chemists noticed a relation between the presence of the "Benzene Ring" in organic chemicals, and that they had discernible odors. Over time, chemists came to understand other chemical structures and compounds that had distinct odors, and likewise further understand the relationship between the odor of a compound, and its chemistry. Some examples of "Aromatic" compounds are shown in Exhibit G, part 4. Also note Exhibit H, fig. 4, which shows the "orbital" structure of the Graphene Unit.

There is also a class of organic compounds called "Polymers". Polymers are large molecules composed of a repeating smaller molecular compound. The "monomers" as they are called are attached to each other repeatedly, and typically "end-to-end" like a chain is made of individual links.

The length of the "chain" and the composition of the "links" are highly customizable, and the Plastics industry relies on this customization heavily to produce a wide variety of plastics with all manner of thermal, physical, and chemical properties.

The relevance to this matter is that the "distinct smell of burning opium" is explained by the Latex sap of the Poppy plant, (the same chemical used to make natural rubber), that carries the drug compound, Morphine. This sap is "PolyIsoprene" (a polymer of the same "Isoprene Unit" that makes up Terpenes).

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The PolyIsoprene molecule may be produced in various sizes by the plant, and the smaller ones will likely have odor, while the larger ones may not, or only a faint odor. Regardless, as the material is combusted at temperatures associated with smoking, the PolyIsoprene itself will evaporate, and will yield smaller terpenoid compounds, and hence the smoke and smell,

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as the PolyIsoprene polymer is broken into smaller particles , (all of which are legal compounds), by the combustion, but not completely combusted into Carbon Dioxide and Water. It is these combustion products of PolyIsoprene, and of the sugars in the sap that give burning Opium its odor. Not Morphine, or any other controlled substance.

VI) Small Molecules

The organic chemicals associated with smell as relevant here would be considered small molecules. One source cites odiferous organic molecules as weighing typically less than 300 Daltons. (*Aroma Chemistry*, Terry Acree, Cornell University, Department of Food Science). Pharmacology dictionaries define organic "Small Molecules" as weighing less than 800 Daltons. (A Dalton is essentially the weight of a Proton or Neutron). Carbon has a nominal atomic weight of 12 Daltons. As a general measure most of the compounds that are drugs under FRS 893.03, are close to or beyond the 300 Dalton weight, whereas the odorants involved, namely Terpenes, solvents, and reagents, are all considerably smaller and less massive than the drug molecules. (THC has a molecular weight of 314.45, while the Cannabis Terpenes listed all have a molecular weight around 136).

The relevance is that in the chemistry of the olfactory interface where "smell" begins, the molecules of "odor" must to some extent fit into the molecules and structures that make up the region where the drug-detecting mechanism comes in contact with the odor molecules suspended in the surrounding fluid. Smaller molecules tend to do this better. Heavier molecules also typically do not evaporate readily because the ambient temperatures available on Earth are not high enough to boil them into normal atmospheric pressures, as described in Vapor Pressure, below.

VII) Vapor Pressure: (See Exhibits B, D)

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The most likely physical property of any chemical that indicates it may have an odor is its vapor pressure. Compounds cannot be "smelled" if they have no vapor pressure. A chemical

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can however have a vapor pressure, but no odor. This is explained further below.

Vapor pressure is a measure of the likelihood that a material will evaporate, also known as its "volatility". In order to be "smelled" a chemical compound is dissolved or diffused into a fluid. (Both air and water are "fluids". One is a gas, one is a liquid. "Fluid" means that the individual particles, atoms or molecules, are not bound to each other and free to move about in space). In the case of a liquid like water, odorant molecules dissolve in the liquid, and ultimately reach the olfactory interface of whatever being or device is doing the smelling. In the case of a gas like air, the instant case, atoms or molecules of the odorant diffuse into the gas. When particles evaporate from a substance into a surrounding gas they exert a pressure against the surrounding gas. Likewise the surrounding gas exerts a pressure on the substance. The analogy of Vapor Pressure is that of a balloon expanding and pushing away the surrounding air. The difference is that because both air, and an evaporating substance are fluids, a distinct surface like that of a balloon is not created when evaporating molecules push away from their source, but rather they push their way into, or "diffuse" into the surrounding gas, with a measurable degree of pressure.

Crystals (of any kind) have a low vapor pressure, if any, because of the energy-stable binding that takes place between the particles that gives rise to its crystal structure.

Compounds like THC, and Morphine, Cocaine, and Amphetamine commonly exist as crystals in their contraband form, and their molecules are considerably larger in size and mass than the Terpenes, solvents, and reagents associated with them. Vapor pressure of a compound typically begins to increase once it is melted into a liquid from a solid, and continues to increase until the material boils. A substance boiling at sea-level, is said to have a vapor pressure of one atmosphere. (Equal to the surrounding atmospheric pressure).

Comparing the vapor pressure of various chemicals that appear in contraband can give an indication of what may be evaporating and what not, and subsequently whether any molecules of such a substance will leave their source, diffuse into the air, and ultimately

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reach the olfactory interface of any drug detecting mechanism.

Attached as Exhibit D, are two graphs showing vapor pressures of various compounds associated with illegal drugs as well as of those associated with the smell of Cannabis. The easiest way to understand the charts is that the farther to the left of the chart that the plot of a given compound is, the more volatile it is. The vertical line near the center of the chart is at a temperature of 25° Celsius. (What chemists refer to as "standard temperature", also known as "room temperature"). The top of the chart represents one atmosphere, (what chemists refer to as "Standard Pressure"), of vapor pressure. The temperature at which the plot of a given compound crosses the top of the chart, is its boiling point at sea-level.

As can be seen from the chart, all the chemicals shown are common, and highly volatile compared to THC, Morphine, Cocaine, and Methamphetamine, all of which have little or no vapor pressure at normal temperatures. The data for the chart were obtained from a table of vapor pressure data (Exhibit B), which shows the relation between temperature and Vapor Pressure of various chemicals from 1 Pascal to 100,000 Pascals (Approximately One Atmosphere). By comparison, THC, Morphine, Methamphetamine, and Cocaine all have vapor pressures below 1 Pascal (1/100,000th of an atmosphere) at standard temperature, and melting and boiling points well above normal temperatures. (Note that the data shown are for the pure or "Base" forms of these compounds, as well as for the Hydrochloride and Sulphate salts if known).

| Compound | Vapor Pressure @ 25° Celsius In Pascals | Melting Point (°C) Base / Hydrochloride / Sulphate | Boiling Point (°C) Of Typical Contraband Form |
|-----------------|--|---|--|
| THC | < .1 | 160 / / | 390.5 |
| Methamphetamine | < .1 | 2 / / | 215.5 |
| Morphine | < .1 | 197 / 200 / 250 | (Decomposes before Boiling) |
| Heroin | < .1 | 159.85 / / | 492.9 |
| Cocaine | < .1 | 89 / / | 395.2 |

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Sources:

- 1) ChemSpider, Royal Chemical Society, <http://www.chemspider.com>
 - 2) Technical Support Document: Toxicology. Clandestine Drug Labs: Methamphetamine. California Office of Environmental Health Hazard Assessment. Sept. 24, 2003. (Exhibit J)
 - 3) Determination of cocaine and heroin vapor pressures using commercial and illicit samples. Dindal et al., Oak Ridge National Laboratory, Chemical and Analytical Sciences Division,
 - 4) Merck Index 13th ed. 2001. (Exhibit C)
 - 5) CRC Handbook of Chemistry and Physics, 91st Edition, Section 6. (Exhibit B)
- Or calculated from data contained therein.

One example of a Chemical that has a Vapor Pressure but no odor is Helium. Helium boils (reaches a vapor pressure of one atmosphere at sea-level), at a temperature close to absolute zero, (-459.67 Fahrenheit). It is a gas at room temperature. But, because Helium reacts with nothing on Earth under natural conditions, it may be fairly safely conjectured that Helium could not have any "odor" to any living being. It may be impossible to prove, but is a reasonable conjecture based on Chemistry because odor is not just a product of vapor pressure but also chemical reactivity as described below.

VII) Chemical Reactivity and Odor

Vapor Pressure affects the concentration of an evaporating substance in a surrounding gas, and in that regard how strong an odor may be. Chemical reactivity must also be taken into consideration regarding odors. Strong acids, halogens and ammonia are all considered highly chemically reactive in that they will react with almost anything one is likely to find on Planet Earth. And likewise, these chemicals will typically permanently alter or destroy whatever they react with. Compounds that can be assimilated, or metabolized by the chemical reactions of living beings may be considered less reactive because they do not typically destroy or permanently alter the molecules of the living being they come in contact with. The significance is that if something can be smelled at all, it implies there is some chemistry taking place. However, chemicals like Hydrochloric and Sulphuric acids, Iodine and Ammonia have very strong odors, and cause irritation and watering of the eyes and nose, choking and even death at relatively low concentrations in air, as a result of their high reactivity, and humans experience an odor-masking effect as a result. Almost anything

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Humans are capable of smelling can be masked by a small amount of Iodine, Ammonia, Hydrochloric or Sulphuric acids. If the Court chooses to consider the sense of smell of a Canine as being analogous to that of humans, one must take into account the presence of these highly reactive compounds as they may exist in illegal chemically-processed drugs, and whatever masking effect it may have a concurring drug-compound, presuming that the drug compound was capable of evaporating at all.

Respectfully Submitted to This Court, This _____ Day _____, 20____.

Mr. Piero A. Bugoni, Amicus.

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Certificate of Service:

Copies of this Treatise have been sent by United States Mail, on _____ to:

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