Review

Air Quality in Auto-Cabin

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Abstract

Air quality in auto-cabin is reported from various viewpoints including recent trends.

Regarding the volatile organic compounds in the auto-cabin, the generating mechanism, method of measurement from within the auto-cabin, method of analysis, method of measuring from the parts, etc. are introduced. Regarding the odor, the generating mechanism, masking function, relation with humidity, etc. are introduced along with the characteristics of the human sense of smell. In addition, the importance of ventilation of the air in the auto-cabin is discussed.

Keywords Air quality, Volatile organic compounds, Odor, Ventilation

1. Introduction

It has been 5 years since the author last reported on the air quality in auto-cabin in a 1998 R&D Review Toyota CRDL.[1) Since that time, people's concern on the subject has undergone a dramatic change. Back in 1998, various standards and a number of research papers were published, but the degree of general concern on the matter remained at a low level. In June 1997, then Ministry of Health and Welfare established indoor guidelines for formaldehyde to prevent sick-building syndrome (SBS). The WHO (World Health Organization) and many overseas governments had already established their guidelines for formaldehyde at the same concentration.

The guidelines for 13 compounds as presented in **Table 1** were established later before 2002.[2) At the same time, newspapers, televisions and other mass media began to report on the matter more frequently, subsequently forming greater public concern on the problems of chemical contamination on indoor air quality. In wider interpretation of SBS, sick-house syndrome is called the entire syndrome caused by indoor environmental pollution in Japan.

Moreover, the air quality in auto-cabin has been drawing attention for several years from the same standpoint as on the indoor air quality in buildings and houses. Accordingly, various researchers began to investigate the chemical contamination problems of the indoor climate close to home and disclosed the data of their measurements. When these results were reported, the number of cases seen as problems increased dramatically. It should be noted, however, that these figures were leaked unintentionally, usually without disclosing the measuring conditions or method of analysis.

Under the circumstances, Toshiro Matsumura, Japan's forerunner in chemical substance measurement of indoor air quality and developer of various analytical methods since 1980s, reported detailed measuring data. The measurement data given in his research reports indicated a high level of knowledge and skill with respect to measuring chemical substances in the air.[3) Also gleaned from this data was the knowledge that chemical concentration varies much by the measuring environment. Successive measurements by the authors over a week under the same conditions indicated over 10 times as many variation of concentration.[4) Due to the fact that measuring conditions affect the measurements more greatly inside an auto-cabin than inside a building, care should be taken at various points.

This paper reports the content of studies the author have made thus far concerning the air quality in the auto-cabin, simultaneously discussing his viewpoints on the subject.

2. Volatile organic compounds (VOCs)

2. 1 Current situation

Volatile organic compounds (VOCs) constitute most of the chemial pollution found in indoor climate and pose a problem that is currently drawing attention. Similarly, VOCs pose a major problem to the auto-cabin.

Conventionally, people enjoyed the odor of VOCs as that of a new vehicle. It was one of the factors that pleased purchasers of new vehicle. In recent days, with the change of times, increasing number of people dislike the odor. In the indoor climate of the auto-cabin, such a VOCs concentration can

Table 1 Guideline value by Ministry of Health, Labour and Welfare of Japan.

Volatile Organic Compound	Guidieline value (μg/m^3)	Established day
Formaldehyde	100	1997.6.13
Acetaldehyde	48	2002.1.22
Toluene	260	2000.6.26
Xylene	870	2000.6.26
p-dichlorobenzene	240	2000.6.26
Ethylbenzene	3800	2000.12.15
Styrene	220	2000.12.15
Chlorpyrifos	1, 0.1 (child)	2000.12.25
Di-n-butyl phthalate	220	2000.12.15
Tetradecane	330	2001.7.5
Di-2-ethylhexyl phthalate	120	2001.7.5
Diazinon	0.29	2001.7.5
Fenoxycarb	33	2002.1.22
TVOC (Total Volatile Organic Compound)	400 (provisional guideline value)	2000.12.15

be easily changed to that of the outside air by opening windows or setting the air conditioning system to "fresh mode." In addition, the VOC concentration in a new vehicle can be reduced to less than 1/100 of its original value within several months of purchase through the opening of doors when entering and leaving the vehicle. Considering the fact that the air conditioning system of most of the vehicles driving in urban areas is set to recirculation mode, it is necessary to reduce VOCs in the auto-cabin as it is in a building. VOCs indicated here is one of the following three types:

VVOCs (Very Volatile Organic Compounds)
VOCs (Volatile Organic Compounds)
SVOCs (Semi Volatile Organic Compounds)

These compounds all vaporize in air.

2. 2 Source mechanisms and measures

Compared with indoor air, VOCs in auto-cabin air have are numerous, counting in the hundreds. For example, many types of sulfur compounds originating from vulcanizing agents and amine compounds for the hardening catalysts exist in the auto-cabin climate due to the urethane foam and rubber materials popularly used for interior trim material.

In addition, solvents such as toluene, ethylbenzene, xylene, tetradecane, etc. to which guideline values are given also exist. Since these solvents are originally used as mixture, however, any single one alone does not have a high concentration in the auto-cabin. In other words, if a high concentration of tetradecane is detected, decane, undecane, dodecane and their isomers are likely to be detected in large numbers.

Diffusion of these VOCs is greatly affected by the cabin temperature of vehicle. Around 25°C, the concentration level is 100 ppb with passengers riding. This level can reach dozens of ppm in a new vehicle parked under the scorching sun. Depending on the component, humidity may greatly affect the diffusion of VOCs.

Generally speaking, the diffusion behaviors of these VOCs resulting from the interior trim material are classified into two types. One type is found with solvents used for paint materials and adhesives. Upon application, these components vaporize rapidly, and are thus called vaporization rate controlled components. The other type is found in additives, unreacted components, etc. Diffusion behaviors of these components depend on the rate of diffusion in the materials and are thus called diffusion rate controlled components. This kind of component diffuses over an extended period of time. These classifications are made for the sake of convenience, but they are the basis for understanding diffusion behavior and taking necessary countermeasures.

Actual diffusion behavior, however, strongly reflects the application method of the chemical substance and chemical characteristics. For example, toluene, used as a solvent for part surface coating materials, is a vaporization rate controlled component. However, when used as a solvent for the adhesive agent between the door-trim surface material and the base material in multi-layer molds, toluene acts as a diffusion rate controlled component. The same component can show different behavior depending on the application method.

In addition to the application method, chemical characteristics of the component greatly affect diffusion behavior. Toluene is a substance having high vapor pressure with a boiling point at 111°C. Being a nonpolar compound chemically, it is difficult to readsorb once vaporized. Therefore, it is always detected, even if the auto-cabin has low temperature or high humidity. Compounds that are chemically polar or easily polymerized show different diffusion behavior from toluene. Formaldehyde is one of these compounds. It is chemically polar, has high affinity with base materials such as pulp, and its diffusion rate is low inside of materials. In addition, if vaporized, it becomes readsorbed as the cabin temperature drops or the humidity varies. This re-adsorption is called the sink effect.

Therefore, the key for chemically polar compounds with major sink effect, additives and unreacted components in the material is to reduce from raw materials. On the other hand, ventilation and/or aging are effective means for reducing VOCs from components having minor sink effect or vaporization rate controlled components. This concept is like that of house where improvement of materials and ventilation are the basic means of VOCs reduction. Generally, post treatment techniques often prove ineffective in reducing those components. In the case of an adsorption type component, it becomes saturated within a short span of time, causing an odor problem as described later on. Even with a reactive type component, a considerable amount of energy is required to decompose macromolecular components such as SVOCs, making onboard application impractical.

2. 3 Measuring method of the air in auto-cabin

Japan has no uniform method established regarding the measurement method for air in the auto-cabin. This section outlines the method the authors are using.

As the preparation for the measuring, it is necessary to close the vehicle windows and doors completely and then turn on and set the air conditioning system to recirculation mode. **Figure 1** shows the sampling of the air in the auto-cabin.[5)] For sampling, Teflon tubing (10 dia.) is used and small length of silicon tube is used for the joints. Sampling is primarily performed outside the vehicle. The Teflon tubing is led outdoors from the upper corner of the door. The tube deforms due to this, but it does not affect sampling. Also, the deformation of the door weather strip rubbers shut off the auto-cabin completely from outside. The Teflon tube is reused after being cleaned with pure nitrogen gas. The silicon tube is disposable. In Europe, a stainless steel tube heated to about 40°C is used in fear of possible adsorption caused by the lowering of the temperature.

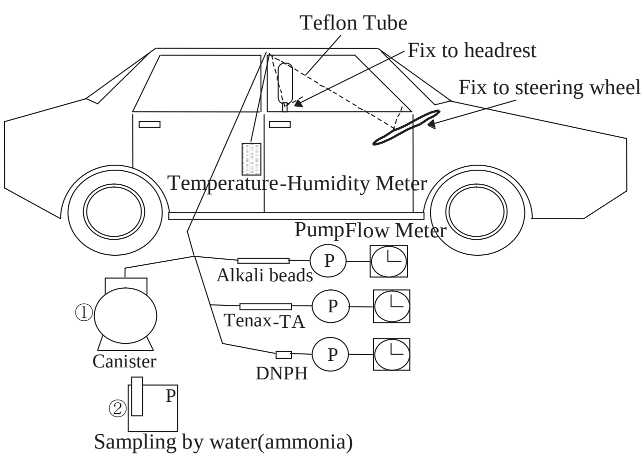

Fig. 1 Gas sampling

Even in light of this argument, it is believed that Teflon tube will do fine if several liters of the air are extracted from the auto-cabin before sampling. The air in the auto-cabin is generally heated with infrared lamps, each installed on the front and rear glass surfaces. Similar to Europe, measuring is conducted under various cabin temperature conditions of the vehicle with a maximum temperature of 65°C. To obtain correct VOCs diffusion, it is necessary to measure the ventilation of the auto-cabin. When the test vehicle becomes pressurized because of the rise of the cabin temperature, extra air is purged through a valve system installed to the vehicle. Also, the amount of ventilation differs depending on the use of the air conditioner. Since it is quite difficult to measure ventilation on individual vehicle models, sampling is actually conducted under a set condition. In consideration for the test scale for the day, sampling is generally made two hours after the cabin temperature has reached a constant level.

2. 4 Method of analysis

As stated in the preceding report, the authors use the U.S. Environmental Protection Agency's Toxic Organic Method (TO method) for analysis.[6)] It utilizes the TO-1 method, using Tenax-TA for adsorbent, the TO-16 method, using a special surface treatment canister, and the TO-11 method, using a DNPH (Dinitrophenylhydrazine) carrying silica cartridge. The analyzing systems are GC-MS (Gas Chromatograph-Mass Spectrometer) and HPLC (High-Performance Liquid Chromatography).

VOCs analysis method with Tenax-TA and aldehyde analysis method using DNPH cartridge are adopted in Europe. They are international methods for analyzing many and unspecified components. Naturally they are official method of analysis for sick-house in Japan.

The authors use both the canister and Tenax-TA to acquire the breakthrough data of Tenax-TA as the analysis method of VOCs. Breakthrough refers to a phenomenon in which VOCs in the air pass through the adsorbent without being arrested. It is difficult to obtain accurate analytical values from the air in the auto-cabin where VOC components of some several hundred types exist and the temperature and humidity change drastically. To cope with this, the analytical values from both methods are examined constantly for comparison. While Tenax-TA has good characteristics for analyzing wide range of substances, it requires caution for degradation. As a Poly 2,6-Dipheyl-p-Phenylene Oxide, Tenax-TA is degraded by its own decomposition byproducts and adsorbed substances. On the other hand, the canister can make accurate analysis of heptane and hexane, etc., but has difficulty in analyzing water-soluble components and SVOCs, etc. As thus far described above, it is also necessary to understand the characteristics of analytical methods to increase accuracy of analytical results.

In addition to the above, to prevent breakthrough of Tenax-TA, we use sampling glass tube filled with 500 mg of Tenax-TA. This volume is several times that of the commercial product. The DNPH cartridge is also accounted for by using long types.

The next problem concerns residual contaminant on the analysis system. Through thermal desorption from Tenax-TA to GC-MS, many units have the transfer lines installed. Subsequently, tetradecane, phthalic acid ester and other SVOCs remain between them. Thus care must be taken with the residue and blank test must always be conducted. In addition, since sensitivity of GC-MS changes greatly depending on the contamination of ion source and/or leakage, it is also necessary to constantly measure the standard sample. The sensitivity also changes by substance. For the standard sample, it is better to use the standard gas for toxic air contaminant in mixture of 44 or 58 components.

Incidentally, the analysis of specific individual components such as lower fatty acid compound, lower amine compound, lower sulfur compound and so forth, the official method of analysis for the Offensive Odor Control Law of Japan is used. In addition, it is possible to refer to the list of methods of analysis of 189 toxic air pollutants in the Clean Air Act of the United States.[7)]

2. 5 Method of measurement from parts and materials

To reduce VOCs from the auto-cabin, it is necessary to measure VOCs evaporation from the parts and materials. German automotive manufacturers have the established Automobile Industry Standards (Verband der Automobil-industrie). For the measuring method of samples of several milligrams to several grams, they adopted the Head Space method and Gerstel's thermal desorption unit. For aldehyde, they adopt a method using a glass bottle. This method is similar to the desiccator method used in Japan.

Automobile parts characteristically emit various components from VVOCs to SVOCs. This is due to the large number of multi-layer moldings, surfaces covered with polymeric material sheets and sources. Therefore, the above-mentioned minor tests pose the problem of being unable to understand exact state of vaporization.

To compensate for this disadvantage, VDA276 establishes a test method using a 1m^3 chamber.[8)] This method is essential in measuring accurate evaporation from the parts. Since the chamber method is accompanied by a problem of effect from pollutants and environment, however, a measurement time of 2 to 3 days is required per sample per unit of measuring equipment.

As a simple method, there is a method using a bag. This method can measure VOCs and aldehydes at the same time, and a number of samples simultaneously.

Conversely, this method has disadvantage of lower accuracy because of evaporated components from the bag and environmental problems. Since parts are manufactured in various factory environments, they adsorb various types of VOC components present in the workshop. With consideration given to these effects, the authors believe that the simple method can fully serve the purpose.

3. Odor

3. 1 VOC components in auto-cabin and odor

As stated earlier, vaporization rate controlled components consisting mainly of solvent are rapidly reduced. Depending on the environmental and service conditions, it is reduced to 1/100 of initial value within several months in summertime. On the other hand, the initial value of diffusion rate controlled components remains almost unchanged after several months of evaporation. As the result, in terms of concentration, diffusion rate controlled components exceed the vaporization rate controlled components. **Figure 2** shows a schematic diagram of the above-mentioned state of reduction. The vertical axis represents concentration and the transverse axis, passage of time. In terms of component, toluene, xylene and other aromatic hydrocarbons and high volatile ammonia and amine reduce rapidly, and the higher amine, higher alcohol, higher aldehyde, etc. contained in the materials are constantly vaporized. At the same time, components from passenger's body odor and favorite foods brought onboard increase. By component, aldehyde having about 4 and over number of carbon, limonene as perfume, p-dichlorobenzene as insecticide, etc. will be detected.

The human sense of smell adjusts itself to VOC components of a new vehicle (by fatigue or adaptation) and time passes without them noticing variation in the VOC components.[9, 10] Some people, however, can sense odors that are different from conventional ones as the result of an increase in the ratio of diffusion rate controlled components and human body odor components. If a person has aversion to this odor, odor becomes a problem. Generally, threshold value of human sense of smell is small compared to components having lipophilic property and some minor hydrophilic property. For example, butyric acid and isovaleric acid, etc. have standard threshold values of several ppb. After several months, the odor components of the diffusion rate controlled components having medium to high boiling points plus human body odor, etc. become blended. The odor is generally expressed as that of soiled socks, the smell of a dust cloth, the stench of decay and so forth. The concentration

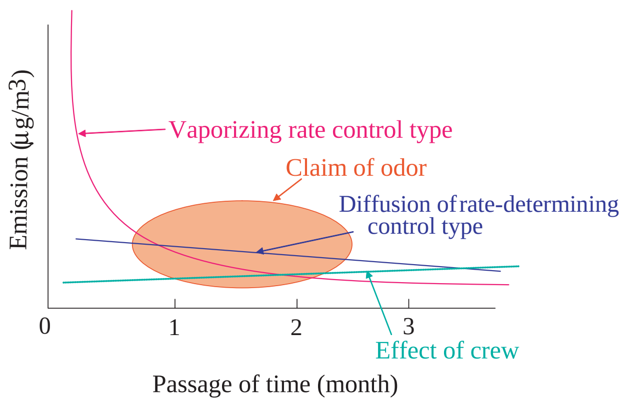

Fig. 2 Happened claim of odor.

level of VOCs in this case is below 1/100 of the initial value, but human sense of smell can still detect it. The sense of smell differs much by individual and concentration varies by 10,000 fold. Therefore, the odor problem does not occur for every person. At present, the functional mechanism of human sense of smell to complex odor mixtures remains almost totally unclear,[11] and it is yet to be solved which combination of components in the cabin stresses an offensive odor.

3. 2 Masking function

Used since ancient age, masking of odor with perfume is indispensable for today's living. Thus limonene, acetophenone and other perfume components are always detected from inside the auto-cabin where the masking was applied as a result of masking offensive odor with perfume. Wolkoff, et al. reported, however, possible generation of substances causing sick house syndrome through the reaction between terpene and ozone present in the indoor.[12] Chemically, ozone is a substance that breaks the sigma-bond by adding itself to unsaturated bonds.[13] Since higher concentration of ozone is present naturally in the auto-cabin than in the house, there is high possibility of generation of substances causing the sick house syndrome. Applying large quantity of perfume in the auto-cabin accelerates the risk. It should be considered that perfume is a chemical substance, and full caution should be taken for the concentration exposed. The notion does not hold good that perfume is safe because it is natural chemical substance. Limonene too is a natural carcinogen, and it may possibly form formaldehyde and other irritating substances upon reaction with ozone. In addition, styrene having unsaturated bond makes similar reaction. Naturally, these are essential components for reduction.[14]

A masking function is also found in new vehicle. Of the vaporization rate controlled components, vehicles having large quantities of aromatic hydrocarbons are assessed as having more comfortable odor than vehicles having less aromatic hydrocarbons. Apparently, the effect of masking using aromatic hydrocarbons (odor of thinner) has been recognized.[15]

As shown in Fig. 2, there is some concern in reducing only aromatic hydrocarbons to reduce VOCs as it may increase the problem of odor instead. Therefore, VOCs including odorous substances of high boiling points should be reduced across the board.

Besides, we have to remember the characteristics of the sense of smell we often experience during a sensory assessment of odor. One of them is that odor becomes habitual to the sense of smell. Compared with people in general, developers of diesel engine and materials always assess odor as one rank lower if it is a conventional odor of the same type. Considering that the sense of smell is on a logarithmic scale, this represents quite a large difference in concentration. Another characteristic is a psychological problem. When others claim offensive odor in repetition, one starts sensing it psychologically. Accordingly, sensory assessment should basically adopt a single blind test by people in general.

3. 3 Humidity

Characteristics of human sense of smell for offensive odor change largely by the condition of humidity. The degree of offensiveness tends to increase under high humidity. **Figure 3** shows the result of an odor assessment test using inorganic powdered reagent.[16] The result indicates a strong sense of odor from the inorganic reagent as the result of humidification. In the background of this test, we can suppose that the degree of offensiveness increases by humidity and that humidity increases the quantity of inorganic reagent that reaches the human olfactory cells. At any rate, considering the fact that the sense of smell is on the logarithmic scale, we can state that the degree of offensiveness rises by humidity. This phenomenon is recognized with offensive odor emitted immediately after turning on an air conditioner. When the engine stops in an automobile, odorous components and humidity that have condensed inside the air conditioner and/or evaporator fill up the ducts. These substances are discharged simultaneously when the air conditioner is turned on, subjecting the passengers to an unpleasant, musky smell. In this case, measuring the chemical components in the discharged air indicates several times the concentration while the components themselves remain almost unchanged. Considering from this point as well, the authors are confident that humidity increases offensive odor.

3. 4 Other, importance of ventilation

Various chemical substances flow in to the auto-cabin from the driving environment. They mostly consist of exhaust gas components. Many people dislike the exhaust gas components of diesel-powered automobile. Therefore, as stated previously, the air conditioning system of the vehicles driving urban areas is mostly set to recirculation mode. When set to this mode, CO_2 concentration exceeds 5,000 ppm due to the crew's own exhalation as shown in **Fig. 4** depending on the vehicle type and the number of passengers.[17] An example of our examination results will be given about the effect of this CO_2 concentration on driving. The vertical axis in **Fig. 5** represents the apparent ratio of α brain wave and the transverse

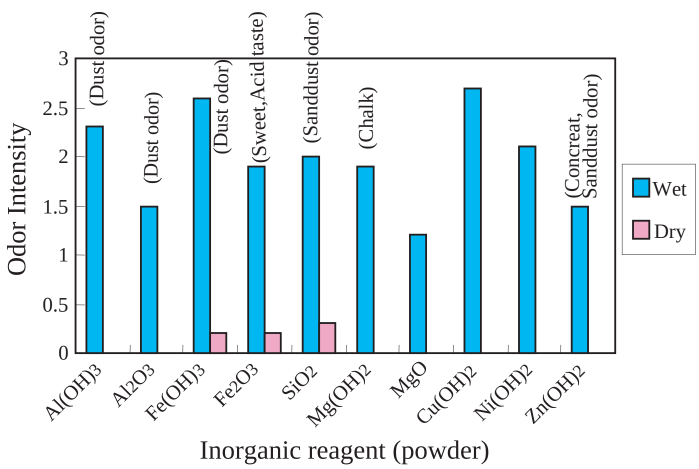

Fig. 3 Effect of humidity.

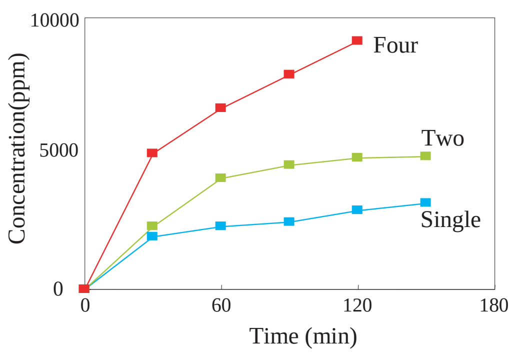

Fig. 4 Change of CO_2 concentration (recycle mode, idle).

axis, the test time. As Fig. 5 is self-explanatory, the apparent ratio of α brain wave rises in the air containing CO_2 concentration of 10,000 ppm, indicating that the crew tends to be in a careless state. Success in a simultaneously conducted collision evasion game also dropped, indicating the importance of ventilation.

Recently, vehicles with devices for automatically selecting the air inlet mode according to the information provided by the hydrocarbon sensor and NO*x* sensor, etc. have been increasing. The air quality in this type of vehicle has reached the level of the atmosphere, proving that the device is an effective method for improving the air quality in the auto-cabin. People still sense the odor of exhaust gas because of the difference between the sensor information and the human sensing characteristics of smell. In addition, there is a possibility of an odor problem when outside air is inlet while the crew's sense of smell is adjusted to the air inside the cabin. Human sensing characteristics of smell should be also given full consideration in this case.

4. Future trends

Improving the air quality in the auto-cabin is important for the reduction of volatile organic compounds and it is an area that will advance in the future. In the author's opinion, the improvement of the air quality in the auto-cabin will be developed from the viewpoints of passengers' improved safety, health and recovery from fatigue.

It is believed that clarification of various characteristics including that of the human sense of smell are necessary for improvement to proceed. In handling odor problems, is perfume-masking really a good solution? Will eliminating germs from the air in the auto-cabin lead to a safety and comfortable driving? These are additional problems that require wide-ranged study on the effect on human beings.

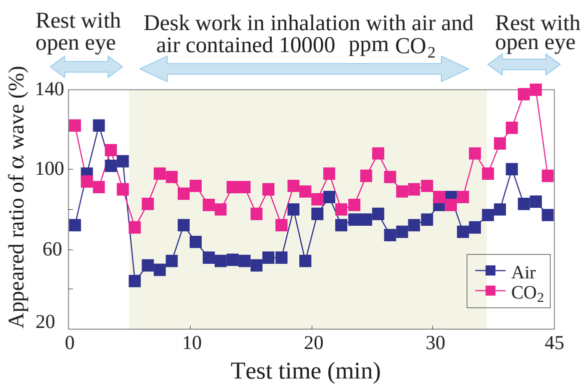

Fig. 5 Appeared ratio of α brain wave.

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