Development of Low VOC-Emission Products and Analyses of Emitted VOCs and Aldehyde

*Fumiha Aoki *, Kenji Iizuka *, Mariko Wakae *, and Atsushi Higashiura **

ABSTRACT There is worldwide demand to reduce volatile organic compounds (VOCs) such as toluene and xylene as well as aldehyde such as formaldehyde. These compounds are emitted from building materials, vehicle cabin components, or home appliances, and cause a health hazard.

We have attempted to reduce VOC and formaldehyde emission from our product line-up related to building materials, automotive, electrical, and electronic equipment. This report introduces our product developments for low VOC emission, sensitive analyses through the collection and concentration of emitted VOCs and aldehyde in the respective product groups, and a simplified VOC analysis at the development stage. In addition, we mention the grasped points of these analyses.

1. INTRODUCTION

Table 1 shows the guideline values for a concentration of chemical substances in the indoor atmosphere [1] released by the Ministry of Health, Labor and Welfare. This was presented in response to the outbreak of sick building syndrome which became a social problem in the 1990s, and with an aim to reduce chemical substances in the indoor atmosphere. The amended Building Standards Law regulates formaldehyde emission [2), 3)] (Table 2), and the "Standards of School Environmental Sanitation" [4] makes inspections on formaldehyde and toluene mandatory. Furthermore, the Japan Automobile Manufacturers Association, Inc. (JAMA) self-regulates VOC in the vehicle cabin [5] and the Japan Electronics and Information Technology Industries Association (JEITA) does in similar way personal computers [6]. The respective industry segments have thus formulated their own measuring methods for VOC and aldehyde emission.

We have developed analysis techniques on VOC and aldehyde emission in order to achieve lower VOC emission for our products.

Table 1 **Guideline values for concentration of chemical substances in indoor atmosphere by Ministry of Health, Labor and Welfare.**

Chemical substance	Guideline value for concentration in indoor air (μg/m^3)	Main usage (Emission source)
Formaldehyde	100	Plywood, adhesive
Toluene	260	Adhesive, paint
Xylene	870	Adhesive, paint
Paradichlorobenzene	240	Insect repellent
Ethylbenzene	3800	Heat insulation material, paint, floor material
Styrene	220	Heat insulation material, paint, floor material
Chlorpyrifos	1	Termite insecticide
Di-n-butylphthalate	220	Plasticizer for PVC
Tetradecane	330	Adhesive, paint
Di-(2-ethylhexyl)phthalate	120	Plasticizer for PVC
Diazinon	0.29	Termite insecticide
Acetaldehyde	48	Plywood, adhesive
Fenobucarb	33	Termite insecticide
(Nonanal)	Interim target 41	Plywood, adhesive
Total Volatile Organic Compounds (TVOC)	Interim target 400	

Table 2 **Classification and regulation for formaldehyde emission from building products by the Building Standards Law.**

Emission factor μg/(m^{2}h) *	JIS symbols for indication	Area limit of building materials
Less than 5	F☆☆☆☆	No limit
5-20	F☆☆☆	With area limit
20-120	F☆☆	With area limit
Over 120	No indication	Banned

* Refer to the definition of emission factor in Table 6.

* Ecology & Energy Lab., R&D Div.

2. OUR PRODUCTS AND MEASURING METHODS OF VOC AND ALDEHYDE EMISSION

Table 3 summarizes our product line-up on which we strive for the reduction of VOC and aldehyde emission as well as relevant analysis methods.

Table 3 Summary of our product line-up involved with reducing VOC and aldehyde emission and analysis methods specified in each field.

Product	Field	Measuring method of VOC and aldehyde emission
Fireproof putty for building ductwork Interior wiring products	Building materials	JIS A 1901 Small chamber method
Wire harness Steering roll connector	Vehicle cabin components	Sampling bag method JASO M902 Method by respective companies Closed chamber method
Heat conductive parts Electromagnetic shielding material	Electrical and electronic equipment	JIS C 9913

For building materials and electrical and electronic equipment, Japan Industrial Standards (JIS) specifies measuring methods of VOC and aldehyde emission under the assumed temperature, humidity, and ventilation for indoor environments [7), 8)]. As for vehicle cabin components, measuring methods specified by automotive manufacturers are classified into two methods: sampling bag method and closed chamber method. However, the society of Automotive Engineering of Japan (JASO) adopted the widely used sampling bag method as the industry standard [9)]. Table 4 is a compendium of sampling test conditions.

Any of the testing methods are performed using the equipment shown in Figures 1 through 3. Figure 4 shows a schematic of sampling and analysis.

For the emission test (small chamber method), VOCs and aldehyde are analyzed in the process shown in Figure 4 (a) with the instrument shown in Figure 1.

For the sampling bag method, VOCs and aldehyde are analyzed in the process shown in Figure 4 (b).

After VOCs are collected in a Tenax tube, they are analyzed and measured by thermal desorption-gas chromatograph/mass spectrometer (GC/MS) shown in Figure 2. For highly volatile and unstable aldehydes, they are derivatized right after they are collected in a DNPH cartridge. And then aldehyde-DNPH derivatives are extracted with acetnitrile, and analyzed with a High-Performance Liquid Chromatograph (HPLC) shown in Figure 3.

Figure 1 Emission test instrument.

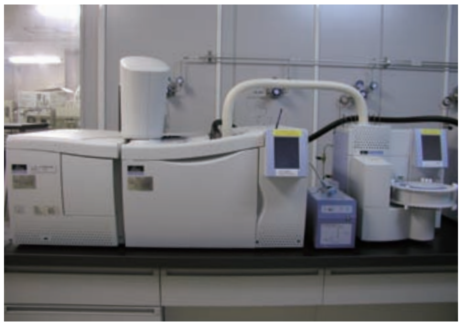

Figure 2 Thermal desorption-gas chromatograph/mass spectrometer for analysis of VOCs.

Figure 3 HPLC for analysis of DNPH-aldehydes.

Table 4 Compendium of testing conditions for sampling VOCs and aldehyde from products.

Product group	Testing method	Temperature (℃) Humidity (% R.H.)	Air exchange rate (times/h)	Sample amount or product loading factor
Building materials	JIS A 1901	28℃, 50% R.H.	0.5	2.2 m²/m³
Vehicle cabin components	Sampling bag method JASO M902 Respective companies' method	65℃ e.g., 65℃	NA	Surface area: 100 cm² e.g., 80 cm²
	Closed chamber method	65℃	NA	Equivalent of 1/100 unit or 1 unit
Electrical and electronic equipment	JIS C 9913	23℃ (28℃ Ok) 50 % R.H.	0.5 or 1	0.01 < (Volume of measured equipment / Volume of chamber) < 0.25

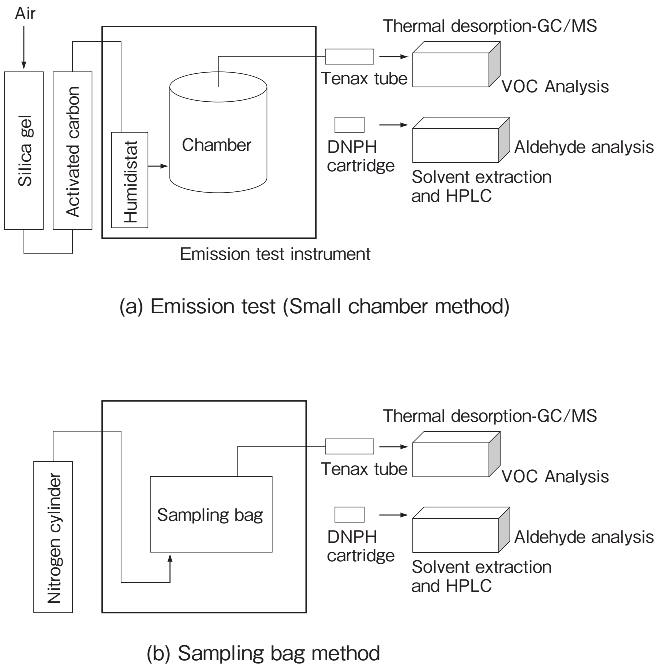

Figure 4 Schematic of emission test, sampling and analyses.

The aforementioned analyses, using a sampling tube and a DNPH cartridge for collecting and concentrating emitted VOCs and aldehyde, feature high sensitivity. However, they are time-consuming analyses going through test preparation, respective sampling operations, and analyses for VOCs and aldehyde.

3. SIMPLIFIED VOC ANALYSIS: HEADSPACE METHOD

Compared with the JIS or JASO methods, the VOC analysis by Headspace auto sampler (Figure 5) is a simple and brief method.

In the Headspace method (HeadSpace, HS), a headspace vial (Figure 6) containing a sample is sealed and heated to introduce a portion of vapor phase including the generated gas into an analytical column.

But emission of VOCs is not quantitatively evaluated by the Headspace method (as explained in Section 8. (5)).

Figure 5 Headspace auto sampler.

Figure 6 Headspace vial.

4. DEVELOPMENT OF FIREPROOF PUTTY FOR BUILDING DUCTWORK (BUILDING PRODUCTS)

4.1 Target Specification for Development

Fireproof putty for building ductwork is applied to the gap of pass-through cables and bus ducts in the houses. In the event of fire, its thermal expansion blocks up and prevents the fire from spreading. It also shows excellent performance in sound insulation. In addition to improvements of conventional features such as lighter weight and better thixotropy (no drooping after application), we decided to challenge the issue for lower VOCs and formaldehyde. We set our target specification: F☆☆☆☆ for formaldehyde and the equivalent level to F☆☆☆☆ for four VOCs [10]. This is shown in Table 5.

Table 5 Target specification for development.

	Notation or code of building materials	Emission factor (μg/(m^{2}h))*
Formaldehyde	F☆☆☆☆	5 or below
Toluene	T	38 or below
Xylene	X	120 or below
Ethylbenzene	E	550 or below
Styrene	S	32 or below

* Refer to the codicil for emission factor in Table 6.

As a result of evaluation by the official method of JIS A 1901 (small chamber method), the toluene emission factor substantially exceeded the target value in our first prototype (No.1), necessitating reduction measures. Through HS-GC/MS measurement, we found that raw material A accounted for the cause of toluene.

Next, prototype evaluation was made on a toluene-controlled sample (No.2) using raw material as an alternative to A. The result was successful and we could clear the target.

With an example of development for fireproof putty, we describe the analysis of VOC and aldehyde emission from building materials by JIS A 1901 and simplified VOC analysis of raw materials by Headspace GC/MS measurement.

4.2 JIS A 1901 Small Chamber Method

4.2.1 Flow of Measurement

Figure 7 [11] shows a flow of JIS A 1901 “Determination of the emission of volatile organic compounds and aldehydes for building products - Small chamber method” (2003). Table 6 describes the important terms of the emission tests.

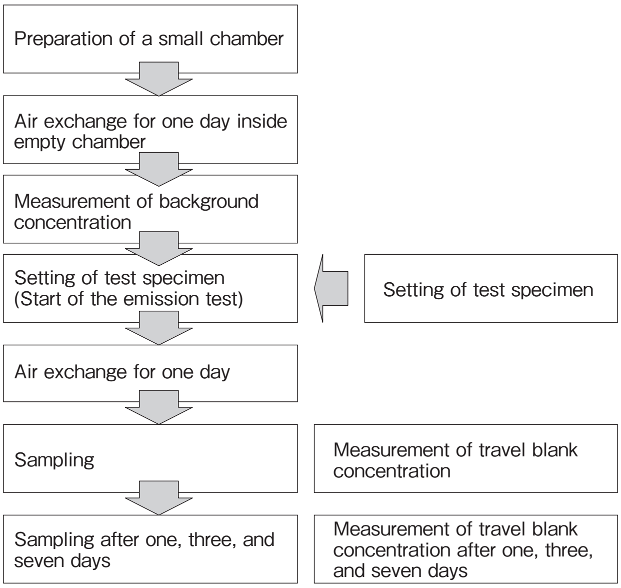

Figure 7 Flow of JIS A 1901.

Table 6 Key technical terms and the definitions.

Emission factor

This is a mass of VOC, formaldehyde, and other carbonyl compound emission per unit time during the specified time from the start of test. Since building materials such as flooring materials and wallpapers to be the subject of JIS A 1901 are used per unit area, the emission factor is expressed in the mass per unit time and unit area. The unit is $\mu g/(m^2h)$.

Codicil: Following F☆☆☆☆ (read as "formaldehyde four stars") in the formaldehyde regulation of the Construction Standards Act, a VOC emission factor standard equivalent to F☆☆☆☆ has been specified for four VOCs (toluene: T, xylene: X, ethylbenzene: E, styrene: S) [10].

Air exchange rate

This is a value obtained by dividing air volume supplied to the small chamber per unit time (ventilation rate) by chamber volume. The unit is times/h.

Codicil: 0.5 time/h of air exchange rate means half of the ambient atmosphere inside the chamber is exchanged with fresh air every hour. In the case of a 20-liter chamber, 10 liters are exchanged and the air exchange flow requirement will be 166 ml/min (20,000 ml x 0.5 = 10,000 ml = approx. 166 ml/min x 60 min).

Product loading factor

This is a ratio of the small chamber volume to the surface area of the test specimen. The unit is m^2/m^3. When comparing the results obtained from different small chambers, the product loading factor and air exchange rate must be under the same conditions because they may affect emission factors.

Codicil: The product loading factor must be set at 2.2 m^2/m^3. In the case of a 20-liter chamber, it can be obtained by making the product surface area 440 cm^2 (0.044 m^2 / 0.02 m^3 = 2.2 m^2/m^3) with two sets of squares with 147 mm sides, placed vertically (147 cm x 147 cm x 2 = 432 cm^2).

4.2.2 Setting of Test Specimen

Set the test specimen in the seal box exposing the emission measurement face (Figure 8), and set the box in 20-liter chamber with a support (Figure 9). The product loading factor is required to be set at 2.2 m^2/m^3 (see Table 6).

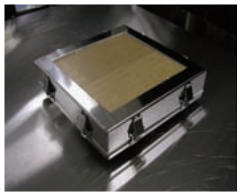

Figure 8 Seal box set.

Figure 9 The sets in chamber.

4.2.3 Emission Test

Set the inside of 20-liter chamber at 28°C 50% R.H. and air exchange rate of 0.5 time/h (reference; Table 6 Air exchange rate), stabilize for 30 minutes and start the emission test. Figure 10 shows the inner view of the emission test instrument.

The emission test generally continues for 7 days and sampling operation is performed after the elapse of one, three and 7 days. (The emission of our prototype (No.1) after the elapse of 7 days exceeded the target, so the test was extended to 30 days.)

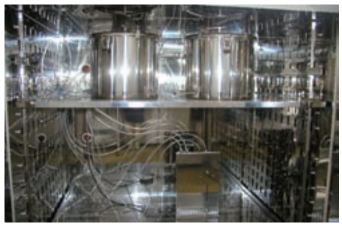

Figure 10 Inner view of emission test instrument.

4.2.4 Sampling Operation

For VOCs, collect 3.2 liters into a Tenax TA tube with a sampling pump (Figure 11).

For aldehyde, collect 10 liters into a DNPH cartridge with a sampling pump (Figure 12).

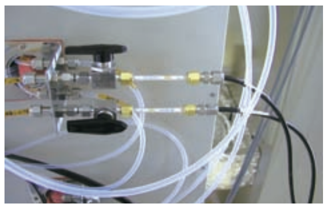

Figure 11 Sampling operation for VOCs into Tenax TA tube.

Figure 12 Sampling operation for aldehyde into DNPH cartridge.

4.2.5 Analysis and Measurement

The Tenax TA tube after sampling is set to the measurement by Thermal desorption-GC/MS.

After acetonitrile extraction of aldehyde-DNPH derivatives in the cartridge, the extract is set to the measurement with a High-Performance Liquid Chromatograph.

4.2.6 Results of the Emission Test for Prototype No.1

Figure 13 shows the total ion chromatograms of VOC emission from our prototype No.1 by Thermal desorption-GC/MS. The results of blank measurement, after the elapse of one day, 7 days, and 30 days of emission tests are shown in this order. The result shows that VOC emission is decreasing day by day. Toluene showed notable detection at 9.2 minutes of retention time.

Table 7 summarizes VOC and aldehyde emission factors of our prototype No.1. Upon the elapse of 7 days, formaldehyde and three VOCs other than toluene achieved the development targets. The emission factor of toluene was measured as 204 μg/(m^{2}h). It failed to achieve the target value of 38 μg/(m^{2}h).

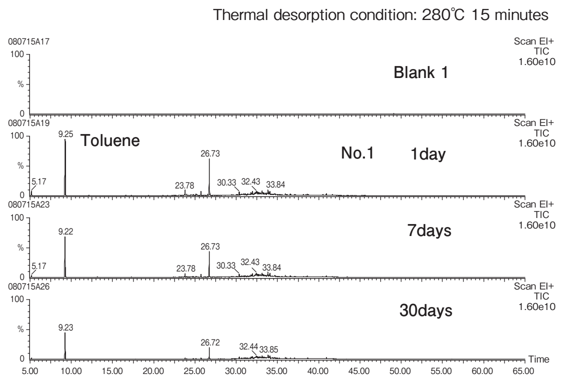

Figure 13 Total ion chromatograms of emitted VOCs from our prototype No.1, by TD-GC/MS.

Table 7 The emission factors of formaldehyde and four VOCs from our prototype No.1.

	Emission factor (μg/(m^{2}h))					
	Target	Measurement results according to JIS A 1901				
	☆☆☆☆	1 day	3 days	7 days	24 days	30 days
Formaldehyde	5 or below	1.4	*	1.0	*	*
Toluene	**38 or below**	**326**	**261**	**204**	**-**	**108**
Xylene	120 or below	0.08	0.06	0.08	-	*
Ethylbenzene	550 or below	0.5	0.4	0.4	-	0.1
Styrene	32 or below	0.01	0.01	0.01	-	*

*: Less than determinate quantity limit -: Not measured

4.3 Results of Simplified VOC Analysis for Raw Materials by HS

Figure 14 shows the results of HS-GC/MS measurement for raw materials A to H. With these results, we could specify the raw material A to be the cause of toluene for our prototype (No.1). In the raw materials B and C, VOCs other than the chemical substances specified in the guidelines for indoor concentration were detected.

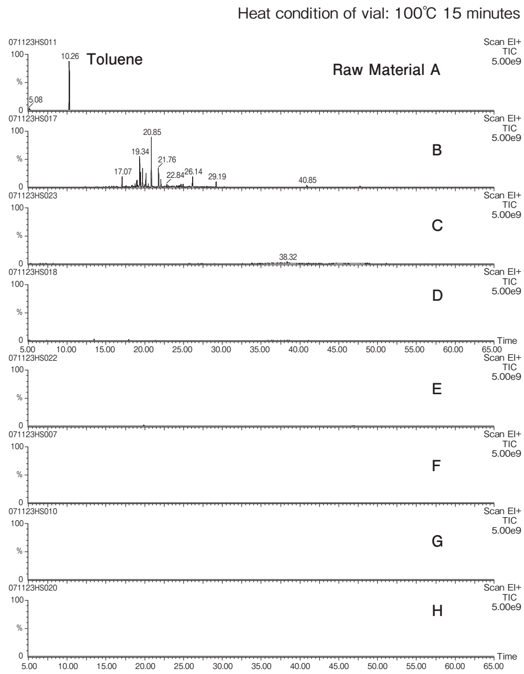

Figure 14 Total ion chromatograms of raw materials of A to H, by HS-GC/MS.

4.4 Toluene-Controlled Prototype (No.2)

Prototype No.2 uses new material for low toluene in place of the raw material A. Figure 15 shows the results of the emission test (total ion chromatograms by Thermal desorption-GC/MS). Table 8 summarizes the emission factors of formaldehyde and VOCs for respective targets. Targets were achieved including toluene.

Figure 16 shows time attenuation of the toluene emission factor.

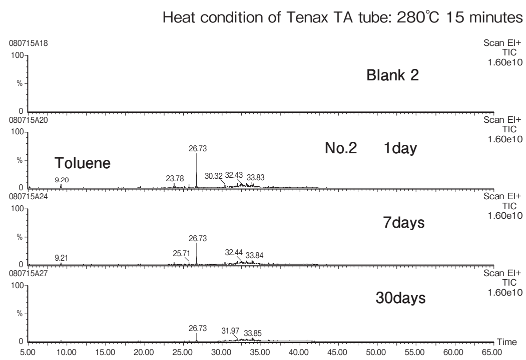

Figure 15 Total ion chromatograms of emitted VOCs from our prototype No.2, by TD-GC/MS.

Table 8 Emission factor of formaldehyde and four VOCs from our prototype No.2 (Toluen-controlled).

Emission factor (μg/(m²h))						
	Target	Measurement results according to JIS A 1901				
	☆☆☆☆	1 day	3 days	7 days	24 days	30 days
Formaldehyde	5 or below	0.84	0.62	0.07	*	*
Toluene	38 or below	17.2	10.6	7.8	-	3.0
Xylene	120 or below	0.34	0.23	0.21	-	0.08
Ethylbenzene	550 or below	0.42	0.31	0.29	-	0.08
Styrene	32 or below	0.07	0.01	0.01	-	*

*: Less than determinate quantity limit -: Not measured

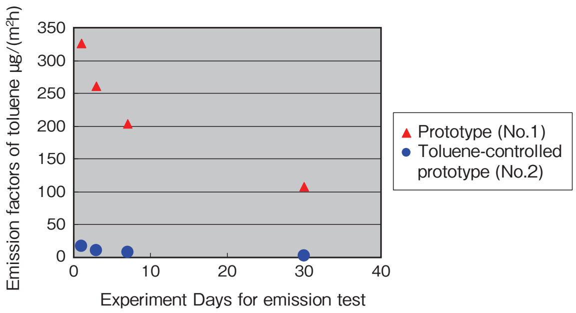

Figure 16 Comparison for emission factors of toluene from our prototype No.1 and No.2.

4.5 Overview for the Development of Fireproof Putty for Building Ductwork

1) Target values were achieved for toluene-controlled prototype No. 2.
2) Further consideration on selection of materials and on manufacturing conditions is our challenge for the reduction of VOCs even for non-targeted chemical materials.
3) Commercialization of the product is targeted for fiscal 2010.

5. WIRE HARNESS, SRC (VEHICLE CABIN COMPONENTS)

With the concept that the vehicle cabin atmosphere is no different from the indoor atmosphere, JAMA has set a self-imposed regulation since April 2007. The regulation aims at maintaining the concentration of VOC and aldehyde emission inside the cabin of passenger vehicles for the Japanese market at levels below the guideline values released by the Ministry of Health and Welfare. For the measuring method of VOCs and aldehyde for automotive components of the vehicle cabin, JASO has specified the sampling bag method as the industry standard (Table 4 JASO M902).

The wire harness is our product which comprises a bundle of cables settled in the vehicle cabin to transfer electric signals and electric power. Thus it is called the "nerves of automobile" or the "blood vessels." We have been striving for a VOC reduction for these components. For example, some of the materials used in the ink printed on the surface of cables contain VOCs. These materials have been replaced with lower VOC materials which are now applied to such products.

We introduce an example of the procedures for VOC and aldehyde analyses by sampling bag method which was adopted by automobile manufacturer A:

Cut out the tip of a resin bag with a 10-liter capacity. Put the test specimen (surface area 80 cm^2) into the bag. Seal the cut-out part with a bag clip. Expel all air from the bag and fill it with nitrogen, and repeat this action three times. Then make sure that the bag is filled with 4 liters of nitrogen gas. Perform a closed-vessel heating test at 65°C for 2 hours (see Figure 17). After the test, collect 1 liter from the bag into a Tenax tube and set it to the measurement by Thermal desorption-GC/MS. Collect the remaining 3 liters in a DNPH cartridge and set the acetonitrile extract to HPLC analysis.

Next, we introduce VOC measurement procedures for vehicle cabin components with the closed chamber method specified by automobile manufacturer B. The sample taken here is a steering roll connector (SRC). SRC is a rolling connector mounted on a steering wheel part, which transmits electric signals from a collision sensor to the airbag and conveys electric power to cause the airbag inflator to explode. Our products dominate the world market partly because of our low VOC line-up.

First, one unit of the sample is set in a 20-liter chamber. The air in the chamber is ventilated with clean air of 50% R.H. Then the chamber is closed and heated at 65°C for 1 hour. 1 liter of the air is collected in a Tenax TA tube, and 10 liters of the air are collected in a DNPH cartridge. The collected air is analyzed respectively.

Figure 17 Sampling bag.

6. HEAT CONDUCTIVE PARTS AND ELECTROMAGNETIC SHIELDING MATERIALS (FOR ELECTRICAL AND ELECTRONIC EQUIPMENT)

We manufacture heat conductive parts (product name: F-CO TM Sheet) and electromagnetic shielding materials for electrical and electronic equipment. We are promoting technical innovation for lower VOCs for those products as well. Some electrical and electronic equipment are designed with a waterproof and airtight feature appropriate for daily use (meaning such cases as spilling juice on the equipment). All of the parts in outdoor monitors, for example, have such waterproof and airtight designs, which may result in VOC emission caused by a rise in temperature during operation of the product. This emission might in turn cause deterioration of product performance or safety, which is what we want to avoid.

For equipment such as personal computers and televisions, JIS C 9913 specifies VOC and aldehyde measuring methods. Assuming indoor atmosphere, it specifies the temperature and humidity conditions for the emission test to be 23°C and 50% R.H. (28°C and 50% R.H. is acceptable), an air exchange rate of 0.5 time/h or 1 time/h, and a sampling volume of 0.01 < the volume of measured equipment / the volume of the chamber < 0.25.

Evaluation of VOCs and aldehyde on our heat conductive parts and electromagnetic shielding materials is either based on the specification of JIS C 9913 or based on the assumption of the temperature rise during operation of the product, depending on the situation.

7. OTHER - ANALYSIS WITH A 150-LITER CHAMBER

We have a stainless chamber with a volume of 150 liters to prepare for the measurement of relatively large products (Figure 18). It has a capacity large enough to accommodate an entire personal computer, and has a cable inlet to enable emission tests on energized equipment. With 150-liter chamber, we can evaluate the whole wire harness with the closed chamber method.

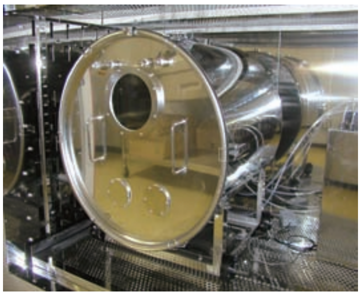

Figure 18 150-liter stainless chamber.

8. POINTS TO CONSIDER ON VOC AND ALDEHYDE ANALYSES

We list five points of consideration observed during VOC and aldehyde analyses of our products.

1) Contamination of products and storage

Toluene is sometimes detected in products which should have no toluene in the materials. In our investigation, absorption or contamination of toluene to the product is suspected to occur in manufacturing where toluene is used in other lines or in storage, for example.

Considering that VOC emission and contamination start right after manufacturing, we wrap up samples with aluminum foil to shield them from light, put them in a polyethylene bag with a zipper, and store them in a cool place avoiding direct sunlight until measurement of the samples.

2) Difference in analysis results caused by manufacturing process

There are cases in which the results of detected toluene largely differed from sample to sample. In our investigation of manufacturing sites, we found that the viscosity of raw materials is adjusted by adding toluene in the manufacturing line to prevent solidification with the passage of time, and that it was not an error in the analyzed data.

3) Points to note on sampling bag method

Since the sampling bag is made of resin, emission of chemical substances from the bag itself need to be considered. In order to eliminate N,N-dimethylacetamide and phenol emission from the Tedlar bag, we performed the test after a heating operation applying clean air to the Tedlar bag.

4) Use of acetonitrile for aldehyde analysis

For acetonitrile extraction of a DNPH cartridge, acetonitrile for aldehyde analysis should be used. We have tried less expensive acetonitrile intended for environmental analyses, but discontinued its use because of the high blank value of acetaldehyde.

5) Headspace method mainly as simplified VOC analysis

While the Headspace method is useful for simple and prompt VOC analyses or a brief view of manufacturing conditions, we would like to note that it is almost impossible to make an absolute quantitative judgment with this method.

Quantitative determination can be performed only when the volatile composition of a sample (solid or liquid) is vaporized and in equilibrium (gas-solid equilibrium or gas-liquid equilibrium). Generally, equilibrium is not reached with raw materials such as a resin pellet. Even if equilibrium is reached, the distribution coefficient will be different between the raw material matrix and the product matrix.

9. CONCLUSIONS

To develop eco-friendly and safe products, optimum selection and control of raw materials and of manufacturing conditions are essential for the reduction of VOCs.

Therefore, we have built these VOC analytical techniques. We would like to make the most of such analytical techniques, and further enhance them in order to continue to make excellent products.

REFERENCES

1) Ministry of Health, Labor and Welfare; "Summary of the 8th and 9th Interim Reports of Investigation Commission on Sick House Syndrome," February 8, 2002. (in Japanese)
2) Ministry of Land, Infrastructure, Transport and Tourism; Paragraph 7, Article 20 of the Ordinance of Building Standard Law, "Technical Standard for Formaldehyde in Construction Materials for Buildings with Living Space." (in Japanese)
3) Ministry of Land, Infrastructure, Transport and Tourism; "Examination Standard for Formaldehyde Emitting Construction Materials," June 26, 2003. (in Japanese)
4) Ministry of Education, Culture, Sports, Science and Technology; "Standards of School Environmental Sanitation: Atmosphere in the Class Rooms," February 10, 2004. (in Japanese)
5) Japan Automobile Manufacturers Association; "Automobiles and Environment: Voluntary Activities for Reducing In-Vehicle VOC Emission." (in Japanese)
6) Japan Electronics and Information Technology Industries Association; "Guidelines for VOCs from Personal Computers." (in Japanese)
7) JIS A 1901:2003; Determination of the emission of volatile organic compounds and aldehydes for building products -- Small chamber method
8) JIS C 9913:2008; Measuring method of volatile organic compounds and carbonyl compounds emissions for electronic equipment -- Chamber method
9) JASO Standards No. M902-07; "Road vehicles — Interior parts and materials — Measurement methods of diffused volatile organic compounds (VOC)"
10) Study Group for Standardizing VOCs Emission Factors from Construction Materials, Japan Testing Center for Construction Materials; "Standard for VOCs Emission Factors from Construction Materials." Formulated on April 1, 2008. (in Japanese)
11) Japanese Standards Association; How-to-Use-JIS Series, "The Small Chamber Method Serving for Countermeasures against Sick House Syndrome," Practical Guide for JIS A1901. (in Japanese)