

[Environmental Technology Verification]  
Summary of the Verification Report for FY 2009

Simplified VOC Measurement Technologies  
(Draft)

Ministry of the Environment, JAPAN



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## I. Introduction

This report summarized the outline of verification test results completed in Fiscal Year 2009 for the “Simplified VOC measurement technology field” in the “Environmental Technology Verification Project” of the Ministry of the Environment (MOE).

### ■ What is the Environmental Technology Verification (ETV) Project?

Advanced environmental technologies, even though they are commercial-ready and considered to be useful, have not necessarily been pervasive widely because objective assessments on environmental conservation effects, etc., have not been made and end users such as local governments, companies, and consumers cannot use it without anxiety. The Environmental Technology Verification (ETV) Project is a project in which third-parties objectively verify the environmental conservation effects, etc., of these advanced technologies that have not spread yet. It is expected by implementing this project that the spread of environmental technologies developed by venture companies, etc., is promoted and economic activities are stimulated through environmental conservation and the development of environmental industries.

In fiscal year 2009, the project was implemented targeting the following nine technology fields.

- (1) Human Waste Treatment Technologies in Natural Area
- (2) Organic Wastewater Treatment Technologies for Small-Scale Establishments
- (3) Water Purification Technologies for Lakes and Reservoirs
- (4) Water Environment Improvement Technologies in Enclosed Coastal Seas
- (5) VOC Emission Reduction / Deodorizing Technologies (VOC Emission Reduction / Deodorizing Technologies for Small / Medium-Scale Establishments)
- (6) Simplified VOC Measurement Technologies
- (7) Heat-Island Mitigation Technologies (Technologies for Reducing Air Conditioning Loads

by Using Building Envelope Systems)

- (8) Heat-Island Mitigation Technologies (Technologies for Reducing Artificial Exhaust Heat from Offices, Houses, etc.): Green Technologies for IT Equipment
- (9) Heat-Island Mitigation Technologies (Technologies for Reducing Artificial Exhaust Heat from Offices, Houses, etc.): Heat Pump Air Conditioning Systems Using Underground Heat, Wastewater, etc.

## ■ Procedure of the Project

For target verification technology fields which MOE selected with the advice of experts, third party organizations selected by open invitations (hereinafter "Verification Organizations") issue open invitations for target verification technologies to Verification Applicants (developers, vendors, etc., having technical skill), and perform verification tests. For a technology for which a verification test has been performed, "ETV Project Logo" (Fig. 1) and a verification number are issued as the certificate of the technology verified in this project by MOE to promote its spread. Under this project, "verification" means the process by which objective data based on tests, etc., for the environmental conservation effects of an environmental technology, its secondary environmental impacts, etc., are indicated by third parties, who are neither developers nor users of the technology. "Verification" differs from "certification," whereby certain evaluation standards are established and then compliance is judged based on those standards.



Fig. 1: Logo of the Environmental Technology Verification Project (Common Logo)

(Logo design varies depending on technology fields)

(1) Implementation system of the project (Fig. 2)

Until a verification system is established, that is, in principle by the end of two years from the start of each technology field, MOE will cover the costs of verification tests (“government-sponsored system”). After the period, the system will shift to a “fee-based system,” that means, the Verification Applicant pays all fees including the costs of verification tests based on the policy of “beneficiary liability.”

For the project management of each technology field (preparation of verification test guidelines (hereinafter “Protocols”), selection of Verification Organizations, etc.), MOE will conduct it in the case of the “government-sponsored system,” while a “Verification Management Organization“ will do it in the case of the “fee-based system,” including setting of fees and collection of them from Verification Applicants. MOE selects Verification Management Organizations by open invitations in view of ensuring impartiality and fairness, also considering their implementation system, technical capability, etc.

Open invitations and selection of target verification technologies, verification tests, preparation of verification test result reports, etc., are implemented by Verification Organizations regardless of whether they are done in the “government-sponsored system” or the “fee-based system.” MOE or a Verification Management Organization selects Verification Organizations by open invitations in view of ensuring impartiality and fairness, also considering their implementation system, technical ability, etc.

For overall operation of the project, MOE is receiving advice from the Advisory Committee on the ETV Project composed of experts, as well as sectoral working groups (WGs) under it from a technical point of view.

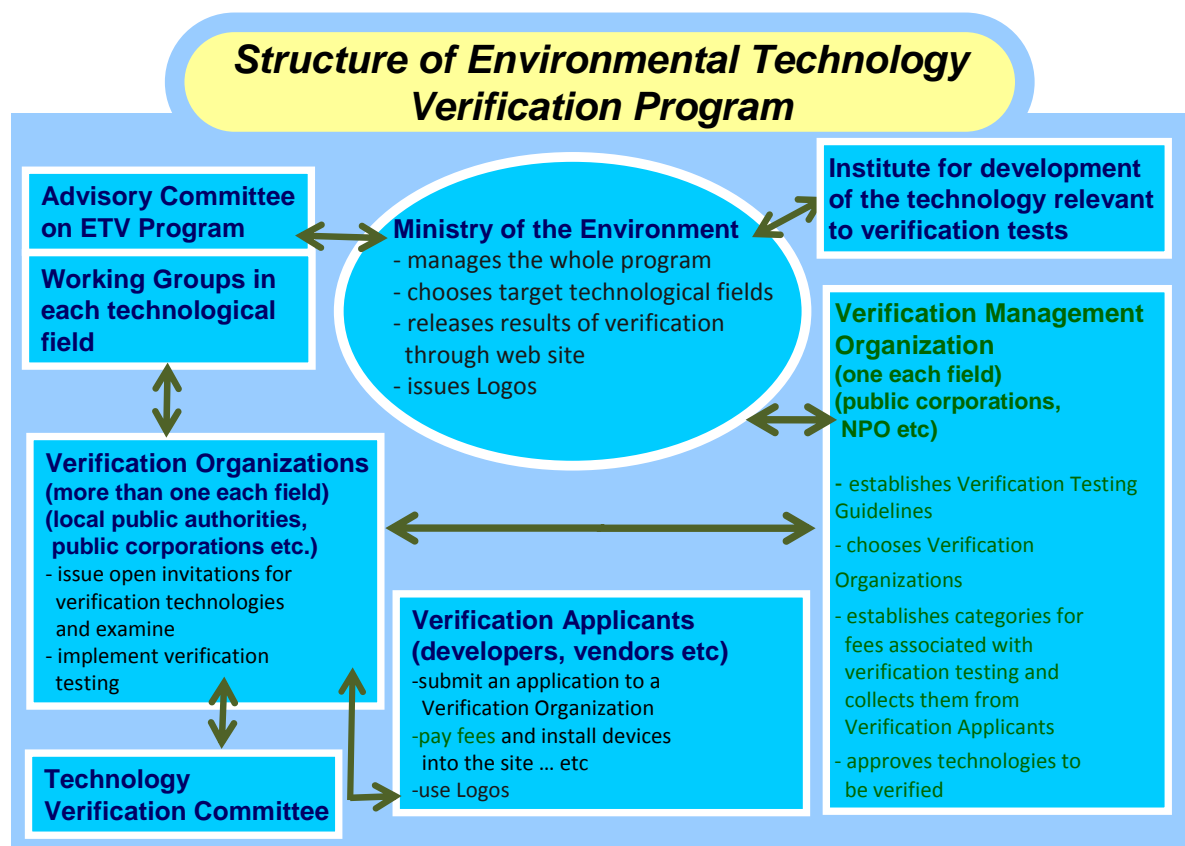


Fig. 2: Implementation system of the ETV Project (fiscal year 2009)

(The green parts apply to the “fee-based system”)

(2) Flow of the Project

Verification tests are implemented according to the following steps mainly (Fig. 3).

○ Selection of target verification technology fields

MOE selects target verification technology fields from technology fields for which technology verification has not been performed by other existing institutions based on the discussions in the Advisory Committee on the ETV Project in view of verification needs, effectiveness of the technology verification for promoting the spread of technologies, feasibility of verification, etc.

○ Verification Management Organizations (fee-based system only), preparation of Protocols, and selection of Verification Organizations



For each technology field, one Verification Management Organization and a necessary number of Verification Organizations (the number is determined by discussions in the WG of the field within the budget) are selected. A Protocol defining basic approaches to implementation of verification tests, test conditions, test methods, etc., is prepared.

- Open invitations for target verification technologies and preparation of Verification Test Plans

A Verification Organization issues open invitations for target verification technologies and makes a selection based on discussions in the Technology Panel composed of experts. Then, the Verification Organization confers with the Verification Applicant, holds discussions in the Technology Panel, and prepares a Verification Test Plan.

- Implementation of verification tests

A Verification Organization implements verification tests based on a Verification Test Plan.

- Preparation and approval of verification test result reports

A Verification Organization analyzes and verifies verification test data, and then prepares a verification test result report. MOE approves the report based on discussions in the WG of the field. The approved report is submitted from the Verification Organization to the Verification Applicant, and is also released to the public.あ

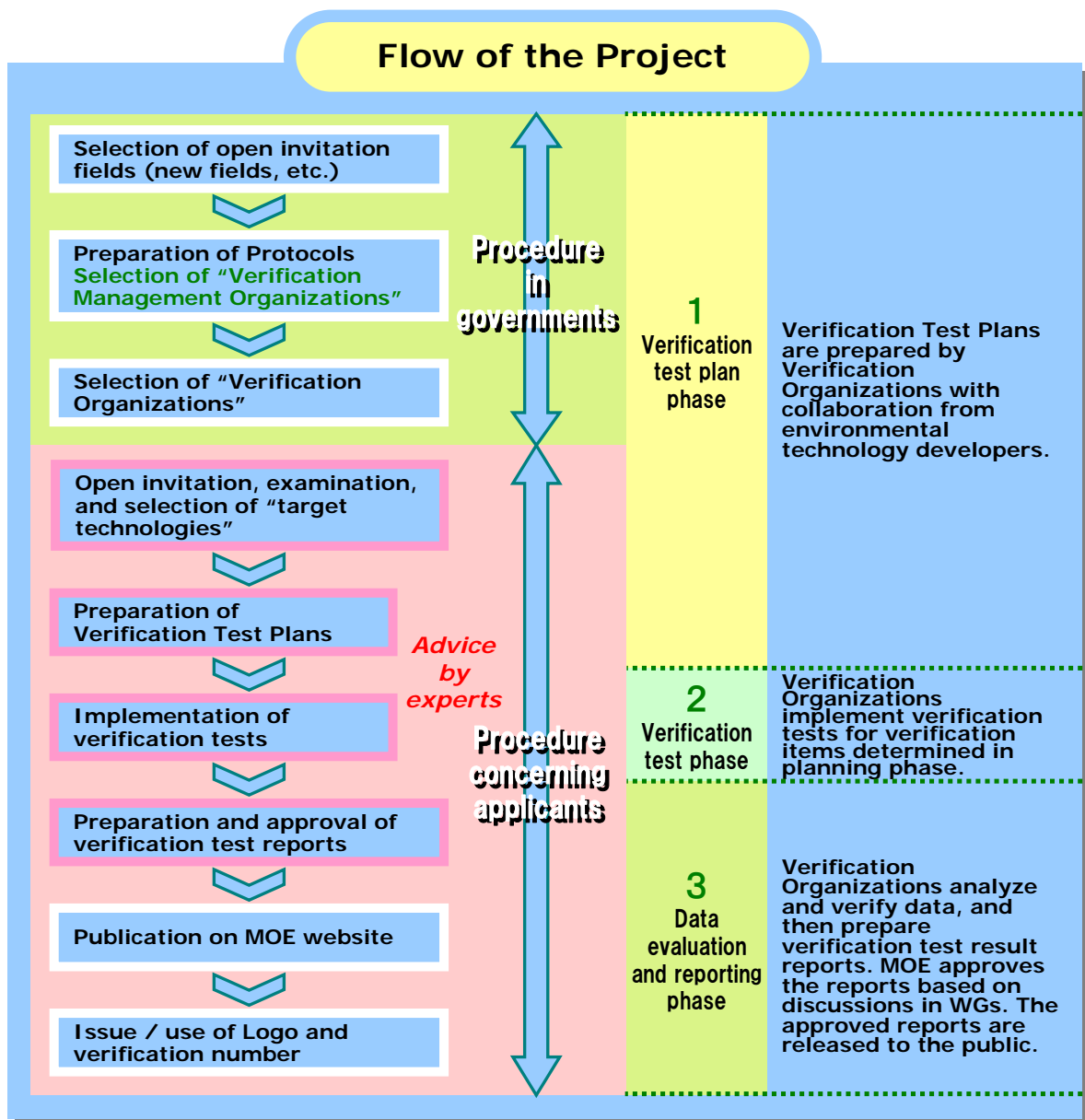


Fig. 3: Flow of the Environmental Technology Verification Project

(Selection of "Verification Management Organizations" applies to "Fee-based system.")

### ■ ETV Project Website

The ETV Project has an ETV Project website (<http://www.env.go.jp/policy/etv/>) as a database of the project, providing the following information. For the detail of the project, see the website.

#### [1] Verification technology list

Technologies verified in this project and their verification results such as environment conservation effects ("Verification Test Result Reports") are provided.

[2] Protocols / Verification Test Plans

For each technology field, a “Protocol” defining basic approaches to implementation of verification tests, test conditions, test methods, etc.; and a “Verification Test Plan” defining detailed test conditions, etc., for each target technology based on the Protocol are provided.

[3] Information on Verification Management Organizations, Verification Organizations, and open invitations for target verification technologies

For each technology field, information is provided on the Verification Management Organization, the Verification Organizations, and the procedure of open invitations when the organizations issue open invitations for target verification technologies.

[4] Information on Advisory Committee, etc.

Materials and the outline of discussion subjects of the Advisory Committee and each WG are provided.

## II. About Simplified VOC Measurement Technology Field

### ■ What are simplified VOC measurement technologies?

The simplified VOC measurement technologies targeted in this project are technologies with characteristics that their operation and management are easy, or quick quantity determination is possible, and which are useful for voluntary efforts to reduce VOC emission, such as process / equipment management in enterprises that deal with VOCs.

VOC measuring methods are divided into two types: methods measuring the concentration of each component of VOCs, and ones measuring a total VOC concentration inclusively. For the former, the Industrial Safety and Health Act (Working Environment Measurement Standards) defines the measuring method for each component of VOCs. For the latter, a notification of MOE defines a method, following the revision of the Air Pollution Control Act.

Under the VOC concentration measuring method defined by MOE (hereinafter called “official method”), it is prescribed that measurement should be performed not for each substance because many kinds of VOCs are contained in emission, but should be inclusively done as the number of carbon. In this method, the unit used to represent the concentration obtained is carbon equivalent ppm (ppmC).

As a premise, simplified VOC measurement technologies targeted in this project must be such that they can measure plural components of VOCs at the same time. However, it is not requisite to determine quantity inclusively (that is, to represent measurement results with the ppmC unit), which is required in the official method, so that the methods can be used in voluntary efforts corresponding to the actual situation of each enterprise, e.g., the type of solvent used. In principle, there is no limitation on measurement principles.

Compared with the official method, which is the method for regulations, equipment for these simplified measuring methods is relatively inexpensive generally, and measurements with the methods are simple.

- Why simplified VOC measurement technologies were selected as a target verification technology field?

VOCs (Volatile Organic Compounds) are substances that produce photochemical oxidants and suspended particulate matters (SPM) by photochemical reactions, physical reactions, etc., in the air. The goal of the total VOC emission reduction was set to 30% during the period from fiscal 2000 to 2010, which should be attained by the VOC emission regulations defined in the Air Pollution Control Act and emission reduction done voluntarily by enterprises. Of that reduction quantity, it is estimated that about 10% should be reduced by the regulations, while about 20% by voluntary efforts. Support to further promote voluntary efforts in small / large-scale facilities which are not covered by the regulations is required.

Enterprises emitting VOCs will be able to take optimum VOC reduction measures voluntarily by accurately grasping their emission quantity in daily management, etc. As a result, it is expected that the efforts will conduce to not only VOC emission reduction but also merits such as further improvement of working environments, reduction in solvent costs, and ensuring of CSR by clarification of environment information.

However, although various types of simplified measuring equipment are sold that can be used in voluntary efforts, data on their accuracy, operability and costs required for analyses is limited to those shown by the manufactures. Therefore, this field was selected as a target technology field in order to contribute to promotion of voluntary efforts by VOC emitting enterprises using simplified measuring equipment, by the government's verification on simplified VOC measurement technologies for providing objective technical information on their usability, etc.

## Revised Air Pollution Control Act (enforced in April 2006)

	Large-scale enterprises	Small / medium-scale enterprises
<b>Coating</b>	Ventilation capacity is 100,000m <sup>3</sup> /h or more (spray); 10,000m <sup>3</sup> /h or more (coating drying)	Ventilation capacity is less than 100,000m <sup>3</sup> /h (spray); less than 10,000m <sup>3</sup> /h (coating drying)
<b>Storage</b>	Tank volume is 1,000kL or more	Tank volume is less than 1,000kL
<b>Chemical production</b>	Ventilation capacity is 3,000m <sup>3</sup> /h or more	Ventilation capacity is less than 3,000m <sup>3</sup> /h
<b>Printing</b>	Ventilation capacity is 27,000m <sup>3</sup> /h or more (gravure); 7,000m <sup>3</sup> /h or more (offsets)	Ventilation capacity is less than 27,000m <sup>3</sup> /h (gravure); less than 7,000m <sup>3</sup> /h (offsets)
<b>Adhesive bonding</b>	Ventilation capacity is 5,000m <sup>3</sup> /h or more (drying adhesive tapes); 15,000m <sup>3</sup> /h or more (drying other materials)	Ventilation capacity is less than 5,000m <sup>3</sup> /h (drying adhesive tapes); less than 15,000m <sup>3</sup> /h (drying other materials)
<b>Washing in industry</b>	Washing tank liquid surface area is 5m <sup>2</sup> or larger	Washing tank liquid surface area is smaller than 5m <sup>2</sup>
	<b>Under the regulation</b>	
<b>Other VOC emitting enterprises</b>	<b>Expect voluntary efforts</b>	

Fig. 1 Prescription on "voluntary efforts" in the Revised Air Pollution Control Act

(Source: Material 5 of the 3rd VOC Treatment Technology Working Group, 2005)

### III. Verification Test Methods (Fiscal Year 2009)

#### ■ Outline of verification tests

The verification tests are performed based on the “Protocol” defined in the simplified VOC measurement technology field. The following items are verified for the target verification product submitted from a Verification Applicant.

- Reliability of product performance
- Practicality when the targeted VOCs are measured at an enterprise using VOCs
- Convenience of product operation

A manufacture having a simplified VOC measurement technology fills in the outline of the technology whose verification is desired on a verification application form, and files an application with a Verification Organization. The Verification Organization examines the contents of the application, and prepares a Verification Test Plan if no problem is found in the technology. A verification test is performed based on the Verification Test Plan. In this verification test, measurement is performed using a sample gas (simulant gas) containing components which are assumed to be emitted at an actual worksite (process). Optionally, measurement using an actual gas emitted from an enterprise may be performed.<sup>1</sup> The Verification Organization analyzes and verifies the verification test data, and then prepares a verification test result report.

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<sup>1</sup> Actual gas measurement in a working environment or at an exhaust port, etc., (optional verification items) was not performed in Fiscal 2009.

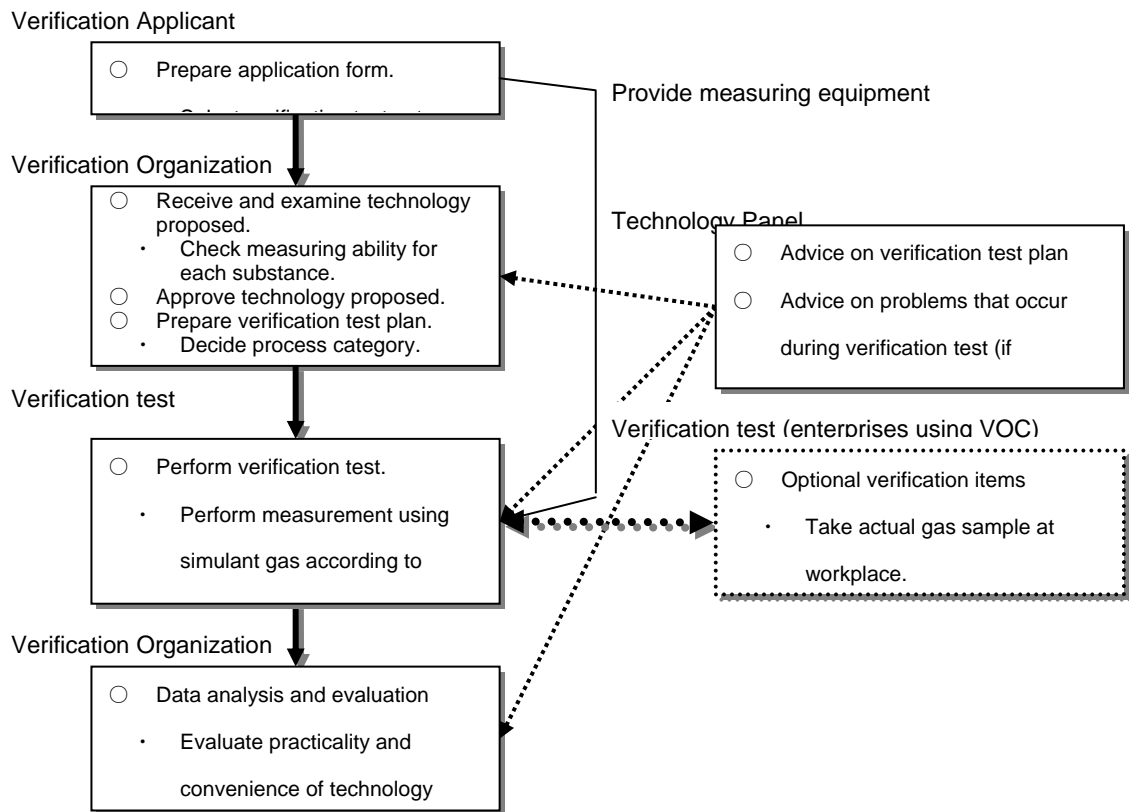


Fig. 5 Flow of the verification test

## ■ Verification items

In the verification test for simplified VOC measurement technologies, measurement is performed using a sample gas (simulant gas) containing components which are assumed to be emitted at an actual worksite (process). In general, several kinds of VOCs exist at the same time at an enterprise (process) using VOCs. In this verification test, therefore, inclusive measurement is performed using a mixed gas simulating these components (simulant gas). Verification test categories have been defined for convenience sake to perform the test in a condition close to an actual worksite. A simulant gas measured in this test is prepared corresponding to one of these verification test categories.



Table 1 Verification test categories

Verification test category	Test-targeted VOCs	Remarks
General facilities targeted by regulations	Hydrocarbon series, alcohols, ketone series, ester series, etc.	Test of VOCs used at enterprises related to coating, adhesive bonding, or printing
Enterprises where halogen series VOC is used in considerable quantity	Halogen series, petroleum-derived mixed solvents, etc.	Test of VOCs used at enterprises related to industrial washing
Others	Determined in consultation with Verification Organization	Test of VOCs not covered in above categories

\* An applicant shall select a verification test category considering the performance of his target verification product.

\* Plural categories can be selected.

A simulatant gas composed of several kinds of VOCs is measured in this verification test. Measuring ability for each substance is checked based on the document submitted by an applicant in principle. In addition, an actual gas emitted at an enterprise may be measured optionally. Verification items related to these verifications are shown in Table 2.<sup>2</sup>

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<sup>2</sup> For these verification test items, a Verification Organization can add or modify test items if necessary, considering the principle of the verification product targeted, technical specifications, etc.

Table2 Example of viewpoints and methods by verification item

Item	Index	Viewpoint			Method	
		Reliability	Practicality	Convenience	Document	Test
<b>1. Evaluation items concerning measurement for each substance (checked based on document)</b>						
(1)Measuring range		○			○	—
(2)Repeatability	Deviation etc.	○			○	—
(3)Linearity	Correlation, etc.	○			○	—
(4)Interference effect test	Ratio, etc.	○			○	—
(5)Response time	Time	○			○	—
(6)Relative sensitivity	Ratio, etc.	○			○	—
<b>2. Evaluation items concerning measurement for a mixed gas (actual measurement)</b>						
(1) Measuring range		○	○		○	◎
(2)Repeatability	Deviation etc.	○	○		○	◎
(3)Linearity	Correlation, etc.	○	○		○	◎
(4)Interference effect test	Ratio, etc.	○	○		○	○
(5)Response time	Time	○	○		○	◎
(6)ppmC equivalent		○	○		○	◎
<b>3. Evaluation items concerning measurement for actual gas sampled at an enterprise (option)</b>						
(1) Reproducibility	Deviation etc.	○	○		—	◎
(2) Comparison with other analysis methods (official method, GC-MS, etc.)	Correlation, etc.	○	○		—	◎

Note: ◎ marks in the method field mean items considered to be important in verification. Data shall be obtained by actual measurement, etc.

For 1 and 2, measurement shall be performed using a gas prepared with analysis-target substances or commercial standard substances similar to them. For 3, it shall be done using a gas actually taken at an enterprise.

Detail of the verification items are described in a “Protocol” defining basic approaches to implementation of verification tests, test conditions, test methods, etc., and a “Verification Test Plan” defining detailed test conditions, etc., based on the Protocol. For them, see the website of the project (<http://www.env.go.jp/policy/etv/>).

## IV. Fiscal Year 2009 Verification Test Results

In fiscal year 2009, the project was implemented according to the government-sponsored system.

### ■ Verification Organization

- Japan Environmental Technology Association

### ■ Outline of target verification technologies

Verification number	Environmental technology developer	Target verification technology	Measurement principle	Verification test period
100-0901	Komyo Rikagaku Kogyo, K. K.	Simplified VOC measurement system (Model VOC-1)	Catalyzed oxidation - detector tube method	Jan 18, to Feb 4, 2010
100-0902	O.S.P. Inc.	Handy VOC sensor (Model VOC-121H)	Interference Enhanced Reflection (IER) method based on swelling of a thin polymer film	Jan 18, to Feb 4, 2010
100-0903	Figaro Engineering, Inc.	Handy TVOC monitor (Model FTVR-02)	Oxide semiconductor type gas sensor	Jan 18, to Feb 4, 2010
100-0904	RIKEN KEIKI Co., Ltd.	Gas leakage detector (Model GL-103)	Flame ionization detector (FID)	Jan 18, to Feb 4, 2010

< Verification Organization: Contact Information >

Japan Environmental Technology Association

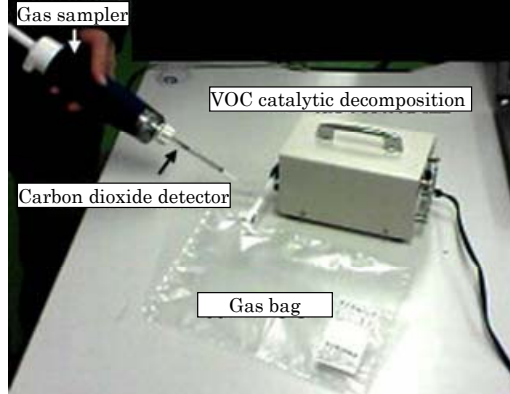
Toranomon KT bldg, 5-11-15, Toranomom, Minato-ku, Tokyo, 105-0001

Tel: +81-3-3431-5462 Fax: +81-3-5472-0909

## ■ Outline of verification test result reports

Target verification technology / environmental technology developer	Simplified VOS measurement system (Model VOC-1) Komyo Rikagaku Kogyo, K. K.
Verification Organization	Japan Environmental Technology Association
Verification test period	Jan 18 to Feb 4, 2010

### 1. Outline of Target Verification Technology

	<p><b>Measurement Principle</b></p> <p>Carbon equivalent concentration (ppmC) is measured by oxidizing VOCs with a catalyst (300°C, platinum catalyst) and measuring the concentration of carbon dioxide generated with a detector tube. Carbon dioxide concentration in a sample gas is measured in advance with the tube, and it is subtracted from the above result.</p> <p>Halogen series VOCs such as methylene chloride cannot be measured with this method.</p>
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### 2. Outline of Verification Test

#### ○ Specifications of Technology to be Verified

Model	VOC-1
Measurement principle	Catalyzed oxidation - detector tube method
Gases to be measured	VOCs other than halogen series (methylene chloride, trichloroethylene, tetrachloroethylene, chlorobenzene, etc.)
Measurement range	200 to 4000 ppmC* (using carbon dioxide SF type detector tube) * Including carbon dioxide in the air
Gas sampling method	Sampling into a VOC sampling bag using a gas sampler (AP-20) (using an airtight vessel for suction) Sampling volume: 100ml or 50ml
Power supply of equipment	AC 100V

Note 1) A sample containing exhaust combustion gas with very high carbon dioxide concentration cannot be measured.

Note 2) A sample containing a silicon coating agent used in gravure printing, etc., may degrade the catalyst.

#### ○ Verification Test Implementation Site

Basic performance test: Conducted at Reference Gas Testing Laboratory, Environmental Science Research Institute, Yokohama City.

Measuring test of a sample taken at an enterprise: A sample was taken into a bag at Coating Testing Facility of Tokyo Metropolitan Industrial Technology Research Institute, and measurement was conducted at Reference Gas Testing Laboratory, Environmental Science Research Institute, Yokohama City.

### 3. Verification Test Result

For each test method, see “5. Verification Test Implementation Method” of the original test result report.

#### ○ Repeatability Test

As the result of a repeatability test, dispersion was about ±5%. However, it was about ±10% in the case of a simulant gas (containing five component VOCs).

Deviations (%) of indicated values from gas concentrations and were +15% at a maximum in the case of toluene, but they were as high as +85% in the case of the simulant gas.

According to the publication of the applicant, the accuracy of the product to be verified is within ±35% of each indicated value for 200~700 ppmC, while ±35% for 700~4000 ppmC. (“3.4 Performance Data”) For toluene, the measurement results of this test were within the accuracy indicated by the environmental technology developer.

On the other hand, the test results for the simulant gas (five component VOCs) showed high indicated values. The cause would be purging performed with the sample gas before the measurement. It is presumed that gases, among the five components of the VOCs, whose catalytic combustion reaction rates are lower than that of toluene, such as isopropyl alcohol and ethyl acetate, remained in the VOC catalytic decomposition equipment during the purging operation (the suction rate was relatively high then), and these gases were then oxidized in combustion and solved out at the measurement (the suction rate was relatively low then), which caused the high indicated values. These phenomena were not observed when measuring toluene alone.

Purging was performed with the sample gas in this verification test. However, the Verification Applicant has submitted to us data which shows that this kind of problem never occurs if purging is performed with air (ambient air) (reference: page vi of Reference Information; and other information from the applicant)

The test was not conducted for trichloroethylene because the applicant told that it degraded the catalyst.

#### ○ Reproducibility (Drift) Test

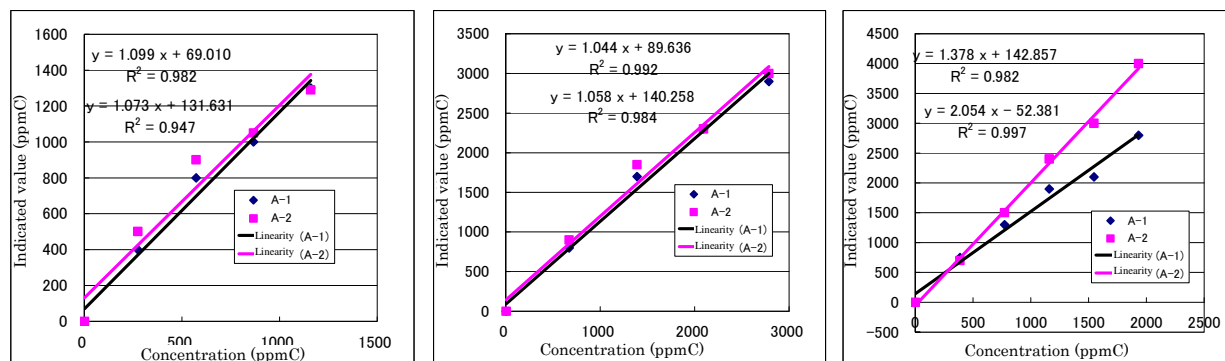
During the test period (two weeks), toluene in a high pressure vessel (about 275 ppm (1900 ppmC)) is fed three times and indicated values were read. Deviations, from the first indicated value, of the other values were as good as 3% or lower.

#### ○ Linearity Test

The results of the linearity test were about -5 to +20%. For toluene, a significant positive value was observed at a midpoint (2/4). However, the results were within the nominal accuracy of the product to be verified as a whole.

For the simulant gas (five component VOCs), considerable dispersion of values was observed in two of the test equipment. It is presumed to be caused by the purging method described in the repeatability test.

Correlated distribution diagrams are shown below to indicate the results of the linearity test.



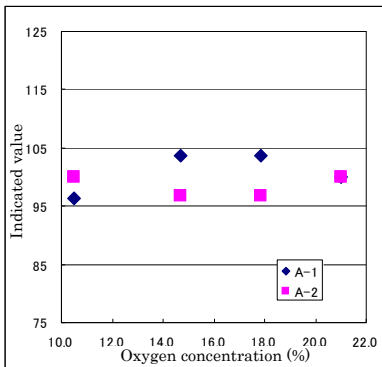
Toluene 1160ppmC

Toluene 2800ppmC

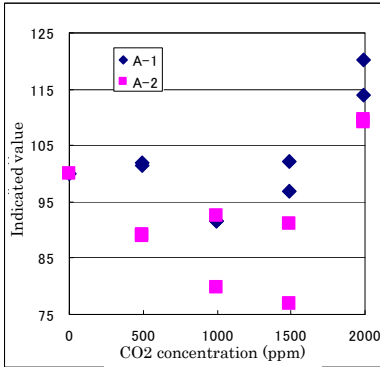
VOCs (five components)

○ **Interference Effect Test**

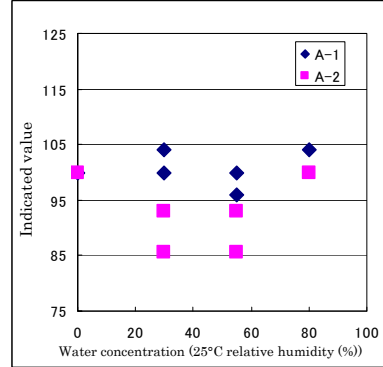
Test results for the effects of oxygen, carbon dioxide, and water are shown below. They were all within the nominal accuracy of the product to be verified. The effects of these substances were not observed very much.



Test result for effects of oxygen



Test result for effects of carbon dioxide



Test result for effects of water

○ **Measurement Test Using a Sample Gas Taken at an Enterprise**

As the result of a repeatability test using the gas in the sampling bag, dispersion was about -20 to +35%, which are relatively large values. It would be caused by the fact that the difference between the background CO2 concentration and VOC concentration was small (measured concentrations were low). For details, see Table 6-8 of the original test result report.

Gas concentrations at the test using the sampling bag, and deviations (%) of the average indicated values of the test equipment are shown below. Some indicated values were as low as about -25%.

Kind of gas	Name of gas	Concentration (ppm)	Concentration (ppmC)		Comparison equipment		Test equipment	
					HOR-made	TD-made	VOC-1	
					NDIR	FID	catalyzed oxidation + detector tube	
					A	B	A-1	A-2
					ppmC	ppmC	ppmC	ppmC
Gas in high pres. Vessel	C7H8	273	1911	Indicated value	1911	1911	2000	2000
				Deviation (%)	0.0	0.0	4.7	4.7
Bag (1)	Sample (1)	120.8	750	Indicated value	752	748	617	556
				Deviation (%)	0.3	-0.3	-17.7	-25.9
Bag (2)	Sample (2)	127.2	845	Indicated value	856	834	626	649
				Deviation (%)	1.3	-1.3	-25.9	-23.2

○ **Summary of Verification Tests**

Viewpoint	Summary of results
Reliability	<p>Technologies on detector tubes for carbon dioxide have already been established, and the reliability depends on how it is appropriately combined with catalyzed oxidation equipment. With regard to the performance of catalyst, oxidation efficiency may differ depending on the components of measured gas, compared with the oxidation efficiency defined in the official method NDIR (where methane must be oxidized by 95% or more). Therefore, care should be exercised, such as checking the components of measured gas in advance. It is expected that a simple check method for catalyst efficiency is established.</p> <p>It is required that purging before measurement is performed with ambient air, not the sample gas.</p>

Practicality	Since measurement based on “ppmC” can be performed, as with the official method, this method is useful when measurement results are published or evaluated. As carbon dioxide always exists in a sample gas as a background, measurement of air, a background gas, should be performed along with measurement of a VOC sample. Care should be exerted to ensure accuracy when concentration of VOCs is lower than that of carbon dioxide.	
Convenience	There was no particular problem, although it is required to get accustomed to a series of operation procedures. Part of “Reference Information” is extracted below as evaluation items on convenience.	
	Price	300,000 Yen
	Weight	About 5 kg (when set in an attache case)
	Power supply	AC 100 V
	Warming-up time	15 minutes

### [Reference Information]

The following reference information is based on the application by the environmental technology developer on his own responsibility. Ministry of the Environment and the Verification Organization do not assume any responsibility on this information.

#### o Product Data

\* Accuracy is evaluated pursuant to the general standards for detector tubes defined in JIS K0804.

For detector tubes used for VOC-1, the following values apply.

200 to 700 ppmC: within  $\pm 35\%$  of each indicated value; 700 to 4000 ppmC: within  $\pm 25\%$

Item	Description
Name of company	Komyo Rikagaku Kogyo, K. K.
	URL <a href="http://www.komyokk.co.jp">http:// www.komyokk.co.jp</a>
Address	1-8-28, Shimonoge, Takatsu-ku, Kawasaki, Kanagawa, 213-0006
Contact person (affiliation, name,)	Chemical Department, Koji Kawamura
Point of contact	TEL/FAX Tel: +81-44-833-1245 Fax: +81-44-833-3126
	E-mail <a href="mailto:kawamura@komyokk.co.jp">kawamura@komyokk.co.jp</a>
Product name	Simplified VOC measurement system
Model	VOC-1
Distributor / maker	Komyo Rikagaku Kogyo, K. K.
Weight (g)	About 5 kg (when set in an attache case)
Price	300,000 Yen
Substances to be analyzed	VOCs other than halogen series (methylene chloride, trichloroethylene, tetrachloroethylene, chlorobenzene, etc.)
Application (assumed)	For simplified VOC measurement in voluntary efforts for VOC emission reduction based on the Air Pollution Control Act
Is there any reference	Yes ( Already prepared / Not prepared yet ) / <u>No</u>

material for calibration?	
Sampling method	<p>Sampling into a gas bag using a gas sampling case and a vacuum-method gas sampler</p> <p>[Specifics]: A gas sampling case (internal volume: 1.2 L) is used as a fixed vessel, and a gas bag (volume: 1 L; made of polyvinylidene difluoride) with a cock is put in it. Sampling is performed by letting out air in the vessel using a vacuum-method gas sampler (AP-20: generally used as a gas sampler for a gas detector tube). Air of 700 mL in total is sent out with the vacuum-method gas sampler (draw the handle of the sampler seven times).</p> <p>The gas bag into which a sample gas is sampled by the above method is connected to VOC catalytic decomposition equipment and a CO2 detector tube, and then measurement of VOC concentration is performed.</p>
Operation environment (room temperature)	0 °C to 40°C
Operation environment (relative humidity)	10% to 90%
Operation environment (others) (environments where this method cannot be used, etc.)	The following samples cannot be measured: those containing halogen series VOCs or a silicon coating agent used in gravure printing, etc., or those containing exhaust combustion gas with very high concentration carbon dioxide
Product storage conditions (maintenance methods, etc.)	<p>Product storage conditions : to be stored in a cool, dark place (0 to 25°C) (CO2 detector tube)</p> <p>Maintenance: it is recommended that catalyst performance should be checked using air-based isobutene of about 1800 ppmC.</p>
Product warranty period	<p>CO2 detector tube: two years after production</p> <p>Other equipment: the period is not specified</p>
Response time	<p>Measurement using CO2 detector tube: 2 min</p> <p>Warming-up time of equipment: 15 min</p>

○ **Other Information from the Verification Applicant**

(Describe comments on verification test results, the results of additional tests performed at the Verification Applicant, etc.)

(1) About the test using a simulant gas (five component VOCs)

Responding to the verification test results in which considerably high indicated values were observed for a simulant gas (five component VOCs), the effect of purging operation using a sample gas on measurement values were checked. A stimulant gas (five component VOCs) with concentration of 1,945 ppmC was prepared using the bag method (gas components are as follows: isopropyl alcohol 471 ppmC, ethyl acetate 246 ppmC, toluene 398 ppmC, n-hexane 293 ppmC, and methyl ethyl ketone 537 ppmC). Purge operations were performed using a sample gas or ambient air, and indicated values obtained were compared. Tests were conducted twice with the same equipment (A-2) (Test I and II). Measurements were performed three times in a row, and purging was done immediately before the first measurement. In the result, as shown in the table below, indicated values were close to gas concentration (1,945 ppmC) when purged with ambient air, while they were higher by about 60% when purged with the sample gas.

The reason is considered as follows: In the purging operation, catalyst aeration speeds (about 100mL/2s) were by far higher than those in normal VOC decomposition (about 100mL/60s)



when purged with the sample gas. Therefore, VOC components were not fully oxidized, which produced highly adhesive components such as aldehydes. The components remained in the catalytic decomposition equipment, which affected the subsequent measurements.

In the case the second and third measurements were performed in a row after purging with the sample gas, it is presumed that indicated values became lower (i.e., close to the actual gas concentration) because adhered VOCs were gradually decomposed.

Consequently, it was confirmed that the reason considerably high indicated values had been measured in the verification test using a simulant gas (five component VOCs) was the purging with a sample gas, and no problem would arise if purging was performed with ambient air. (\* It is designated as the normal usage of VOC-1 that purging should be performed with ambient air.)

			VOC-1	
			Purge method	
Num. of measurement	Gas concentration (ppmC)		Sample gas	Ambient air
1st meas.	1945	Indicated value (ppmC)	3180	1930
		Deviation (%)	63.5	-0.8
2nd meas.	1945	Indicated value (ppmC)	2380	1980
		Deviation (%)	22.4	1.8
3rd meas.	1945	Indicated value (ppmC)	2180	1980
		Deviation (%)	12.1	1.8

\* Purging was performed only once before the first measurement.

			VOC-1	
			Purge method	
Num. of measurement	Gas concentration (ppmC)		Sample gas	Ambient air
1st meas.	1945	Indicated value (ppmC)	3080	2020
		Deviation (%)	58.4	3.9
2nd meas.	1945	Indicated value (ppmC)	2380	2180
		Deviation (%)	22.4	12.1
3rd meas.	1945	Indicated value (ppmC)	2080	1980
		Deviation (%)	6.9	1.8

\* Purging was performed only once before the first measurement.


## (2) About check of catalyst efficiency

It is recommended in the specifications of VOC-1 to perform a catalyst performance test with air-based isobutene of about 1,800 ppmC twice a year. The manufacturer provides reference gas to users who cannot prepare it.

Target verification technology / environmental technology developer*	Handy VOC sensor (Model VOC-121H) O.S.P. Inc.
Verification Organization	Japan Environmental Technology Association
Verification test period	Jan 18 to Feb 4, 2010
Aim of this technology	Simplified VOC measurement that can be used for voluntary efforts for VOC emission reduction

\* The handy VOC sensor (Model VOC-101H) of O.S.P. Inc. and the handy VOC sensor (Model VOC-201H) of Able Corporation were recognized as products of the same standards.

## 1. Outline of Target Verification Technology

	<p><b>Measurement Principle</b></p> <p>The Interference Enhanced Reflection method (IER method) is a method where the following two phenomena are combined to measure VOC concentration: a thin polymer film, contacting to VOCs (substances to be measured), absorbs the VOCs and swells responding to the concentration; and the reflection and interference of light is varied according to the degree of swelling. This principle was applied to this VOC sensor.</p> <p>There are two types of measurement modes. The point measurement mode is the manual measurement mode where starts of measurement and cleaning are operated with the Start button, while the interval mode is the automatic measurement mode where an intermittent continuous operation, in which a sequence of zero point calibration -&gt; measurement -&gt; cleaning is repeated at constant intervals, is performed by selecting a monitoring cycle in a menu.</p>
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## 2. Outline of Verification Test

### ○ Specifications of Equipment to be Verified

Model	VOC-121H
Measurement principle	Interference Enhanced Reflection (IER) method based on swelling of a thin polymer film
Gases to be measured	Almost all VOCs
Measurement range	Select one of the following three measurement ranges when purchasing the equipment. Spec-1 chip: 1 to 2,500 ppm (toluene equivalent) Spec-2 chip: 3 to 7,500 ppm (toluene equivalent) Spec-3 chip: 10 to 25,000 ppm (toluene equivalent)
Gas sampling method	A built-in diaphragm type suction pump is used. Flow rate of sampling: 200 to 300mL/min
Power supply of equipment	Four AA alkaline cells, four nickel metal-hydride batteries, or AC 100V (using the AC adapter provided)

### ○ Verification Test Implementation Site

Basic performance test: Conducted at Reference Gas Testing Laboratory, Environmental Science Research Institute, Yokohama City.

Measuring test of a sample taken at an enterprise: A sample was taken into a bag at Coating Testing Facility of Tokyo Metropolitan Industrial Technology Research Institute, and measurement was conducted at Reference Gas Testing Laboratory, Environmental Science Research Institute, Yokohama City.

### 3. Verification Test Result

For each test method, see “5. Verification Test Implementation Method” of the original test result report.

#### ○ Repeatability Test

As the results of a repeatability test, dispersion was as good as  $\pm 1\%$  for all test items.

Deviations (%) of indicated values from toluene concentrations were relatively low values and dispersion of -2 to -20% was observed depending on measurement concentrations and types of chips. Because the test equipment has low and high ranges which are switched internally, it is presumed that the dispersion was caused by difference in manufacturer’s calibration (calibration gas concentration, etc.). However, since the system accuracy of the equipment to be verified is  $\pm 20\%$  as shown in “3.3 Product Data” of the original test report, the results were all within the accuracy range.

For the simulant gas (five component VOCs), indicated values were around 85 ppm, which were considerably lower values compared with gas concentration (444 ppm). It would be caused by the fact that gases other than toluene (conversion factor: 1.0), that is, isopropyl alcohol (10.5), n-hexane (10), ethyl acetate (5.6), and methyl ethyl ketone (6.0), have large conversion factors.

A predicted value for the indicated value was calculated using the conversion factor and the deviation of the indicated value for toluene in a high pressure vessel. The result is about 93 ppm, which is considered to be a reasonable value.

(Predicted indicated value =  $(124/10.5 + 62.6 / 10 + 94.2 / 5.6 + 111 / 6.0 + 52.7 / 1.0) * 240/273 = 93.3$  ppm)

For trichlorethylene, indicated values were around 200 ppm, which were also considerably lower values compared with gas concentration (484 ppm). Along with the above case, a predicted value for the indicated value was calculated using the conversion factor (2.0) and the deviation of the indicated value for toluene in a high pressure vessel. The result is about 213 ppm, which is also considered to be a reasonable value.

#### ○ Reproducibility (Drift) Test

During the test period (two weeks), toluene in a high pressure vessel (about 275 ppm (1900 ppmC)) is fed three times and indicated values were read. Deviations, from the first indicated value, of the other values were -12% at a maximum. Although they were slightly large, the values were all within the accuracy range of the product to be verified.

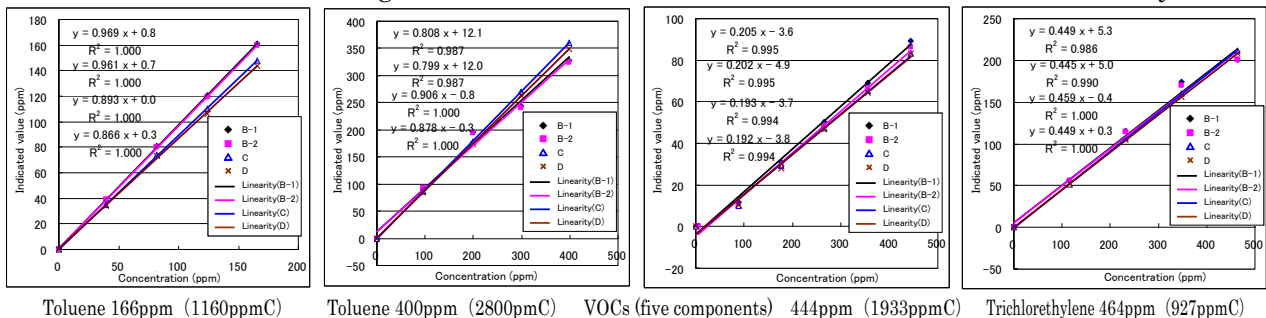
#### ○ Response Time Test

Measurement of the product to be verified is performed according to the sequence mentioned above (automatic zero point calibration -> measurement -> automatic cleaning). For all four units tested, 98%-response times were not longer than two sequences (about 120 min). This test was performed for a system including a gas supply line for testing, not for the equipment alone.

#### ○ Linearity Test

The results of the linearity test were about  $\pm 10\%$ . It is estimated that the dispersion is caused by internal switching between low / high range described in the repeatability test. However, the results were within the nominal accuracy of the product to be verified as a whole.

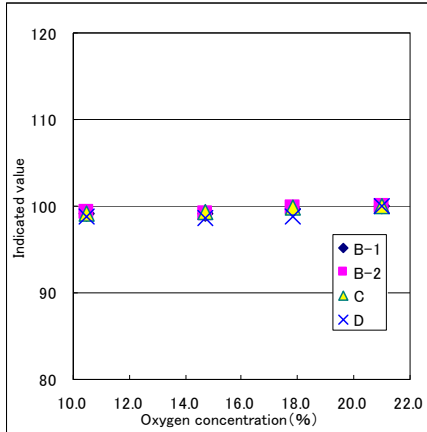
Correlated distribution diagrams are shown below to indicate the results of the linearity test.



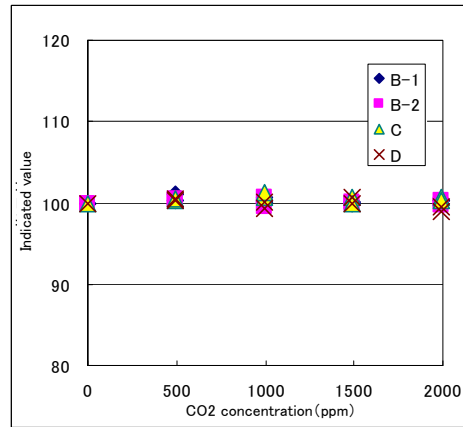
○ **Interference Effect Test**

Test results for the effects of oxygen, carbon dioxide, and water are shown below.

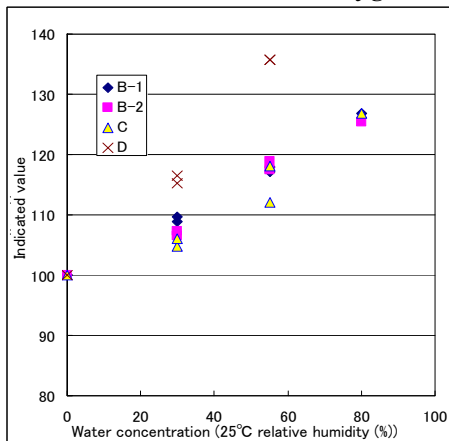
The effects of oxygen and carbon dioxide were not observed. For water, large positive effects on the zero point and the span were observed. The effect on the span when the interference effect on the zero point is compensated for is also shown in the figure. In addition, a test to know the effect of water on the sensor itself was performed with dry air supplied to the zero point calibration line. In normal measurement, an activated carbon tube to purify air is used at the zero point calibration line. Therefore, positive and negative effects will be exerted in the region where relative humidity is around 50%.



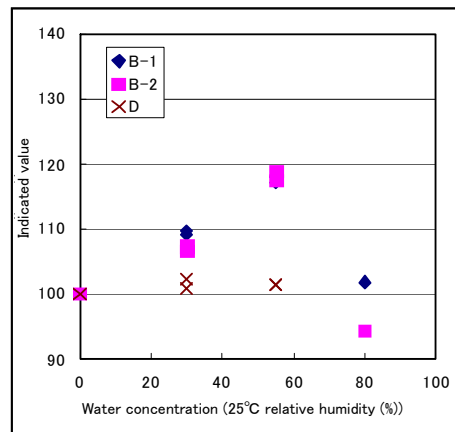
Test result for effects of oxygen



Test result for effects of carbon dioxide



Without zero compensation



With zero compensation

Test result for effects of water

○ **Measurement Test Using a Sample Gas Taken at an Enterprise**

Gas concentrations at the test using the sampling bag, and deviations (%) of the average indicated values of the test equipment are shown below.

Kind of gas	Name of gas	Concentration (ppm)	Concentration (ppmC)	Comparison equipment		Test equipment				
				HOR-made	TD-made	VOC-121H				
				NDIR	FID	Interference enhanced reflection (IER)				
				A	B	B-1	B-2	C	D	
				ppmC	ppmC	ppm	ppm	ppm	ppm	
Gas in high pres. vessel	C7H8	273	1911	Indicated value	1911	1911	210	209	222	206
				Deviation(%)	0.0	0.0	-23.1	-23.4	-18.7	-24.5
Bag (1)	Sample (1)	120.8	750	Indicated value	752	748	139	152	109	142
				Deviation(%)	0.3	-0.3	14.8	25.7	-10.1	17.3
Bag (2)	Sample (2)	127.2	845	Indicated value	856	834	244	252	222	279
				Deviation(%)	1.3	-1.3	91.5	98.0	74.3	119.3

As the result of a repeatability test using the gas in the sampling bag, dispersion was about ±3%, which was an excellent result.

For the bag (1), indicated values showed relatively large dispersion, -10 to +25%, depending on

the test equipment. For the bag (2), dispersion was as large as +75 to +120.

Conversion factors are: toluene (1.0), xylene (0.35), ethylbenzene (0.2), n-butyl alcohol (1.1), and formaldehyde (3.4). A predicted value for the indicated value was calculated using the conversion factor and the deviation of the indicated value for toluene in a high pressure vessel. The results are about 133 ppm for the bag (1) and about 260 ppm for the bag (2), which are considered to be reasonable values.

○ **Summary of Verification Tests**

Viewpoint	Summary of results								
Reliability	<p>The equipment showed excellent performance for repeatability, linearity, and response time.</p> <p>Regarding the interference effect test, an effect of water was observed. Care should be exercised although no problem would arise in measurement in normal environments because the order of the effect is small.</p> <p>It is desirable to establish a simple span check method to ensure the accuracy and reliability of the indicated value itself.</p>								
Practicality	<p>This equipment is useful when components of VOCs are clearly known and they do not change at a measurement site, or in the case of a single component VOC. Measurement results are indicated as toluene equivalent ppm values. For VOCs other than toluene, therefore, conversion using a conversion factor is required for each component. For multi component VOCs, or when components of VOCs change, measurement should be performed after understanding the characteristics of the indication sufficiently, checking components of the gas measured in advance.</p> <p>Among the chips specified, concentration measurement ranges of the spec-2 chip (Equipment C) and the spec-3 chip (Equipment D) were high. Although measurement with them was possible in the concentration range of this verification test, they are suited to process management (on site) rather than use in measurement for regulations of the Air Pollution Control Act.</p>								
Convenience	<p>Operation procedure is simple and easy. Sequence indication and the transition of concentration are provided during continuous measurement. The indication would become more convenient if there is a function of holding the measured value.</p> <p>Part of “Reference Information” is extracted below as evaluation items on convenience.</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tbody> <tr> <td style="width: 50%;">Price</td> <td>Open pricing</td> </tr> <tr> <td>Weight</td> <td>About 400 g</td> </tr> <tr> <td>Power supply</td> <td>Four AA alkaline cells, four nickel metal-hydride batteries, or AC 100V (using the AC adapter provided)</td> </tr> <tr> <td>Warming-up time</td> <td>Not required</td> </tr> </tbody> </table>	Price	Open pricing	Weight	About 400 g	Power supply	Four AA alkaline cells, four nickel metal-hydride batteries, or AC 100V (using the AC adapter provided)	Warming-up time	Not required
Price	Open pricing								
Weight	About 400 g								
Power supply	Four AA alkaline cells, four nickel metal-hydride batteries, or AC 100V (using the AC adapter provided)								
Warming-up time	Not required								

**[Reference Information]**

The following reference information is based on the application by the environmental technology

developer on his own responsibility. Ministry of the Environment and the Verification Organization do not assume any responsibility on this information.

○ Product Data

\* System accuracy (indication error, etc.) is  $\pm 20\%$ .

Item	Description
Name of company	O.S.P. Inc. URL <a href="http://www.osp-inc.co.jp">http://www.osp-inc.co.jp</a>
Address	2-14, Higashi-mitsugi, Sayama, Saitama, 350-1302
Contact person (affiliation, name,)	VOC Sensor Division, Kyoko Yamaguchi
Point of contact	Tel / Fax E-mail
Product name	Handy VOC Sensor (three types (spec-1, spec-2 and spec-3) with different sensor elements)
Model	VOC-121H
Distributor / maker	O.S.P. Inc.
Weight	About 400 g
Price	Open pricing
Substances to be analyzed	Almost all VOCs
Application (assumed)	<ul style="list-style-type: none"> <li>• Grasping of current status of VOC emission, continuous monitoring, and check of effectiveness of various VOC reduction measures at enterprises that emit VOCs in industries such as coating, printing, adhesive bonding, washing, storage, and chemical production</li> <li>• Simplified check, monitoring, etc., of VOC concentration at inlet / outlet of VOC treatment / recovery equipment</li> <li>• Simplified screening of VOC leakage into or contamination of industrial waste water, soils, groundwater, rivers, etc.</li> <li>• Simplified concentration measurement in working environments</li> <li>• Simplified check of residual solvent concentration in films or water-base solvents</li> </ul>
Is there any reference material for calibration?	Yes (Already prepared) / No
Calibration method	Use automatic span calibration mode by toluene reference gas (in a bomb or disposable can)
Sampling method	A built-in diaphragm type suction pump is used.
Operation environment (room temperature)	0 °C to 40°C
Operation environment (relative humidity)	0% to 95%

Operation environment (others) (environments where this method cannot be used, etc.)	<ul style="list-style-type: none"> <li>Gas temperature: 5 °C to 50°C, gas relative humidity: 10% to 95%</li> <li>It is desirable that temperature difference between clean air for automatic zero point calibration and sample gas is within <math>\pm 10\%</math>, and difference in relative humidity is <math>\pm 20\%</math>.</li> <li>When measuring high temperature dry exhaust gas, etc., extend the gas tube with a Teflon tube, etc., to cool the gas before the sensor part.</li> <li>When low humidity gas (relative humidity is 15% or lower) is measured, zero point calibration should be performed with a silica-gel tube and dry zero gas such as dry air and nitrogen gas.</li> <li>When high humidity gas (relative humidity is 85% or higher) is measured, zero point calibration should be performed with wet zero gas having been passed through a humidifier bottle, etc.</li> <li>Non-condensing</li> <li>The sensor body is not explosion-protected. It should be used outside hazardous areas, or when it is used in such areas, appropriate protection measures should be taken.</li> </ul>
Product storage conditions (maintenance methods, etc.)	<ul style="list-style-type: none"> <li>Storage temperature: 0 °C to 40°C</li> <li>Maintenance: an activated carbon filter for zero point calibration, a PTFE filter (dust prevention), regular cleaning and replacement of sensor chips, etc.</li> </ul>
Product warranty period	<ul style="list-style-type: none"> <li>Main body: twelve months after production</li> <li>Sensor part: one year in climate conditions in Japan</li> <li>Sensor chip: consumables</li> </ul> <p>Element life may differ depending on frequency of use, components of VOCs measured, gas concentration, etc. (The sensor has self-diagnosis function for its life.)</p>
Response time	<ul style="list-style-type: none"> <li>Initial response: 3 s or longer</li> </ul> <p>Each measurement: 10 s or longer (may be longer than 10s in the case of VOC components with high molecular weight)</p>

○ **Other Information from the Verification Applicant**

(Describe comments on verification test results, the results of additional tests performed at the Verification Applicant, etc.)

It was verified in this verification test that characteristics of this VOC sensor technology, such as repeatability (reproducibility), linearity, response time, and interference effects, were excellent, and operation of the equipment was easy.

(For reference, the result of an additional test (a water interference effect test) is attached where zero point calibration was performed with an activated carbon.)

We think it was confirmed by these characteristics obtained in the test that continuous monitoring measurement (intermittent measurement based on intermittent operation), at which this sensor (this technology) excelled, could be performed accurately and quickly.

We have many products to which this sensor is applied, such as stationary monitor type, built-in type, and multi-channel type, and flexibly respond to requests for customization from users.

**Results of Additional Tests Performed at the Verification Applicant**

An additional test to check the effect of water was performed at about 15°C and at relative humidity of about 75, 45, or 25%. The test was performed with three units, B-1, B-2, and C, owing to circumstances of equipment preparation.

An activated carbon tube for zero point calibration was used for zero point adjustment, and the test was performed selecting 'Auto' range.

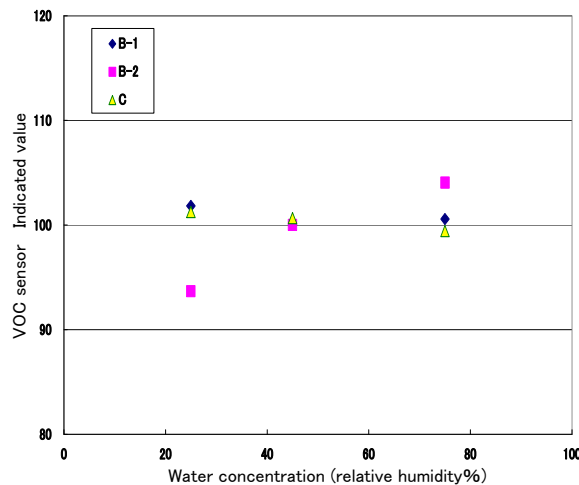
For span gas, toluene gas was prepared in a gas bag filled with humidity-controlled air (relative humidity: 75, 45, and 25%, toluene concentration: 150 to 180 ppm).

For comparison, air for zero point calibration with the same humidity as the span gas was prepared, and zero point calibration and span gas measurement were performed.

The test results are shown in the table and the figure below (calculated so that '100' corresponds to the condition where difference in humidity between air for zero point calibration and span gas is 0%). Under this test condition, the effect of water (difference in humidity) on the span was within  $\pm 10\%$ .

Kind of gas	Name of gas	Concentration (ppm)	Water concentration (%)	Water concentration (%)	Humidity difference (%)	Test equipment		
						VOC-121H		
						Interference enhanced reflection (IER)		
						B-1	B-2	C
						ppm	ppm	ppm
Zero adjustment	Air	0	Zero adjustment	Span		0	0	0
Span	C7H8	154	45	45	0	154	148	151
Span	C7H8	154	50	45	-5	154	148	152
Span	C7H8	178	75	75	0	178	173	173
Span	C7H8	178	50	75	25	179	180	172
Span	C7H8	164	25	25	0	164	158	161
Span	C7H8	164	50	25	-25	167	148	163
↓ Calculated so that '100' corresponds to the condition where difference in humidity between air for zero point calibration and span gas is 0%.								
Span	C7H8	154	45	45	0	100	100	100
Span	C7H8	154	50	45	-5	100	100	101
Span	C7H8	178	75	75	0	100	100	100
Span	C7H8	178	50	75	25	101	104	99
Span	C7H8	164	25	25	0	100	100	100
Span	C7H8	164	50	25	-25	102	94	101

Test date: March 9, 2010 (Tuesday)



\* Hold of measurement values during continuous measurement: When the interval setting is 0 min, measurement indication can be held for 1 min by button operation during zero point calibration. When the interval setting is not 0 min, a measurement value held can be indicated in a standby state during interval time.

\* For reliable measurement, a simple calibration kit is provided. Sensitivity can be checked regularly with reference gas, or span calibration can be conducted with the kit.

\* If components of VOCs and their mixing ratio can be estimated, as in the case of this on-site measurement (at a coating booth), a calculation form (attached) can be used, with which ppmC values are estimated by simple calculation.

Example: The conversion factors (ppm -> ppmC) estimated by calculation based on the component ratio of MSDS of melamine resin coating used this time were about 4.3 for the coating No. 1 and about 2.5 for the coating No. 2. As shown below, the ppmC values calculated with these factors, also considering the deviation of the test equipment, were close to the indicated values of comparison equipment pursuant to the official method:



Coating No. 1: about 786 ppmC

Coating No. 2: about 791 ppmC

**Melamine resin coating No. 1**

Indicated value of measuring equipme 181 ppm-Toluene

True value ppm	127
True value ppmC	786
ppm Conversion factor	0.7
ppmC Conversion	4.34

Name of substance	Conversion factor	Carbon number	Molecular weight	Used amount (weight ratio)	True value ppm	True value ppmC
Toluene	1	7	92.14	24.6	65	453
Formaldehyde	3.4	1	30.03	0.4	3	3
m-xylene	0.35	8	106.17	7.3	17	133
Ethylbenzene	0.2	8	107.17	3.2	7	58
Butanol	1.1	4	74.12	10.6	35	139

**Melamine resin coating No. 2**


Indicated value of measuring equipme 317 ppm-Toluene

True value ppm	119
True value ppmC	791
ppm Conversion factor	0.37
ppmC Conversion	2.5

Name of substance	Conversion factor	Carbon number	Molecular weight	Used amount (weight ratio)	True value ppm	True value ppmC
Toluene	1	7	92.14	0	0	0
Formaldehyde	3.4	1	30.03	0.4	3	3
m-xylene	0.35	8	106.17	24.7	57	456
Ethylbenzene	0.2	8	107.17	10.7	24	196
Butanol	1.1	4	74.12	10.3	34	136

Target verification technology / environmental technology developer*	Handy TVOC Monitor (Model FTVR-02) Figaro Engineering, Inc.
Verification Organization	Japan Environmental Technology Association
Verification test period	Jan 18 to Feb 4, 2010
Aim of this technology	Simplified VOC measurement that can be used for voluntary efforts for VOC emission reduction

### 1. Outline of Target Verification Technology

	<p><b>Measurement Principle</b></p> <p>An oxide semiconductor gas sensor, in which a noble metal added metal oxide is used as a gas sensitive material, is used to measure TVOC concentration. The metal oxide reacts with VOC gas when heated to a predetermined temperature, and its electric resistance rapidly decreases.</p> <p>This equipment adopts a sensor that can measure a wide range of concentration with uniform sensitivity for various types of TOVCs.</p> <p>TVOC concentration is calculated with a calibration curve already calibrated and measurement values compensated by a temperature sensor and a humidity sensor built in the equipment.</p>
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### 2. Outline of Verification Test

#### ○ Specifications of Equipment to be Verified

Model	FTVR-02
Measurement principle	Oxide semiconductor type gas sensor
Gases to be measured	TVOCs (various aromatic hydrocarbons and aliphatic hydrocarbons)
Measurement range	1 to 3,000 ppm (toluene equivalent concentration)
Gas sampling method	A built-in suction pump is used. Flow rate of sampling: 0.8 L/min
Power supply of equipment	Four AA alkaline cells, four nickel metal-hydride batteries, or AC 100V (using the AC adapter provided)

#### ○ Verification Test Implementation Site

Basic performance test: Conducted at Reference Gas Testing Laboratory, Environmental Science Research Institute, Yokohama City.

Measuring test of a sample taken at an enterprise: A sample was taken into a bag at Coating Testing Facility of Tokyo Metropolitan Industrial Technology Research Institute, and measurement was conducted at Reference Gas Testing Laboratory, Environmental Science Research Institute, Yokohama City.

### 3. Verification Test Result

For each test method, see “5. Verification Test Implementation Method” of the original test result report.

When extremely dry gas is used as test gas in this equipment to be verified (FTVR-02), measured values may go out of the calibration curve range. Therefore, a humidistat (humidifier) was connected to the equipment in the test.

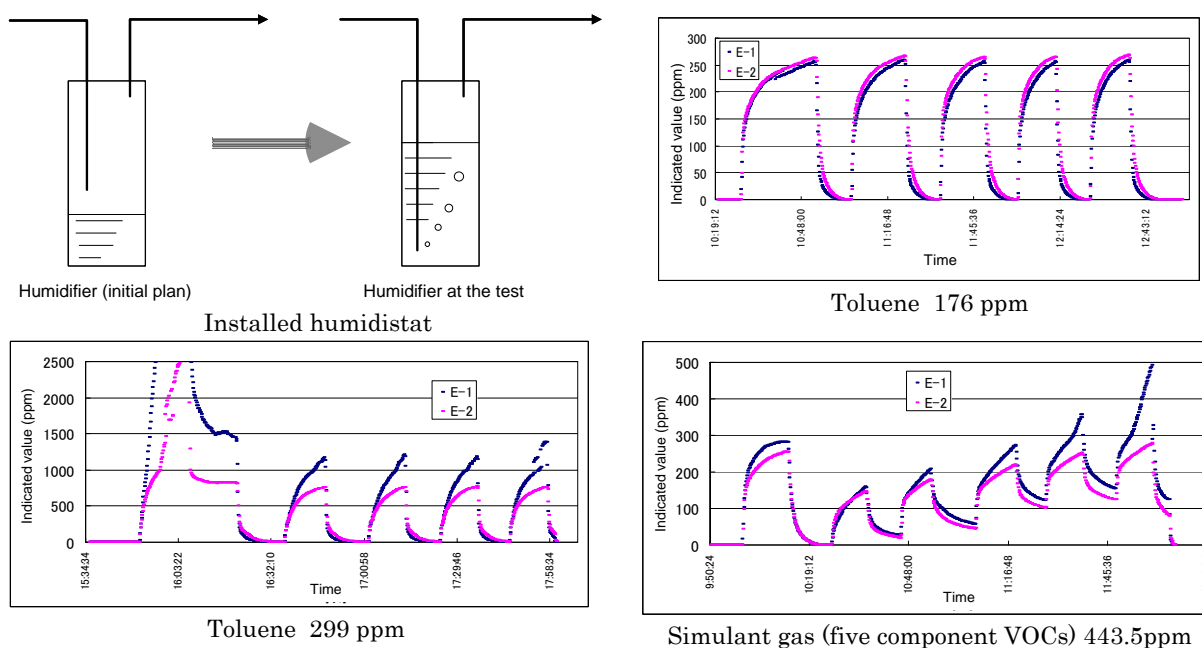
#### ○ Repeatability Test

As the results of a repeatability test at toluene concentration of 176 ppm, dispersion was as low as  $\pm 1\%$ . However, there were large deviations in a high concentration region, etc.

It would be caused by combination of the delay in response time of the sensor itself and the delay by the humidistat inserted before the equipment. At first, it was planned that humidification was performed by passing the gas above water. In the test, however, it was done by bubbling according to the request from the Verification Applicant. Conditions of response are shown in Figs. 6-2 to 6-4.

The first toluene gas of 299 ppm was prepared to a predetermined concentration by inletting high concentration gas and then lowering its concentration. However, because the response was not quick enough, a higher indicated value was observed. In the case of a simulant gas (five component VOCs), because isopropyl alcohol, ethyl acetate, and methyl ethyl ketone, which are water-soluble, were contained, indicated values tended to gradually increase, including the zero point.

In the case of trichloroethylene, indicated values were low, and the value was zero for E-1.



#### ○ Reproducibility (Drift) Test

In the reproducibility (drift) test, toluene gas of about 275 ppm (1,900 ppmC) was fed from a high pressure vessel, and deviations from the first indicated value were checked. However, probably because concentrations were high, indicated values became unstable, sometimes going out of the range of the calibration curve (3,000 ppm). Therefore, evaluation of this test was not possible.

#### ○ Response Time Test

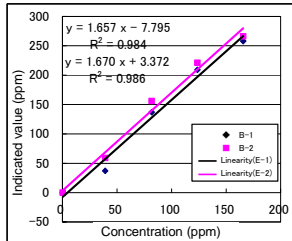
For the measurements of toluene of 176 ppm (1,230 ppmC) and simulant gas (five component VOCs), 90%- and 98%-response times were to be measured. Based on the indicated value 10 min after the gas was fed, which was assumed to be 100%, 90%- and 98%-response times from the time when indicated value began to change were to be measured. However, the indicated value continued to rise after 10 min had passed.

This test was performed for a system including a gas supply line for testing, not for the equipment alone.

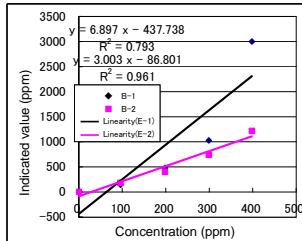
### ○ Linearity Test

The results of the linearity test were about ±10% for toluene of 166 ppm. Regarding toluene with relatively high concentration (399 ppm) and the simulant gas (five component VOCs), the results were -15% to -40%. The reason of this deviation would be difficulty in calibration, caused by the principle of semiconductor sensors (the property is represented by a straight line on a double logarithmic chart). For the test using the simulant gas (five component VOCs), the humidistat was not used because there was a problem of gas dissolution into water during the repeatability test.

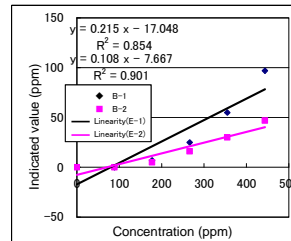
Correlated distribution diagrams are shown below to indicate the results of the linearity test.



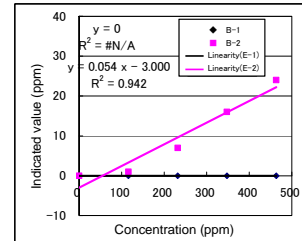
Toluene 166ppm (1160ppmC)



Toluene 400ppm (2800ppmC)



VOCs (five components) 444ppm (1933ppmC)



Trichlorethylene 464ppm (927ppmC)

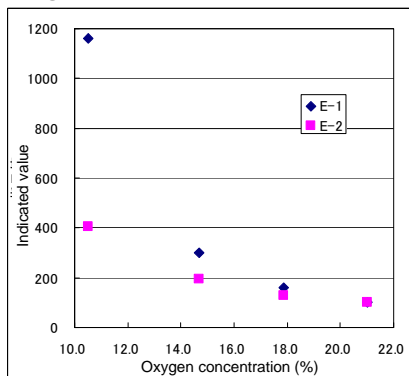
### ○ Interference Effect Test

Test results for the effects of oxygen, carbon dioxide, and water are shown below.

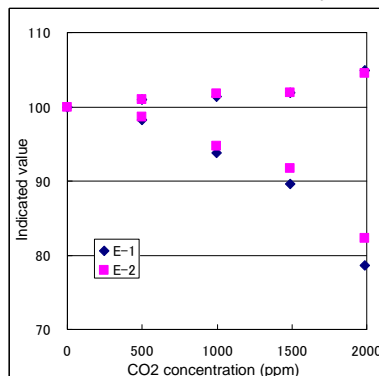
For the effect of carbon dioxide, indicated values increased with time for all data, which seemed to be an unreasonable result.

In principle, semiconductor sensors are not affected by carbon dioxide. Therefore, the cause would be the problem of responsibility described at the section of the repeatability test.

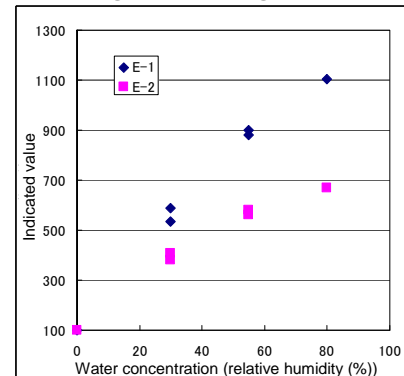
Although effects of oxygen and water on the zero point were not observed, their effects on the span were large. Since semiconductor sensors are considerably affected by water in principle, the equipment has a structure to compensate the effect of water, where a humidity sensor is mounted in the main body and compensation on water can be performed with it. However, in cases where water concentration changes at the sampling gas line (at the probe: semiconductor sensor), as in the case of this test, compensation on water in the sample gas is not possible with this configuration because water concentration at the main body did not change according to it.



Test result for effects of oxygen



Test result for effects of carbon dioxide



Test result for effects of water

### ○ Measurement Test Using a Sample Gas Taken at an Enterprise

Gas concentrations at the test using the sampling bag, and deviations (%) of the average indicated values of the test equipment are shown below.

Kind of gas	Name of gas	Concentration (ppm)	Concentration (ppmC)		Comparison equipment		Test equipment	
					HOR-made	TD-made	VOC-1	
					NDIR	FID	Oxide semiconductor gas	
					A	B	E-1	E-2
					ppmC	ppmC	ppm	ppm
Gas in high pres. Vessel	C7H8	273	1911	Indicated value	1911	1911	3000	716
				Deviation (%)	0.0	0.0	998.9	162.3
Bag (1)	Sample (1)	120.8	750	Indicated value	752	748	61	63
				Deviation (%)	0.3	-0.3	-49.8	-47.7
Bag (2)	Sample (2)	127.2	845	Indicated value	856	834	103	95
				Deviation (%)	1.3	-1.3	-18.8	-24.9

As the result of a repeatability test using the gas in the sampling bag, dispersion was about  $\pm 20\%$ . The humidistat was not used in this case. Indicated values increased with time, which would be caused the delay of response time of the sensor.

Deviations of indicated values were -50 to -20, relatively low values. The reason would be that, compared with toluene, relative sensitivities of other gas components were low. Although it was anticipated that indicated values became lower for the bag (2) which was mainly composed of xylene, the result was not so. Measurement of the bag (2) was performed after the bag (1). Therefore, the reason would be the problem of response mentioned above (indicated values increased with time).

#### ○ Summary of Verification Tests

Viewpoint	Summary of results
Reliability	<p>Reliability of measurement values, such as concentration measurement range, response time, and interference effects by oxygen and water, is in need of some improvements. For toluene, however, a certain level of reliability would be secured in the range not greater than 200 ppm (1,400ppmC).</p> <p>To compensate the effect of water, this equipment adopts a structure where a humidity sensor is mounted in the main body and compensation on water is performed with it. However, compensation on water in the sampling gas line (at the probe: semiconductor sensor) is not possible with this configuration. Since it is easy to enhance the sensitivity of oxide semiconductor gas sensors, the above problem would be considerably solved by combining the equipment with a dilution method, in which sample gas is continuously diluted (1/10 to 1/100) with zero gas made from ambient air by removing VOCs with activated carbon, etc.</p>
Practicality	<p>This equipment is useful when components of VOCs are clearly known and they do not change at a measurement site, or in the case of a single component VOC. Measurement results are indicated as toluene equivalent ppm values. For VOCs other than toluene, therefore, conversion using a conversion factor is required for each component. For multi component VOCs, or when components of VOCs change, measurement should be performed after understanding the characteristics of the indication sufficiently, checking components of the gas measured in advance.</p>

Convenience

Operation procedure is simple and easy. The equipment is useful for continuous monitoring for trend management, etc., because data can be collected with its embedded memory.

Part of “Reference Information” is extracted below as evaluation items on convenience.

Price	198,000 Yen
Weight	About 400 g
Power supply	Four AA alkaline cells, four nickel metal-hydride batteries, or AC 100V (using the AC adapter provided)
Warming-up time	Not required

**[Reference Information]**

The following reference information is based on the application by the environmental technology developer on his own responsibility. Ministry of the Environment and the Verification Organization do not assume any responsibility on this information.

## ○ Product Data

Item	Description
Name of company	Figaro Engineering, Inc.
	URL <a href="http://www.figaro.co.jp">http://www.figaro.co.jp</a>
Address	1-5-11, Senba-nishi, Mino, Osaka, 562-8505
Contact person (affiliation, name,)	Unit Development Department, Yasuhiro Setoguchi
Point of contact	Tel / Fax
	E-mail
Point of contact	Point of contact
Product name	Handy TVOC Monitor
Model	FTVR-02
Distributor / maker	Figaro Engineering, Inc.
Weight	About 400 g (including cells)
Price	198,000 Yen
Substances to be analyzed	TVOCs in exhaust gas
Application (assumed)	<ul style="list-style-type: none"> <li>• Field environment management to prevent health problem at work at factories</li> <li>• Daily management of exhaust gas concentration at factories</li> <li>• Degradation diagnosis of VOC removal filter, etc.</li> </ul>
Is there any reference material for calibration?	<input checked="" type="radio"/> ( Yes ) ( Already prepared / Not prepared yet ) / No
Calibration method	Users can calibrate zero point with a simple zero point adjustment kit. Span calibration: use a replacement sensor probe.
Sampling method	Active sampling (suction amount: about 1 L/min)
Operation environment (room temperature)	0 °C to 40°C
Operation environment (relative humidity)	5% to 95%
Operation environment (others) (environments where this method cannot be used, etc.)	At normal work environments, or measurement of factory exhaust gas (several ppm to several thousand ppm) * Do not expose the sensor to high concentration solvent gas for a long time.
Product storage conditions (maintenance methods, etc.)	Seal the sensor probe part with an aluminum bag attached.
Product warranty period	Twelve months after production

Response time

About 1 min

### ○ Other Information from the Verification Applicant

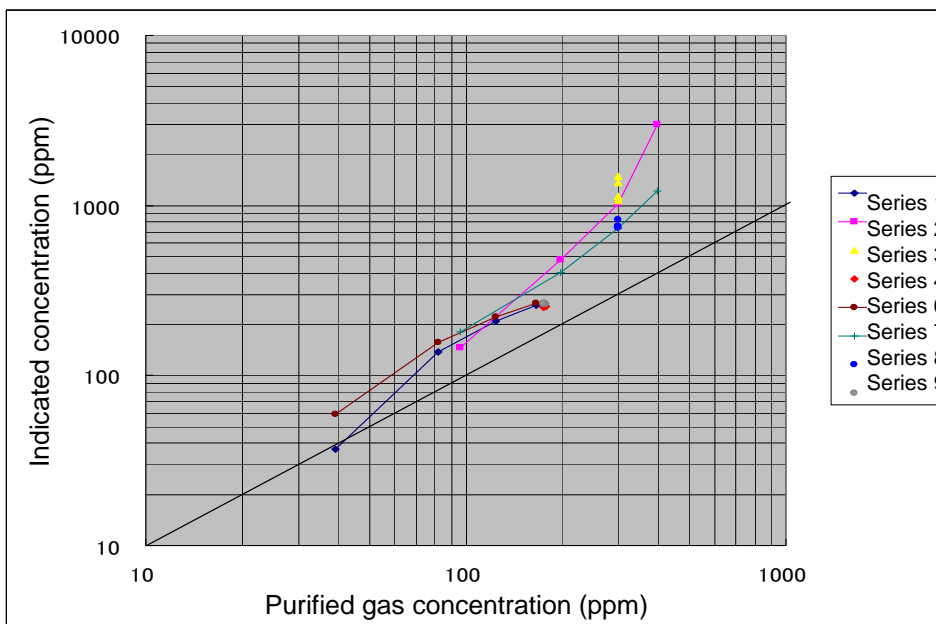
(Describe comments on verification test results, the results of additional tests performed at the Verification Applicant, etc.)

Since there were no official standards on simplified VOC measurement equipment, we used our own test method. Responding to the result of this test, we would like to improve the matters pointed out.

#### ○ About the Results of Repeatability and Linearity Tests

For the behavior of semiconductor sensors, there is a logarithmic relationship between sensor signals (sensor resistances) and gas concentrations. Therefore, when zero point adjustment was made with highly-purified air initially, we suppose cleanliness of the air was too high for the sensor compared with normal atmosphere, and consequently indicated concentration values became considerably high. Thus, we asked the Verification Organization to perform the test in the air using a zero point calibration kit attached.

Regarding the results for toluene, indicated values were mostly higher.



With regard to the lower indicated values for the simulant gas (five component VOCs), although gases for which sensitivity becomes lower were not used in the test (judging from sensitivity data we have), the response wave forms obtained in the test have broad shapes, which would be one of the causes of these lower indicated values.

We were aware of the fact that sensitivity became lower generally for chlorine-based VOCs, but we have not understood the reason why such low values were indicated for trichlorethylene.

#### ○ About the Results of the Interference Effect Test

From the measurement principle, it adds up that oxygen and water affect the result, and CO<sub>2</sub> barely affect it.

Regarding the effect of water, we think it is reproduced that the effect is very low in a dry condition (humidity = 0%), and dependence is small in normal humidity situations.

A humidity sensor is mounted in the main body for a humidity compensation function. This configuration enables compensation in applications where gas in a working environment is sampled.

#### ○ About the Results of the Test at an Enterprise

Regarding the components used in the two tests by the Verification Organization: According to our in-house data, sensitivity becomes low for a small amount of formaldehyde, but sensitivity for other gases is almost the same as that for toluene.



Target verification technology / environmental technology developer*	Gas leakage detector (Model GL-103) RIKEN KEIKI Co., Ltd.
Verification Organization	Japan Environmental Technology Association
Verification test period	Jan 18 to Feb 4, 2010
Aim of this technology	Simplified VOC measurement that can be used for voluntary efforts for VOC emission reduction

## 1. Outline of Target Verification Technology



### Measurement Principle

As with the official method, GL-103 is a flame ionization detector (FID). However, it is regarded as a simplified FID, having basic features of FID.

VOC gas is carried to a nozzle with hydrogen gas, and thermally decomposed into carbon and hydrogen in a high temperature flame. Then, carbon is further decomposed into positive ions and electrons at high temperature. The positive ions and electrons are attracted by electrodes to which high voltage is applied, which mean that current is carried. The magnitude of the current is proportional to the amount of ions, that is, gas concentration of hydrocarbons. Therefore, gas concentration can be obtained based on the magnitude of current.

## 2. Outline of Verification Test

### ○ Specifications of Equipment to be Verified

Model	GL-103
Measurement principle	Flame ionization detector (FID)
Gases to be measured	Almost all VOCs
Measurement range	0 to 100/1,000/10,000 ppmC (methane equivalent)
Gas sampling method	A built-in suction pump is used. Flow rate of sampling: 1L/min
Hydrogen consumption hours	3 hours continuously (using a dedicated bomb)
Power supply of equipment	Four C size batteries; Continuous-use hours: alkaline dry cells 6 hours, manganese dry cells 4 hours

### ○ Verification Test Implementation Site

Basic performance test: Conducted at Reference Gas Testing Laboratory, Environmental Science Research Institute, Yokohama City.

Measuring test of a sample taken at an enterprise: A sample was taken into a bag at Coating Testing Facility of Tokyo Metropolitan Industrial Technology Research Institute, and measurement was conducted at Reference Gas Testing Laboratory, Environmental Science Research Institute, Yokohama City.

### 3. Verification Test Result

For each test method, see “5. Verification Test Implementation Method” of the original test result report.

#### ○ Repeatability Test

As the results of a repeatability test, dispersion was as good as  $\pm 2\%$ . The following figure shows the meter of GL-103. Since indicated values needed to be read in the range no greater than 20% of the maximum value of the meter in this test, high accuracy cannot be expected.

The deviation of an indicated value from actual gas concentration was -18% for a simulant gas (five component VOCs), which was considerably low value. The reason would be that oxygenated compounds (isopropyl alcohol, ethyl acetate, and methyl ethyl ketone) for which relative sensitivity of FID is low were contained.



Meter of GL-103

#### ○ Reproducibility (Drift) Test

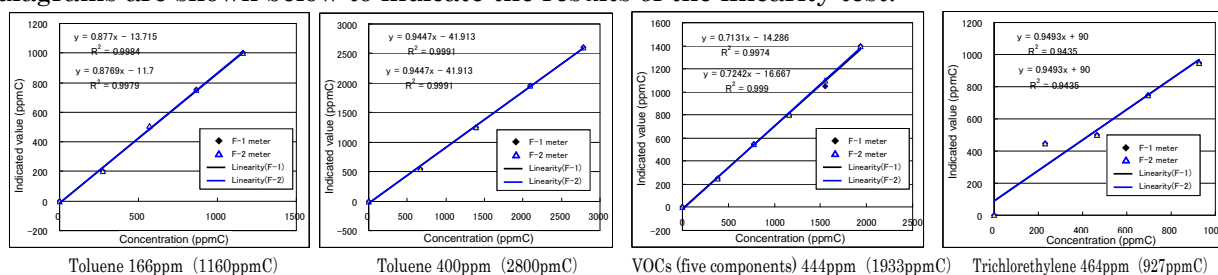
During the test period (two weeks), toluene in a high pressure vessel (about 275 ppm (1900 ppmC)) is fed three times and indicated values were read. Deviations, from the first indicated value, of the other values were -5% at a maximum. It was within the accuracy of reading.

#### ○ Response Time Test

For the measurements of toluene of 176 ppm (1,230 ppmC) and simulant gas (five component VOCs), 90%- and 98%-response times were measured. Based on the indicated value 10 min after the gas was fed, which was assumed to be 100%, 90%- and 98%-response times from the time when indicated value began to change were measured. The results were 50s or shorter for 90%-response time, and 80s or shorter for 98%-response time, which were considered to be good response. This test was performed for a system including a gas supply line for testing, not for the equipment alone.

#### ○ Linearity Test

The results of the linearity test were as good as within  $\pm 5\%$  mostly. In this test, indicated values needed to be read in the range no greater than 20% of the maximum value of the meter. Since the accuracy of reading had restriction in particular in the test of trichlorethylene, there was a measurement point that deviated from the regression line. Correlated distribution diagrams are shown below to indicate the results of the linearity test.



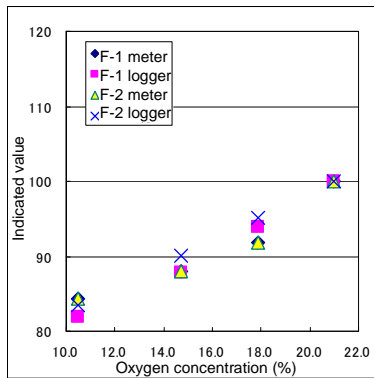
#### ○ Interference Effect Test

Test results for the effects of oxygen, carbon dioxide, and water are shown below.

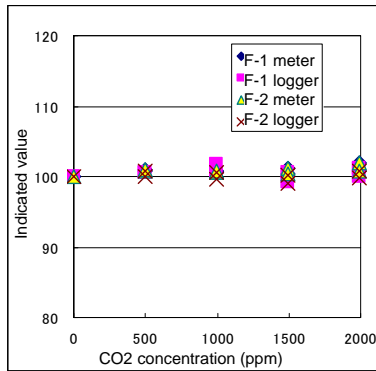
Although the effect of oxygen on the zero point was not observed, the effect on the span was -18% at a maximum, which was a significant value. The effect of oxygen on FID is attributable to its principle. However, the values were larger compared with the case of the comparison equipment with FID based on the official method. In the performance standards of the official method for FID, which is JIS B 7989 (measuring methods for volatile organic compounds (VOCs) in exhaust gas using automatic measuring equipment), it is specified that allowable change is 10% or less.

The effect of carbon dioxide was not observed.

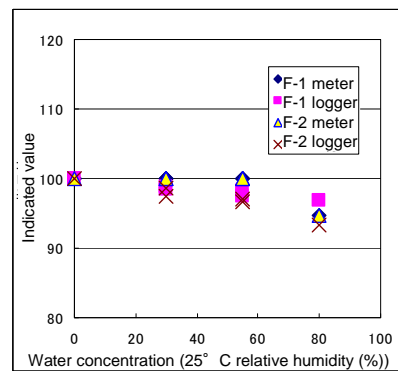
The effect of water was small both for the zero point and the span. The effect on the span was -6% at a maximum.



Test result for effects of oxygen



Test result for effects of carbon dioxide



Test result for effects of water

### ○ Test on the Effect of a (Hydrogen) Bomb

A fuel gas (hydrogen) bomb was connected to the equipment, and it was ignited. Then, after toluene of about 1,200 ppmC was fed, the variation of the indicated value was examined continuously. As a result, one of the two test units had an accidental fire 3 hours 11 min 10 sec later, while the other had it 3 hours 4 min 40 sec later. For both the units, variation of the indicated value or any abnormality was not observed.

### ○ Measurement Test Using a Sample Gas Taken at an Enterprise

Gas concentrations at the test using the sampling bag, and deviations (%) of the average indicated values of the test equipment are shown below.

Kind of gas	Name of gas	Concentration (ppm)	Concentration (ppmC)	Comparison equipment		Test equipment				
				HOR-made	TD-made	GL-103				
				NDIR	FID	Simplified FID				
				A	B	F-1 meter	F-1 logger	F-2 meter	F-2 logger	
ppmC	ppmC	ppmC		ppmC						
Gas in high pres. Vessel	C7H8	273	1911	Indicated value	1911	1911	1800	1967	1800	1962
				Deviation (%)	0.0	0.0	-5.8	2.9	-5.8	2.7
Bag (1)	Sample (1)	120.8	750	Indicated value	752	748	606	725	606	701
				Deviation (%)	0.3	-0.3	-19.2	-3.4	-19.2	-6.5
Bag (2)	Sample (2)	127.2	845	Indicated value	856	834	702	800	677	772
				Deviation (%)	1.3	-1.3	-16.9	-5.3	-19.9	-8.6

As the result of a repeatability test using the gas in the sampling bag, dispersion was about  $\pm 2\%$ , which was an excellent result.

However, this level corresponded to the limitation of the accuracy of meter reading. Deviations of indicated values (average; logger values) were -8% to -3%. It was estimated that relative sensitivity was a little lower compared with the comparison equipment with FID based on the official method. However, the values were within the accuracy range required for general simplified measurement equipment.

### ○ Summary of Verification Tests

Viewpoint	Summary of results
Reliability	The measurement principle is the same as the official method for FID. Although properties concerning the effect of oxygen and relative sensitivity do not satisfy the performance standards of the official method for FID (JIS B 7989: measuring methods for volatile organic compounds (VOCs) in exhaust gas using automatic measuring equipment), the equipment has the basic

	reliability of simplified measurement equipment (measurement accuracy = $\pm$ 20% in general).								
Practicality	Since measurement based on “ppmC” can be performed, as with the official method, this method is useful when measurement results are published or evaluated. The equipment has excellent practicality, such as use of a hydrogen bomb and operation using battery cells. However, its reading error is large because the meter is small, its scale is coarse, and the number of ranges is small (3 ranges). It is desirably to adopt a digital display, or provide external output terminals to connect a digital voltage meter or a tester. In addition, since the built-in pump is noisy, indoor measurement is difficult.								
Convenience	<p>Although it is required to get accustomed to a series of operation procedures, the procedure itself is relatively simple and easy.</p> <p>Part of “Reference Information” is extracted below as evaluation items on convenience.</p> <table border="1"> <tr> <td>Price</td> <td>500,000 Yen</td> </tr> <tr> <td>Weight</td> <td>About 4 kg</td> </tr> <tr> <td>Power supply</td> <td>Four C size batteries; Continuous-use hours: alkaline dry cells 6 hours, manganese dry cells 4 hours</td> </tr> <tr> <td>Warming-up time</td> <td>Not required</td> </tr> </table>	Price	500,000 Yen	Weight	About 4 kg	Power supply	Four C size batteries; Continuous-use hours: alkaline dry cells 6 hours, manganese dry cells 4 hours	Warming-up time	Not required
Price	500,000 Yen								
Weight	About 4 kg								
Power supply	Four C size batteries; Continuous-use hours: alkaline dry cells 6 hours, manganese dry cells 4 hours								
Warming-up time	Not required								

**[Reference Information]**

The following reference information is based on the application by the environmental technology developer on his own responsibility. Ministry of the Environment and the Verification Organization do not assume any responsibility on this information.

## ○ Product Data

\* In measurement principle, substances containing a hydrocarbon can be detected. The measurement range is based on CH<sub>4</sub> equivalent, and the following three ranges can be switched.

0 to 100 ppm / 0 to 1,000 ppm / 0 to 10,000 ppm

Item	Description
Name of company	RIKEN KEIKI Co., Ltd.
	URL <a href="http://www.rikenkeiki.co.jp">http://www.rikenkeiki.co.jp</a>
Address	2-7-6, Azusawa, Itabashi, Tokyo, 174-8744
Contact person (affiliation, name,)	Susumu Yoshikawa
Point of contact	Tel / Fax Point of contact
	E-mail
Product name	Gas leakage detector
Model	GL-103
Distributor / maker	RIKEN KEIKI Co., Ltd.
Weight	About 4 kg
Price	500,000Yen
Substances to be analyzed	Almost all VOCs
Application (assumed)	On-site measurement of VOCs emitted
Is there any reference material for calibration?	<input checked="" type="radio"/> Yes ( <del>Already prepared</del> ) / Not prepared yet ) / No
Calibration method	Calibration using span gas (sold separately)
Sampling method	Suction using a built-in pump
Operation environment (room temperature)	5 °C to 35°C
Operation environment (relative humidity)	5% to 95%RH (non-condensing)
Operation environment (others) (environments where this method cannot be used, etc.)	
Product storage conditions (maintenance methods, etc.)	Zero point adjustment, span adjustment, alarm point adjustment, remaining battery level, remaining hydrogen level in bomb, lightning indication, pump operation check, etc.

Product warranty period	Twelve months after production
Response time	7 sec (90%-response)

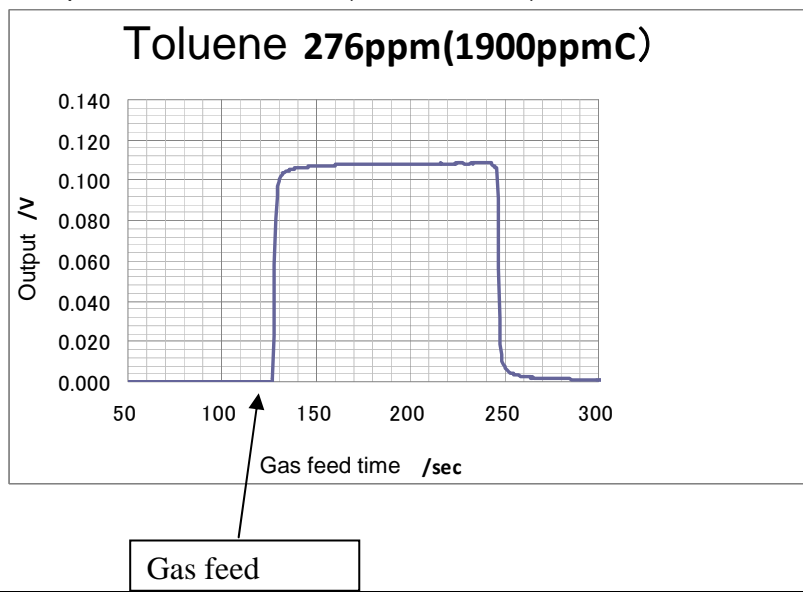
○ **Other Information from the Verification Applicant**

(Describe comments on verification test results, the results of additional tests performed at the Verification Applicant, etc.)

○ Sensitivity Characteristics of Various VOCs

Name of gas	Prepared gas concentration		Measurement voltage		Indicated value (toluene calibration)	
	ppm	ppmC	945010003	945010004	945010003	945010004
			V	V	ppmC	ppmC
air	0	0	0.0003	0	0	0
Toluene	276	1932	0.10837	0.10431	1930	1930
air	0	0	0.00052	0.00033	4	6
Toluene	53.7	376	0.02124	0.02079	374	385
Hexane	62.9	377	0.01877	0.01896	330	351
IPA	128.5	386	0.01775	0.01811	312	335
MEK	96.1	384	0.01716	0.01709	301	316
Ethyl acetate	95.8	383	0.0155	0.01511	271	280
Toluene	53.7	376	0.02095	0.02075	369	384
air	0	0	0.00022	-	-1	-
5 components mix	-	1906	0.08672	0.08664	1543	1603
air	0	0	0.00064	0.00022	6	4

○ Response Characteristics (In-house Data)



< Contact information >

Ministry of the Environment

Kasumigaseki 1-2-2, Chiyoda-ku, Tokyo 100-8975, Japan

Tel: +81-(0)3-3581-3351

- General information on “ETV Project”

Office of Environmental Research and Technology,

Policy and Coordination Division, Environmental Policy Bureau, MOE

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Tel: +81-(0)3-3581-3351

- Information on the simplified VOC measurement technology field”

Office of Environmental Research and Technology,

Policy and Coordination Division, Environmental Policy Bureau, MOE

Godochosha No. 5, Kasumigaseki 1-2-2, Chiyoda-ku, Tokyo 100-8975, Japan

Tel: +81-(0)3-3581-3351

< Website >

For detailed information on this project, see the following website.

<http://www.env.go.jp/policy/etv/>

Protocols, procedure of discussions in the Advisory Committee, verification test results, etc., are provided on this website

