

Feature Article

Portable VOC Analyzer FV-250 VOC Emission Regulations and Product Introduction

Hiroshi Mizutani, Kazuya Matsushita

The Japan's Air Pollution Control Law was revised on June 1 2005 and established emission regulations for Volatile Organic Compounds (VOCs). The Portable VOC Analyzer FV-250, which makes use of the Flame Ionization Detection (FID) method (suitable for both indoor and on-site use), was developed for the purpose of measuring VOCs. This article describes the FID principle, the configuration and the features of the FV-250, and the application of VOC emission regulations to facilities covered by the legislation when they came into effect in April 2006.

Introduction

It is pointed out that Volatile Organic Compounds (VOCs) are the major causative agents of secondary particles such as photochemical oxidants and suspended particulate matter (SPM), both of which have detrimental effects on air and water quality. The Ministry of the Environment has set the goal of cutting VOC emission levels in the year 2000 by 30% by the year 2010, and a revision of the Air Pollution Control Law was announced in May 2004. A government ordinance to regulate the facilities producing VOC emissions (specified facilities) and a ministerial ordinance of the Ministry of the Environment to limit VOC emissions have been enacted. The ordinances took effect from April 2006.

HORIBA produces the Portable VOC Analyzer FV-250 (Figure 1) in compliance with the operating performance standard values for VOC measurement analyzers as defined by the new regulations. The VOC emission regulations and an overview of the FV-250 development are described.



Figure 1 Portable VOC Analyzer FV-250

Current VOC Emissions and Features of the Revised Air Pollution Control Law

According to the inventories of greenhouse gas emissions and absorption which governments submitted to the secretariat in accordance with the Framework Convention on Climate Change, total VOC emissions in Japan were about 1,850,000 tons in 2000. Only ten percent of the emissions came from mobile sources such as vehicles, which indicates that earlier regulatory control of vehicular emissions has proved effective. Ninety percent of emissions came from non-regulated fixed sources, of which over 70 percent comprised solvents used in coating, painting, or cleaning, etc.^{[1][2]}. These percentages represent the present state of VOC emissions in Japan.

The revised Air Pollution Control Law is based on the concept of "Best Mix," a combination of legal control and voluntary compliance. Companies are encouraged to voluntarily reduce emissions in a manner that reflects their circumstances. The new legal controls target facilities that are affecting air quality as a result of producing large quantities of VOC emissions. A feature of the revised law is that it is thus based not only on enforcement, as with existing countermeasures, but on a collaborative approach to voluntary compliance by which companies can take into account their particular business activities in coming up with cost-effective measures to reduce their emissions of harmful air pollutants^[3].

The revised law aims to regulate and reduce the level of emissions at facilities which potentially produce 50 tons

of VOCs per year. At this level of emission there is a particularly large impact on the environment. With the aim of establishing a basic standard for emission control the following nine types of facilities are specifically covered by the new regulations.

- (1) Drying facilities for the manufacture of chemical products using VOC solvents.
- (2) Painting facilities.
- (3) Drying facilities associated with painting.
- (4) Drying facilities associated with adhesives used during the production of printed-circuit copper-clad lamination, adhesive tape/adhesive sheets, and release coated paper/packaging material.
- (5) Drying facilities associated with adhesives used to produce the products in item (4) and wood/wood products.
- (6) Drying facilities associated with printing.
- (7) Printing and drying facilities.
- (8) Cleaning facilities using VOCs industrially.
- (9) Storage tanks of VOCs (gasoline, crude oil, naphtha, etc.) where the stem pressure exceeds 20 kPa at 37.8 °C.

There are several principles involved in the measurement of VOC concentrations. The analyzers that comprehensively measure VOCs as regulated by the Air Pollution Control Law are the flame ionization detector (FID), which detects almost all organic compounds and generates a linear response based on the carbon number, and the subtraction-method non-dispersive infrared analyzer (NDIR), which uses oxidation catalysts. Which analyzer to use is a matter to be decided based on type of the facilities and circumstances of the measurement site. Many VOC emissions from stationary sources can be flammable depending on their concentrations. Some of the exhaust gases from the sources exceed VOC concentrations over their explosion points. The possibility of explosion must be considered when sampling exhaust gas, and a collecting bag should be used so that a sample of exhaust gas can be taken and then analyzed in a safe environment. Moving average deviations are determined based on characteristic VOC emission patterns obtained by carrying out a measurement survey during VOC emission. Analyzing the concentration fluctuations revealed that sample gas should be collected for 20 minutes. Figure 2 shows the method of collecting sample gas.

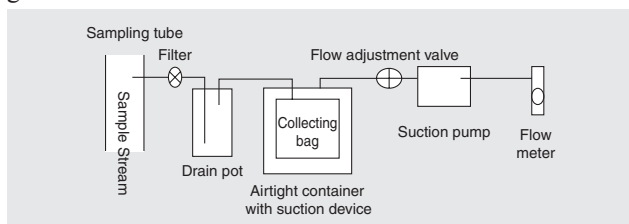


Figure 2 Method of Collecting Gas Samples^[4]

Because of the possibility of VOCs adhering to the collecting bag the type of materials from which the bag can be constructed and the time available from collecting the gas sample to analyzing it are limited. The results of the VOC damping tests show that the time from the end of collecting a sample of gas to the start of analyzing it should normally be less than 8 hours. In extremis, up to 24 hours is feasible. A fluorocarbon polymer film or polyester resin film collecting bag with a volume of 20 L or more should be used. Once used the bag should not be reused.

Measurement Method and Features of the Portable VOC Analyzer FV-250

The FV-250 was developed to meet the specification defined in the official method and be suited to the task of carrying out simplified measurements, which are thought to require an autonomous approach using the ‘Best Mix’ method. Being so designed, the FV-250 can measure sample gas accurately even during simplified measurements.

Measurement Principle

The flame ionization detector (FID), which the FV-250 uses to measure VOC, is based on the ionization of some of the hydrocarbon elements in the sample gas. The ionization occurs as the result of the high-temperature energy (1500K or higher) from combustion when hydrocarbons in the sample gas are mixed with a fuel gas and introduced into a hydrogen flame at the tip of the nozzle. When a direct-current voltage is applied across the nozzle and the electrode, a micro ion current proportionally to the carbon number is produced. This current can be collected and converted into concentration signals. Figure 3 shows the pattern diagram of the FID. To carry out measurements using the FID, hydrogen (the fuel gas) and air (oxygen - the combustion air) have to be supplied continuously during the measuring process.

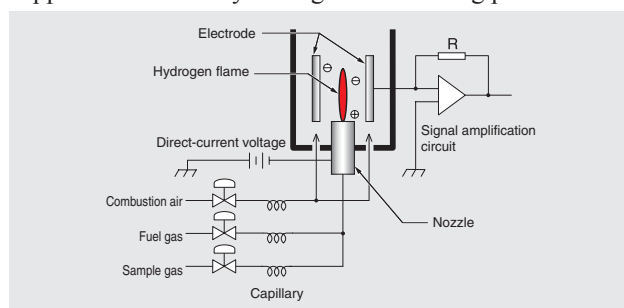


Figure 3 Pattern Diagram of FID

Feature Article

Portable VOC Analyzer FV-250 VOC Emission Regulations and Product Introduction

Adoption of Pure Hydrogen Cylinder Using Metal Alloys for Hydrogen Storage

The FV-250 can be equipped with a pure hydrogen cylinder using MH (Metal Hydride) for hydrogen storage. The cylinder differs from the existing small gas cartridges and the existing small gas cylinders in both capacity and filling pressure. It can store more than 3 times pure hydrogen as a high-pressure small gas cartridge of the same size can, at only one-tenth the filling pressure (approximately 1 MPa). Because of this, the FV-250 does not need high-pressure hydrogen cylinders, which need to be prepared and transported as a separate utility. Equipping the FV-250 with a pure hydrogen cylinder gives it good portability.

Reducing the Use of Heaters and Influence on Ambient Temperature

Existing flame ionization detectors reduced the influence of the ambient temperature by using a heater to maintain the sample gas flow, fuel gas flow, and combustion air flow capillaries at a constant temperature higher than that of the ambient. The FV-250 has a much smaller detection component including both a detector and a capillary for controlling flow rate, and they are located close to the detector with a hydrogen flame which is a heat source. In this way the temperature influence gradient - the influence of ambient temperature on the detector sensitivity - is reduced. The influence of ambient temperature is also reduced via the temperature compensation computed by the temperature sensor equipped analyzer. As a result there is no need for a heater. Figure 4 shows the influence on the FV-250 of ambient temperature before computed temperature compensation.

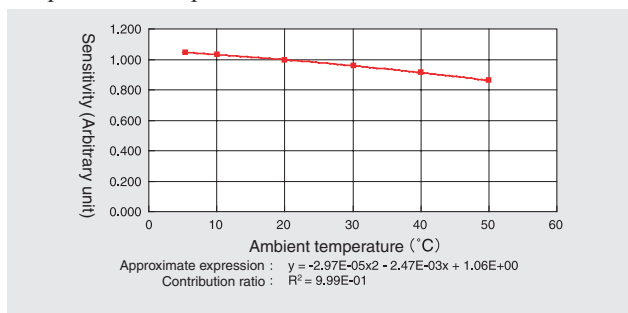


Figure 4 Influence on FV-250 of Ambient Temperature (before computed temperature compensation)

The reduction in the size and weight of the detector and removal of the heater and achieves a reduction of the total weight of the analyzer of about 50% over our conventional analyzers and a power saving of 10%, further improving the portability of the FV-250.

Optimization of Relative Response and Oxygen Interference

The sensitivity of FIDs to hydrocarbons (including VOCs) is based on carbon chain length, and hence FIDs will produce similar results for hydrocarbons with the same number of carbons atoms - a relative response to hydrocarbons. Sensitivity changes depending on the flow mixing ratio of sample gas and fuel gas (pure H₂ or a mixture of H₂ and He)/combustion air, the relative proportions of fuel in the fuel gas, and the material, structure, and dimensions of the detecting component. The sensitivity to oxygenated esters (ethyl acetate: C₄H₈O₂) and alcohols is 30 to 40 percent lower than that of propane (C₃H₈). This is attributed to the fact that the ionization by the hydrogen flame is affected by the physical and chemical nature of gas components.

The material and the shape of nozzle used for the FV-250 have been changed and the flow-mixing ratio of sample gas and fuel gas/combustion air has been optimized so that the device has a relative response characteristic specific to the VOC emission regulations. The relative responses to toluene (C₇H₈), ethyl acetate (C₄H₈O₂), and trichloroethylene (C₂HCl₃), all regulated under the revised law, are within the rated values.

The sensitivity of the FID varies depending on the oxygen concentration in the sample gas. This is called oxygen interference. As with the relative response to hydrocarbons, oxygen interference changes depending on the various elements as flow mixing ratio of the gases, the relative proportions of fuel in the fuel gas, and the material, the structure, and the dimensions of the detecting part, the hydrogen flame pattern, and the temperature distribution. By performing the same optimization of the oxygen interference as that of the relative response, the oxygen interference on the FV-250 is 10 percent or less of full scale (Figure 5).

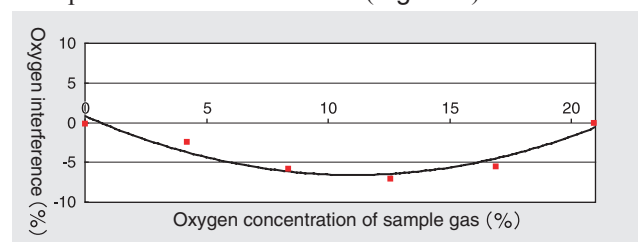


Figure 5 Oxygen Interference Influence on FV-250
Measurement sample: Propane (C₃H₈)

Some of the relative response characteristics, which vary depending on various conditions, are described below.

Figure 6 shows two types of nozzle shapes. Figure 7 shows the relative responses of ethyl acetate and trichloroethylene in air to propane obtained by using a large-bore nozzle and a small-bore nozzle, for each type of nozzle shape. They were obtained while the flow rate

of fuel gas (pure H₂) was changed at constant flow rates of sample gas and fuel gas. The large-bore flat head nozzle was adopted for the FV-250 so that it can meet the specified values at an appropriate flow rate. The specified relative response of ethyl acetate is 0.70 or more and the specified sensitivity to trichloroethylene is from 0.95 to 1.1 inclusive.

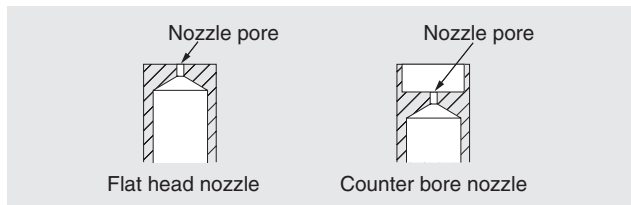


Figure 6 Nozzle Shape

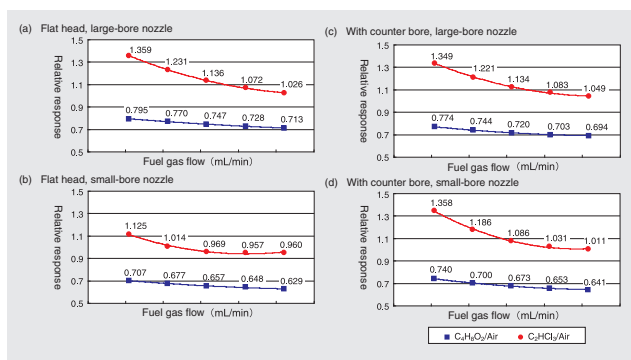


Figure 7 Relative Responses of Ethyl Acetate (C₄H₈O₂) and Trichloroethylene (C₂HCl₃) in Air
Sample Gas Flow: Constant, Combustion Air Flow: Constant, Fuel Gas: Pure H₂

Conclusion

The applications of analyzers are limited, and depend on their measurement principles and specifications. As we have discussed in this article, exactly which analyzer is suitable depends on whether it will be used to measure total VOC concentration or simply a specific component. The analyzer optimized to deal with the control of VOC gas emission from stationary sources has product specifications that comply with the official law. On the other hand, if used under the voluntary compliance guidelines, the product specification must be suitable for the on-site gas measurement and the continuous gas measurement (which is not advocated in the regulations) as well as the sample gas measurement should be performed with a collecting bag in a non-flammable environment. In this case, the analyzer with the following product specifications is strongly recommended:

- (1) Short warm-up time: In the case of on-site gas measurement, the analyzer is brought to the measurement site and then powered on. Once the analyzer has warmed up measurement can start. As a result, it is necessary to minimize the time until the concentration indication is stabilized.
- (2) Reduction of size and weight: For flexibility in choosing sampling points in on-site gas measurement,

the portability of the analyzer must be improved. It is necessary to consider the capacity and the stability of the power supply and reduce the power consumption of the analyzer.

- (3) Continuous measurement and long-term stability. In the case of continuous on-site gas measurement, it is necessary to stabilize the concentration indication of the analyzer for a long time and extend the calibration period.

Along with the FID using FV-250, the subtraction method NDIR analyzer NV-370 (using oxidation catalyst) also has been produced in order to carry out comprehensive measurement of VOCs in line with the Air Pollution Control Law (Figure 8). In this way HORIBA offers the most suitable analyzer for the needs of our customers and is sure to greatly contribute to the future of VOC emission limitation.



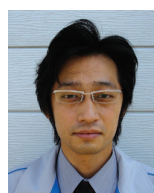
Figure 8 Subtraction Method NDIR Analyzer NV-370 (using Oxidation Catalyst)

Reference

- [1] Investigative Committee of VOC emission limitation in Central Environment Council, VOC emissions in Japan, distributed in the committee at September 29, 2003.
- [2] Masao Nakano, VOC Emission Limitation, *Kangikyou*, 94,3-6 (2004).
- [3] Central Environment Council, Proposal for VOC Emission Limitation at February 3, 2004.
- [4] [M1] Ministry of the Environment, Measurement Method of Volatile Organic Compounds, Announcement No.61 (2005).



Hiroshi Mizutani
HORIBA, Ltd.
Gas Measurement R&D Dept.
Combustion Control
Section Leader



Kazuya Matsushita
HORIBA, Ltd.
Gas Measurement R&D Dept.
Combustion Control