CONTINUOUS ANALYZER FOR VOLATILE ORGANIC COMPOUNDS IN AIR AND WATER

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Environmental pollution caused by volatile organic compounds (VOCs) has become a global environment issue, including issues on effects upon health. This paper introduces a system based on detection and sampling technologies and developed for measuring VOCs in the global environment. Small amounts of VOCs are measured with a gas chromatograph or photoionization detector (PID). VOCs in water are sampled using a sparging method. A small quantity of VOC constituents of more than 20 different types can be measured with a gas chromatograph using a programmed temperature oven. The PID can detect a ppb level of VOCs that are ionized using a vacuum ultraviolet radiation lamp. We expect these devices will be useful for improving the global environment.

INTRODUCTION

High volumes of volatile organic compounds (VOCs), typified by trichloroethylene and tetrachloroethylene, have long been used in various industrial fields for their high degrees of industrial usefulness. On the other hand, there is a growing awareness of environment preservation today, and of the fact that we face serious environmental pollution due to such harmful VOCs. Industries are increasingly active in recovering and preserving the global environment—attempting to clean polluted soil and ground water, minimize emissions from places of business where VOCs are used, and monitor raw water in water purification plants. Accordingly, in many industrial fields there is the need for measuring and monitoring the concentration of such a pollutant as VOCs. Nonetheless, sampling and analysis tasks remain dependent on human labor in most cases. In view of this situation, we have developed a field-installed system for automatically and continuously measuring VOCs in air and water. With the system, we aim to make the activities of preserving and recovering the global environmental more efficient, less labor-intensive and more reliable, by making active use of high-quality surveillance information. Fundamental technologies that support the system are the process gas chromatograph for separating and measuring the constituents of a small amount of VOC, the compact photoionization detector (PID) for quickly detecting a small amount of VOC in air, and the sparging column for continuously sampling VOCs in water. In this article, we will briefly explain these component technologies,

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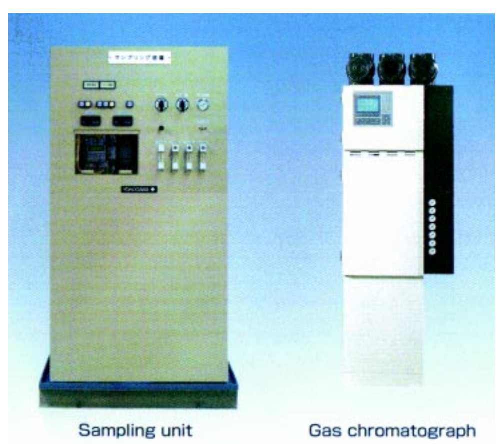


Figure 1 External View of Process Gas Chromatograph Based Continuous VOC Analyzer

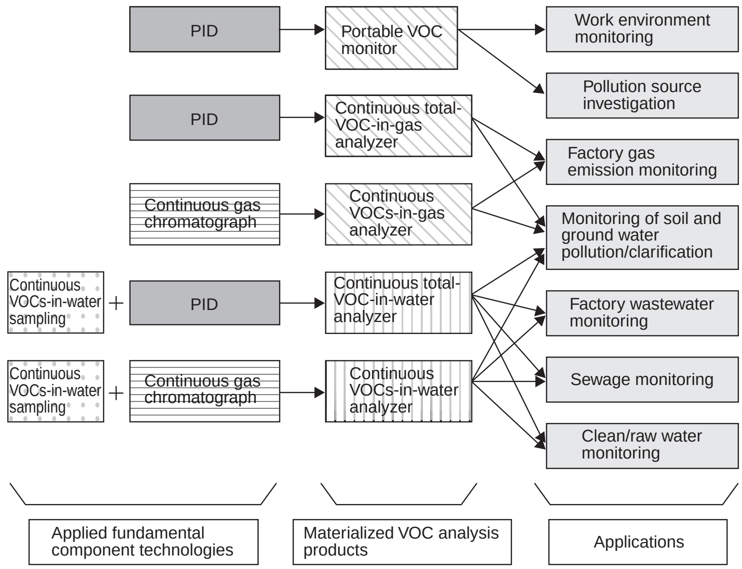


Figure 2 Basic VOC Measurement Technologies, Family of Products and Their Applications

the family of products and their applications. Then, we will introduce a process gas chromatograph based continuous VOC analyzer and a PID-based continuous total-VOC analyzer. Figure 1 shows an external view of the process gas chromatograph based continuous VOC analyzer.

VOC MEASUREMENT TECHNOLOGY, FAMILY OF PRODUCTS AND THEIR APPLICATIONS

Figure 2 schematically shows the fundamental VOC measurement technologies, the family of products based on combinations of the technologies, and their applications. The PID technology has no capability of constituent-by-constituent measurement. This technology is applied to portable VOC monitors and simple and stationary continuous VOC analyzers. In contrast, a gas chromatograph capable of measuring VOCs constituent by constituent is used for applications in which the concentration of a particular constituent in a multicomponent sample is measured or multiple constituents are simultaneously measured. As an environmental pollutant, VOCs are ubiquitous and found not only in air but in soil, rivers, and ground water. Thus, in cases where VOCs are viewed as a measurement object, each measurement project must be able to deal with all possible morphologies of each VOC sample. For this reason, we have developed a continuous VOCs-in-water sampling column for the measurement of VOCs in water. This column, in combination with the PID or gas chromatograph, makes it possible to support all sorts of application, irrespective of whether the sample is a VOC in air or VOC in water. Specific applications include monitoring raw water and sewage in a water purification plant, emissions within a factory, soil and ground water under purification, and a work environment.

PROCESS GAS CHROMATOGRAPH BASED CONTINUOUS VOC ANALYZER

As a highly reliable online continuous VOC analyzer, Yokogawa’s process gas chromatograph has an excellent track record in the field of oil refinery and ethylene processing. A combination of this process gas chromatograph with a VOC sampling unit composes a continuous VOC analyzer. The analyzer thus configured has come into use for continuous monitoring of small amounts of VOC in raw water supplied to a water purification plant or government-regulated VOCs in factory wastewater.

Figure 3 shows how the process gas chromatograph based continuous VOCs-in-water analyzer is configured.

VOCs sampled from the sparging-based continuous VOCs-in-water sampling column are introduced to the process gas chromatograph for continuous analysis. In the gas chromatograph, a

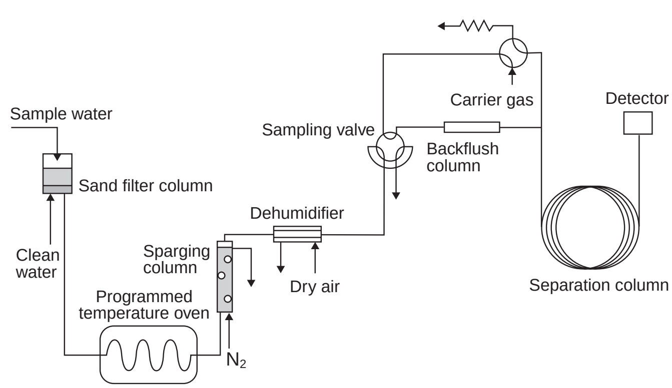


Figure 3 Configuration of Gas Chromatograph Based Continuous VOCs-in-Water Analyzer

certain amount of sample gas is admitted by a sampling valve and introduced to a separation column as the sample gas is driven forward by a carrier gas (nitrogen). In the separation column, the sample gas is separated, constituent by constituent, according to a difference in the speed of elution. Chromatograms are obtained as each VOC separated by a flame ionization detector (FID) at the outlet of the separation column is detected in a time-series manner. Thus, the analyzer continuously measures the concentration of each VOC by automatically repeating the above-noted cycle of operation. By using a programmed temperature column as the separation column, it is possible to simultaneously separate and measure a wide range of VOC constituents, from low boiling point constituents to high boiling point constituents.

Figure 4 is a schematic view explaining the operating principle of the sparging-based continuous VOCs-in-water sampling column. Sample water is continuously supplied into the sparging column and bubbled with a nitrogen gas or air so that VOC constituents in the sample water vaporize and go into bubbles. Consequently, a sample gas containing the VOC constituents is obtained within the head space of the sparging column. A constant sampling rate of the VOC constituents can be made available by keeping constant both the temperature of the sparging column and the flow rates of the sample water and nitrogen gas. This means the column serves as a continuous VOCs-in-water sampling column capable of supporting quantitative analysis.

Figure 5 shows an example of separating and measuring 21 types of VOC constituents in water, each having a concentration of 10 µg/ℓ, by using the process gas chromatograph based continuous VOC analyzer. The figure indicates that each constituent is separated and measured with adequate levels of sensitivity.

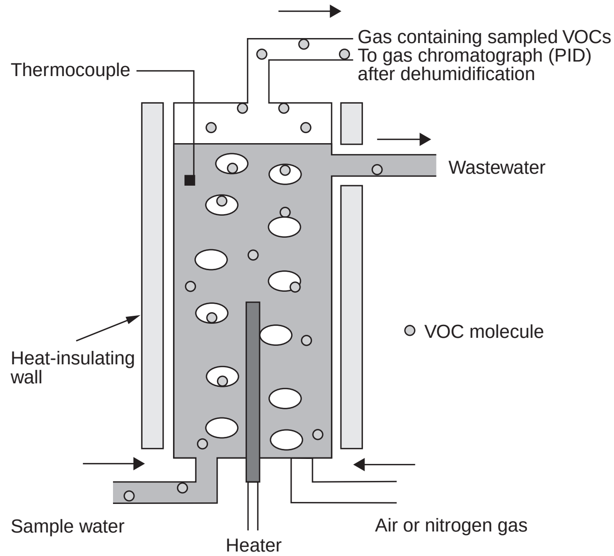
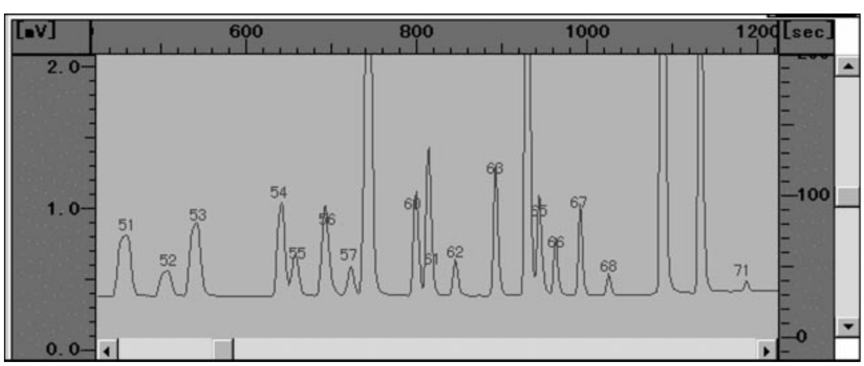


Figure 4 Sparging-based Continuous Total-VOC-in-Water Sampling Column

PID-BASED CONTINUOUS TOTAL-VOC ANALYZER

There is a case where the sample being measured has a simple, known composition of constituents and the concentration of the constituent in question can be determined by measuring the concentrations of all VOCs, rather than measuring the concentration of that particular constituent only. In that case, it is possible to realize a continuous VOC analyzer that is compact, simple and superior in operability and maintainability, by using a PID. In the case of monitoring and cleaning VOCs in soil or water, pollutants are most often limited to such compounds as trichloroethylene and tetrachloroethylene[1]. Consequently, the



51: 1,1-dichloroethylene; 52: Dichloromethane; 53: Trans-1,2-dichloroethylene; 54: Cis-1,2-dichloroethylene; 55: Chloroform;
56: 1,1,1-trichloroethane; 57: Carbon tetrachloride; 58: Benzene + 1,2-dichloroethane; 60: Trichloroethylene;
61: 1,2-dichloropropane; 62: Bromochloromethane; 63: Cis-1,3-dichloropropane; 64: Toluene; 65: trans-1,3-dichloropropane;
66: 1,1,2-trichloroethane; 67: Tetrachloroethylene; 68: Dibromochloromethane; 69: Meta-xylene + Para-xylene;
70: Ortho-xylene; 71: Bromoform; 72: Para-dichlorobenzene

Figure 5 Example of Chromatogram Obtained Using Gas Chromatograph Based Continuous VOC Analyzer
Test sample: 10 µg/ℓ each of 21 different VOC constituents in water

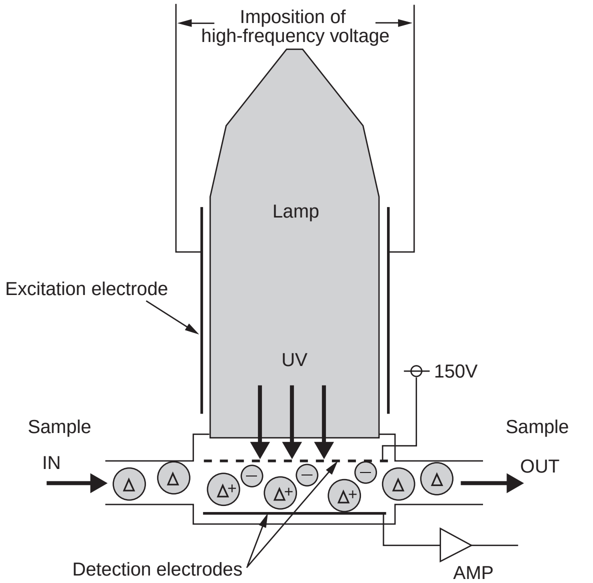


Figure 6 Operating Principle of Photoionization Detector (PID)

degree of purification and the operating condition of purification equipment can be automatically and continuously monitored by simply checking the concentrations of all these VOCs.

Figure 6 schematically shows the principle of PID operation. The PID lamp is filled with a specific gas. When the gas is excited externally by high-frequency electric fields, the lamp emits a vacuum ultraviolet radiation of 10.6 eV. With this ultraviolet radiation, VOC constituents with ionization energy of lower than 10.6 eV are ionized and detected as an ion current.

Figure 7 External View of PID Lamp

Figure 8 External View of PID-based Continuous Total-VOC Analyzer

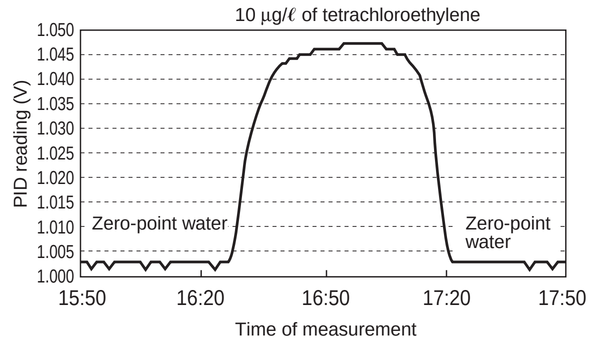


Figure 9 Example of Measurement Using PID-based Continuous VOC Analyzer

Test sample 10 µg/ℓ of tetrachloroethylene in water—environmental-standards concentration of ground water

Although benzene, trichloroethylene and other major harmful VOCs are ionized, such major constituents in air as nitrogen, oxygen, carbon dioxide, methane and water have high ionization energy and therefore are not detected. This is why the PID serves as a VOC detector. This VOC detector is a compact yet high-performance device, featuring excellent response characteristics on the order of seconds and detection sensitivity on a parts-per-billion scale. Figure 7 is a picture showing an external view of the lamp used with the PID. The lamp is a simple, gas-filled lamp having no internal electrodes. Accordingly, it has a service life of greater than one year and can be easily replaced. Figure 8 shows an external view of the continuous total-VOC analyzer for soil gases, prototyped by using the PID module discussed above.

The PID-based continuous total-VOC-in-water analyzer has been realized by connecting the above-mentioned continuous VOCs-in-water sampling column to the front stage of the analyzer for soil gases. Figure 9 shows an example of measuring 10 µg/ℓ of tetrachloroethylene, i.e., an environmental-standards concentration, using the analyzer. The figure indicates that the concentration was measured with an adequate S/N ratio.

CONCLUDING REMARKS

In this article, we have introduced our component technologies for continuous VOC measurement—the process gas chromatograph, photoionization detector (PID), and continuous VOCs-in-water sampling column. We expect that high-quality environment preservation and recovery activities will be promoted through the proliferation and active use of these technologies. We also hope that environmental clarification will be further accelerated on a global scale. ◆

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