Continuous monitoring of volatile organic compounds in industrial waste water

Walter M. Doyle

This paper outlines an integrated system which provides rapid, fully-automatic, monitoring of selected volatile organics in waste water. Many priority pollutants, such as chlorinated hydrocarbons and aromatics are characterized by low solubility and high vapor pressure, making them difficult to measure using traditional techniques. The waste water analyzer employs the sparging-infrared method, coupled with the latest in process analytical software, to overcome these limitations, making possible the simultaneous measurement of multiple species with detection limits in the low ppb range, and updated results every few minutes.

1. Introduction

The discharge of organic chemicals into waste water is an endemic problem in chemical processing. As a result, most plants employ remediation facilities to purify their waste water before discharging it into the environment. However, these facilities can be easily overloaded by a large spill. Conventional detection methods which involve the periodic collection of samples and laboratory analysis by relatively slow techniques such as GC or GC/MS, suffer from a number of limitations;

1. Inability to detect a major spill before it can reach – and possibly damage – the remediation facility.
2. Failure to detect many short term spills due to the low sampling frequency.
3. Inaccuracies such as under reporting of concentrations due to evaporation of volatile pollutants between sample collection and measurement.
4. Inability to detect spills rapidly enough to take effective remedial action.
5. Frequent inability to determine the source of a given chemical spill.

We have developed a fully automated system for the continuous monitoring of volatile organic pollutants based on the sparging-infrared technique. This technique uses a stream of air bubbles to transfer the pollutants from a fixed volume of water to an air stream, where the concentrations can be measured quickly and easily using infrared spectroscopy.[1]

The speed of the sparging-infrared technique enables it to overcome each of the limitations of the previous systems outlined above. In addition, since the system is fully automated, it greatly reduces manpower requirements, resulting in substantial cost savings. Finally, by providing a time-resolved chemical signature of each spill, it makes it possible to trace a spill to its exact location so that action can be taken to prevent a recurrence.

2. System Description

The key hardware elements of the sparging-IR waste water analysis system are illustrated in Figure 1. These include a sparging vessel, a low volume IR gas cell (Axiom Analytical LFT-210), an FT-IR spectrometer (Bruker IR Cube), a water pump, an air pump, and various valves and sensors. These are controlled by the Symbion-DX™ process analytical software suite (Symbion Systems, Inc.). Symbion-DX™ controls and sequences the operation of the spectrometer, pumps, and valves and provides for the analysis, display, alarming, and archiving of data. The system is designed for continuous, unattended 24/7 operation with reporting and alarming via a plant-wide data network.

The author is with Axiom Analytical, Inc., 17751-B Sky Park Circle, Irvine, California 92614. W.M. Doyle's e-mail address is mdoyle@goaxiom.com.

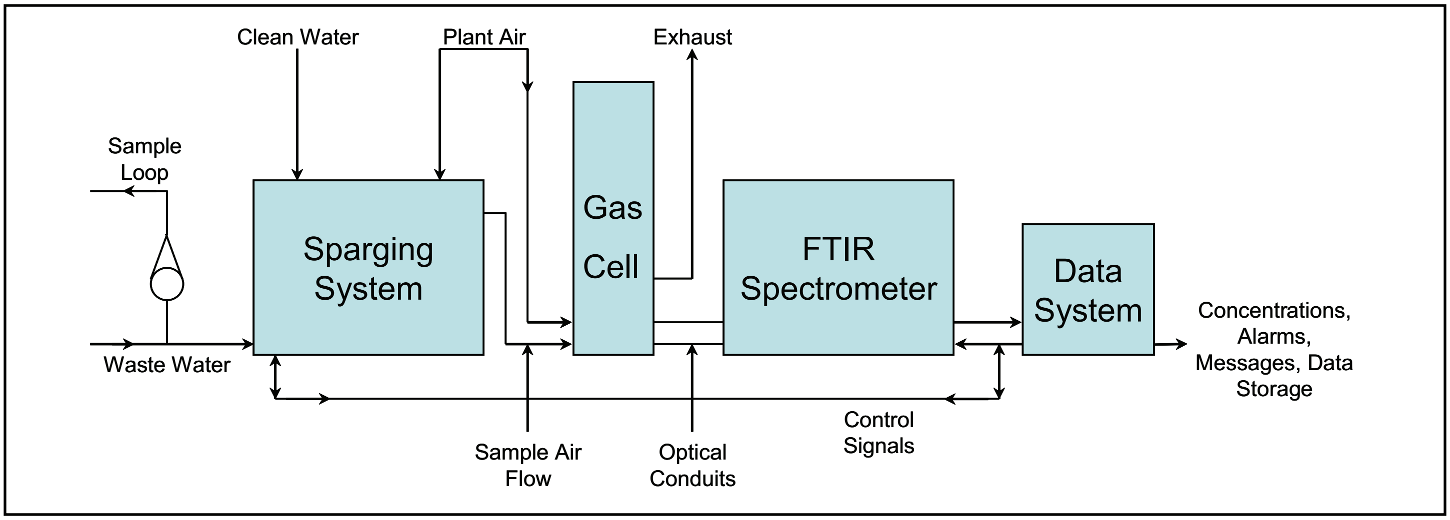

Figure 1. Major elements of the Sparging-IR waste water analysis system.

The system typically makes a discrete measurement every two to three minutes. The measurement cycle involves first pumping a 200 mL sample of waste water from the plant's effluent stream into the sparging vessel. Air is then pumped into the bottom of the vessel at a constant flow rate via a sparging nozzle. The solute containing air emerging from the vessel is directed to the gas cell where it is analyzed by the spectrometer operating in conjunction with the Symbion-DX™ software and a multivariate analysis program.

3. Principles of Operation

The operation of the sparging-IR system is based on the fact that each organic chemical species has a unique infrared spectrum, or fingerprint (Figure 2). Despite the uniqueness of each fingerprint, the direct measurement of low concentrations of volatile organics in liquid water is made extremely difficult by the presence of very strong and broad water absorption in the fingerprint spectral region. The sparging-IR system solves this problem by transferring the organics from the water to a vapor stream. The low solubility of many volatile organics, combined with the fact that their vapor pressures are typically much greater than that of water, leads to a dramatic enhancement of their relative concentrations in the vapor stream. For the chlorinated hydrocarbons and aromatics of greatest environmental concern, the relative concentrations can be many orders of magnitude greater than in the liquid water. At the same time, the spectral absorptions of water vapor are far weaker and narrower than those of liquid water. As a result, these absorptions generally do not overlap those of the species of interest and hence do not limit the system's sensitivity.

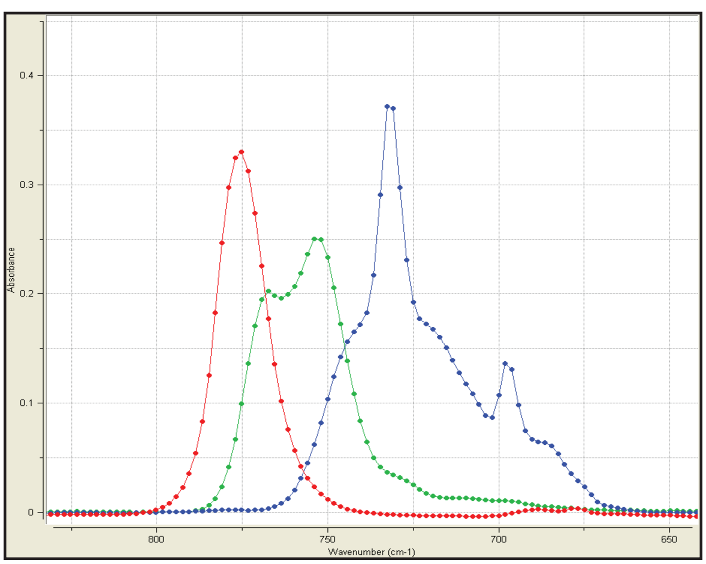

Figure 2. Vapor phase fingerprint region spectra of chloroform (red), DCM (green), and Toluene (blue).

4. Typical Results

The waste water analysis system will usually be calibrated to report on those volatile organics that may be present in a given plant environment. Typically, this will be a small number of components. However, we have measured as many as fifteen different species simultaneously during lab simulation. In routine operation, the measured concentrations are reported via the plant's network. For analytical purposes, the time dependent depletion curves can be monitored on the system's video display. A typical result is shown in Figure 3.

The sensitivity of the system for measuring individual species depends on the solubility and vapor pressure of each species as well as various factors related to the operating requirements such as number of species to be monitored, required speed, and type of infrared detector employed. An example of measurement limits for a particular set of components is given in Table I.

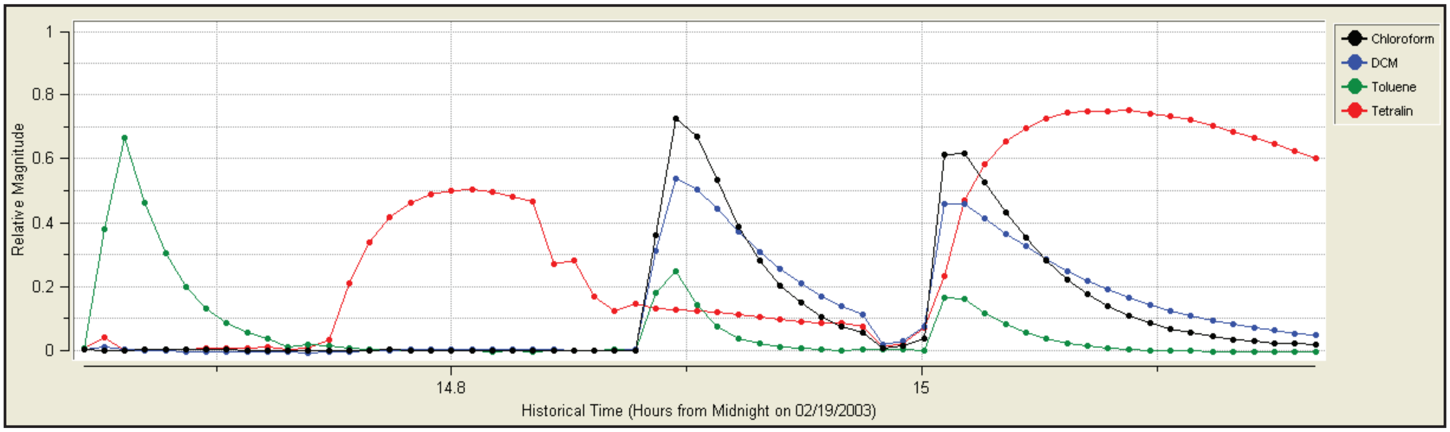

Figure 3. Depletion plots of four organic species in water obtained during laboratory simulation. The y-axis units are ppm.

TABLE I

SELECTED DETECTION LIMITS

Contaminant	Detection Limit (ppb)
Benzene	5
Carbon tetrachloride	0.5
Chloroform	1.5
1,1-Dichloroethylene	5
1,2-Dichloroethylene	12
cis-Dichloroethylene	7
trans-Dichloroethylene	4
Ethyl benzene	6
Styrene	5
Tetrachloroethylene	1
Toluene	4
1,1,1-Trichloroethane	1
1,1,2-Trichloroethane	25
Trichloroethylene	0.6

Figure 4. A fully automatic Sparging-IR system for 24/7 on-line operation.

5. Implementation and Conclusion

The first fully automated sparging-IR waste water system has been in continuous operation for over a year at a major chemical manufacturing complex (Figure 4). It has successfully detected significant spills on a number of occasions in time for appropriate action to be taken. Several additional benefits have resulted from the use of this system. Not only has it eliminated the costs associated with major spills, but it has also made it possible to eliminate the very significant costs associated with the previous approach of discrete daily sampling and off-line analysis. The use of continuous on-line monitoring also revealed inaccuracies inherent in the previous system. These resulted from the evaporation of the volatile pollutants between the time a sample was gathered and its eventual analysis. Finally, by providing a chemical signature of each spill, the system has made it possible to trace the spill to a particular plant location. As a result of these benefits, this particular facility has now changed over to complete dependence on the new sparging-IR waste water system.

References

1. W. M. Doyle, "Continuous Monitoring of Organic Pollutants in Water by Sparging-Infrared", Axiom Analytical, Inc. Technical Note AN-907.