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Membrane Extraction Mass Spectrometry for the On-Line Analysis of Gas and Liquid Process Streams

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A membrane extraction mass spectrometry (MEMS) technique was developed for the on-line analysis of organic components of multiple liquid and gas streams. Silicone hollow-fiber membranes allow for the extraction of organic chemicals from complex and dirty matrices with no sample preparation. Multiple streams of both air and water were analyzed on-line with a single analyzer. This method has been applied in an aerobic biological wastewater treatment process. Mass balance determinations were performed by quantitatively measuring the organic contaminants in the influent wastewater stream, in the effluent water stream, and in the effluent air stream.

INTRODUCTION

The efficiency of chemical processes is becoming an increasingly important issue with the growing push toward waste reduction and minimizing organic emissions in air and water. Analytical chemistry can play a vital role in achieving and maintaining optimum process operating conditions. As opposed to off-line analysis, on-line analysis can provide more efficient use of information about a process in terms of the amount of data, the quality of data, and the ability to respond to changes in the process as exhibited by the data (1). As a simple example, the continuous-temperature measurements obtained with a thermocouple device can provide a more statistically useful data set and more precise indications of changes in the process temperature than intermittent manual measurements with a thermometer. The same is true for other traditionally measured process parameters such as pressure and pH, as well as the more sophisticated measurements of the process composition. Currently, on-line process composition measurements are often obtained from chromatographic (2), spectroscopic (3, 4), or solid-state chemical sensor (5) techniques, as dictated by the nature of the analyte and the process matrix. Although the speed, sensitivity, and selectivity of mass spectrometry make the technique attractive, on-line analysis by mass spectrometry has until recently been limited to clean, well-defined gas-phase streams.

Sampling is generally the most difficult problem associated with the on-line analysis of process streams, regardless of the analytical technique (6). Many gas and liquid process streams are chemically and physically complex and require pre-

treatment prior to analysis. This has been especially true for mass spectrometry, which has generally utilized a capillary or orifice sample introduction system that is limited to filtered gases. Many sampling problems can be circumvented by utilizing membrane extraction techniques. The use of hollow-fiber MEMS for the direct analysis of organic compounds in both air and water was first described in 1974 (7) and the effects of experimental parameters on such analyses have recently been described (8). Advantages of sampling with the silicone hollow-fiber membranes include the simplicity of the membrane extractor device, the high sample surface area-to-volume ratio in the hollow fiber, the ability to obtain high linear flows at relatively low-volume flows, and the ability of the membrane to provide efficient extractions of organic compounds from both air and water. In addition, the inertness of the silicone membrane material makes it suitable for use in many biological and chemically reactive systems. The head space gases in reactors have been successfully monitored by MEMS (9-11), as have liquid streams (12-14). However, the simultaneous on-line analysis of the influent and effluent gas and liquid streams of a reactor have not been previously reported.

While previous work focused on the measurement of compounds in either the effluent gas or the effluent liquid, all streams must be considered for complete process characterization. Assumptions made about the quantity of a compound in the influent stream can yield significant errors in the mass balance determinations. As will be demonstrated below, the measurement of the influent as well as the effluent streams minimizes these errors. This report describes the development of an on-line multi-gas/liquid-stream monitoring technique and its application to the simultaneous trace analysis of complex and dirty streams in three wastewater treatment reactors.

EXPERIMENTAL SECTION

Chemicals. The compounds used in this study were obtained from Fisher Scientific (Fair Lawn, NJ) and Aldrich Chemical Co. (Milwaukee, WI). These compounds were generally nonpolar and relatively insoluble in water, so they were prepared in acetone to facilitate dissolution when spiked into the influent wastewater stream.

Water standards were prepared in a 1-L glass jar of deionized water with the same solutions used to spike the influent water stream. Air standards were prepared in a 100-L Saran (The Dow Chemical Co., Midland, MI) bag filled with air by injecting known volumes of 1:1 mixtures of the two compounds being studied. Standards were prepared and analyzed immediately following each reaction analysis.

¹ Also at Michigan State University.

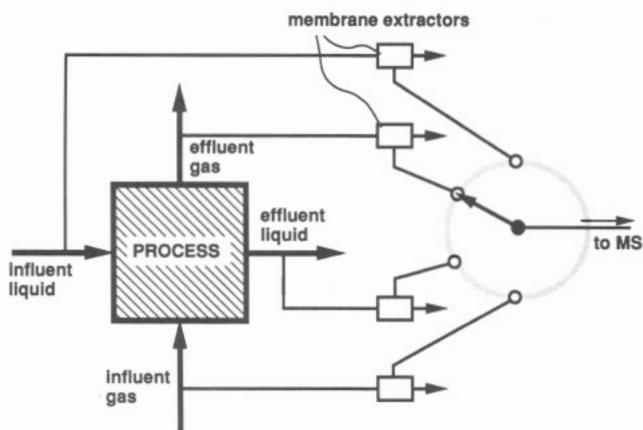


Figure 1. Configuration for the influent and effluent analysis of a multistream, multiphase process by MEMS.

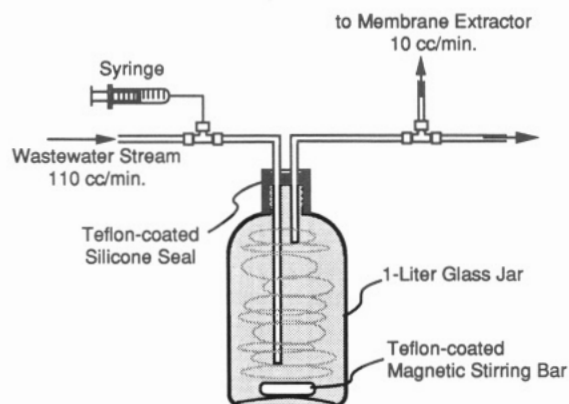


Figure 2. Syringe and mixing jar configuration for spiking organic compounds into liquid streams.

Analyzer. A Balzers QMG 511 quadrupole mass spectrometer was used in this study. The mass spectrometer, sampling valve, and data acquisition were controlled by in-house written software on a PDP 11-73 computer from Digital Equipment Corp. (Maynard, MA). The instrumental conditions were as follows: mass range, 60–200 Da; scan rate, 30 ms/Da, 10 scans averaged; secondary electron multiplier voltage, 1900 V for water streams, 2000 V for air streams; analyzer pressure, 1×10^{-6} Torr for water streams, 3×10^{-6} Torr for air streams. The combination of 10 averaged relatively slow scans was selected because these instrumental conditions provided very good sensitivity for full scans in less than 1 min. To the limit where ion transmissions decay at high scan rates, the use of slow scan rates with a quadrupole mass analyzer will provide signal-to-noise ratios comparable to those obtained from averaging several fast scans over the same duration of time.

Membrane and Sampling System. The process streams were pumped from the reactors through the membrane extractors via 6 m long, $1/8$ in. (0.32 cm) o.d. stainless steel tubes. The silicone hollow-fiber membranes used in this study were constructed by sealing 2.5-cm lengths of Dow Corning (Midland, MI) Silastic medical grade tubing into $1/8$ -in. stainless steel tubing tees, as shown in Figure 3. The two ends of the hollow-fiber membrane are sealed into stainless steel ferrules with Dow Corning Silastic silicone sealant. For sampling the effluent air streams, 0.0305 cm i.d., 0.0635 cm o.d. hollow-fiber membranes were used. The effluent air was pumped through the membrane extractors at the rate of 60 cm^3/min with an air pump from Metal Bellows Corp. (Sharon, MA). Aqueous samples were drawn through 0.147 cm i.d., 0.196 cm o.d. hollow-fiber membranes at the rate of 10 cm^3/min with fluid pumps from Fluid Metering Corp. (Oyster Bay, NY).

A $1/8$ -in. SC-12-HT hastelloy-C rotary switching valve from Valco Instruments Co., Inc. (Houston, TX) was used to interface the membranes to the mass spectrometer. This valve was computer-actuated so that a different stream was sampled every 5

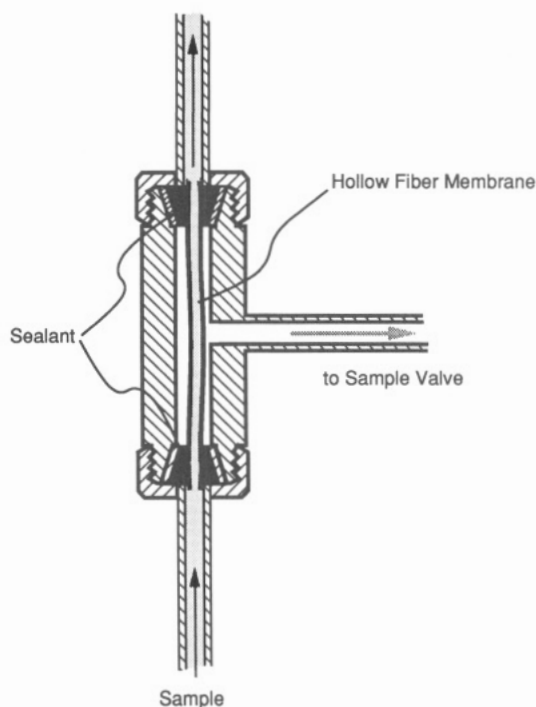


Figure 3. Flow-through hollow-fiber membrane extractor.

min. The analyzer side of all inlets, when not selected for sampling to the mass spectrometer, was continuously evacuated by a vacuum pump to prevent accumulation of permeating species. The membranes and valve assembly were mounted in an oven and maintained at 30 °C. The permeation process is temperature dependent (8); therefore the inlet was maintained slightly above the process and maximum ambient temperatures. The analyzer vacuum chamber and transfer line between the valve and the mass spectrometer were heated to 100 °C.

Wastewater Treatment Apparatus. To demonstrate the utility of MEMS for on-line reaction monitoring of multiple streams, this study was performed with bioreactors in a wastewater treatment pilot plant at the Dow Chemical Co. in Midland, MI. The pilot plant consists of three 75-L reactors, depicted in Figure 4, that were designed to simulate a large-scale treatment process and were stocked with biomass from a general wastewater treatment plant. The flow-through reactors were composed of stirred treatment basins and clarifiers for recycling the biomass back into the basins. The temperature of the reactors was maintained at about 27 °C.

The influent wastewater was first filtered by 100- and 50- μm canister filters and then mixed with the spike solution in stirred 1-L glass mixing jars. A 10- cm^3 syringe with a syringe pump from Sage Instruments (Cambridge, MA) was used to inject the spike solution at a rate of 5 $\mu\text{L}/\text{min}$ into the influent wastewater, which was flowing into the mixing jar at a rate of 110 cm^3/min (see Figure 2). The caps of the mixing jars were fitted with Teflon (E. I. du Pont de Nemours & Co., Wilmington, DE) coated silicone rubber seals to prevent losses due to evaporation. The bioreactor influent stream, flowing at a rate of 35 $\text{cm}^3/\text{minute}$, was drawn from the wastewater stream exiting the mixing jar. A second mixing jar provided an unspiked wastewater stream to a bioreactor used to generate baseline data. The wastewater flows were driven by Masterflex peristaltic pumps from Cole Parmer Instrument Co. (Chicago, IL).

The influent air continuously flowed at a rate of 900 cm^3/min into the bottom of each basin. The tops of the reactors were covered with polyethylene sheeting tight enough to reduce the dilution of the effluent air stream due to air currents in the room, but not so tight as to cause a positive pressure in the reactor head space.

RESULTS AND DISCUSSION

The system developed has been tested and evaluated in the context of process analysis. In many processes, both influent and effluent streams need to be analyzed for complete

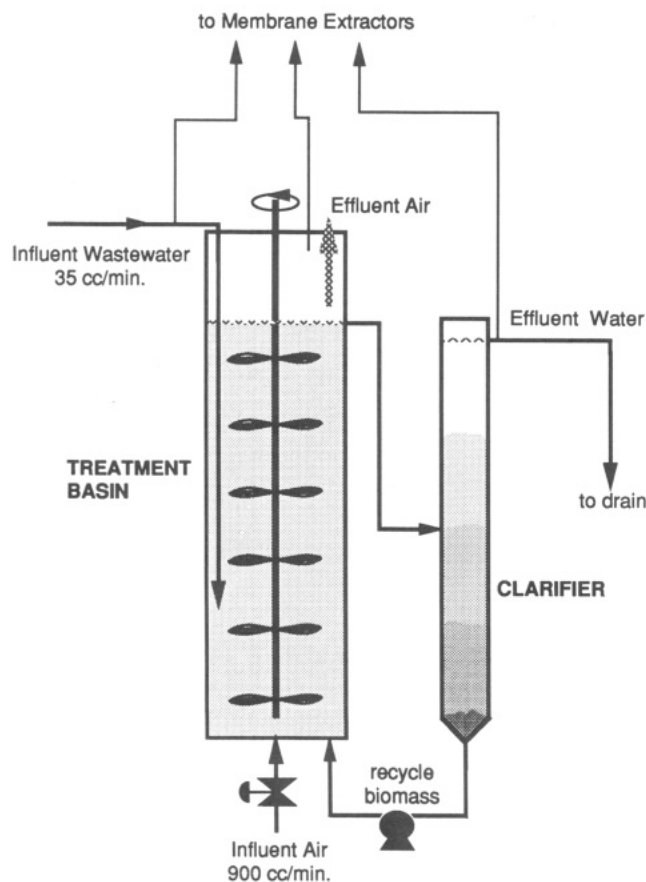


Figure 4. Diagram of the wastewater treatment bioreactor.

characterization of the process and to minimize errors due to impurities or inaccurate assumptions about the influent composition. Results of the technology development, performance tests, and an application of the technique to real processes are described below.

Multi-Gas/Liquid-Stream Analysis. By analyzing the streams influent and effluent to a process, mass balance determinations can be performed and a more complete picture of a process can be obtained. A generic process that has liquid influent and effluent streams and gas influent and effluent streams is illustrated in Figure 1. For a given component entering the process under nonreactive conditions, the steady-state mass balance equation is

$$m_{il} + m_{ig} = m_{el} + m_{eg} \quad (1)$$

and under reactive conditions is

$$m_{il} + m_{ig} = m_{el} + m_{eg} + m_p \quad (2)$$

where m is the mass flow rate for the component in the stream designated by the subscript, and where the subscripts i , e , l , and g designate the influent, effluent, liquid, and gas streams, respectively. The mass flow rate due to uptake of the compound by the process is designated m_p . The values for m_{il} , m_{ig} , m_{el} , and m_{eg} are determined from the on-line extraction and analysis of the streams, and m_p is calculated from eq 2.

The mass flow rates for a component in the different process streams are calculated by multiplying the process stream concentration (mg/L) by the process stream flow rate (L/min). For example, the mass flow rate for a component in the influent liquid stream is determined mass spectrometrically from the following equation:

$$m_{il} = F_{il}C_{il} = F_{il}K_{std,l}I_{il} \quad (3)$$

where F_{il} is the influent liquid flow rate, C_{il} is the concentration of the component in the process stream, $K_{std,l}$ is the analytical

Table I. Spike Sets with Volume Percent in Acetone, Monitored Ions, and Standard Response Factors^a

spike set	% in acetone	m/z	response/mg/L	
			in air	in water
1 toluene	7.6	91	8.8	0.088
dichloromethane	5.0	84	0.6	0.016
2 benzene	7.5	78	9.0	0.10
carbon tetrachloride	4.2	117	2.5	0.034
3 ethylbenzene	7.6	106	7.6	0.055
chloroform	4.4	83	2.1	0.060
4 styrene	12.0	104	10.3	0.092
1,1,2-trichloroethane	7.6	97	2.5	0.030
5 chlorobenzene	6.0	112	1.4	0.018
tetrachloroethene	4.0	129	0.9	0.006
6 bromoform	3.8	173	0.8	0.007
1,1,1-trichloroethane	8.2	97	0.3	0.015

^a Instrumental baseline response was 0.0005.

response factor for the compound obtained from analyzing the liquid standards, and I_{il} is the response for the compound in the process stream. This equation applies in the determination of both liquid and gas-phase mass flow rates after substituting in the appropriate parameters.

It is useful to present the mass balance determinations in eqs 1 and 2 as % recovery or % conversion, defined as follows:

$$\% \text{ Rec} = 100\% (m_{el} + m_{eg}) / (m_{il} + m_{ig}) \quad (4)$$

$$\% \text{ Con} = 100\% m_p / (m_{il} + m_{ig}) = 100\% - \% \text{ Rec} \quad (5)$$

Furthermore, the fate of unreacted materials in the process is determined by calculating the % recovery for the compound in each effluent stream. For example, the unreacted % recovery for the compound in the liquid effluent stream is calculated as follows:

$$\% \text{ Rec}_{el} = 100\% m_{el} / (m_{il} + m_{ig}) \quad (6)$$

The ability to monitor multiple streams and even multiple processes provides the ability not only to make mass balance determinations but also to analyze reference baseline streams (no added reactants) to make these determinations more accurate. The % recovery for process A is obtained from eq 7, where the analytical results from process A are back-

$$\% \text{ Rec}_A = 100\% [(m_{elA} - m_{elB}) + (m_{egA} - m_{egB})] / [(m_{ilA} - m_{ilB}) + (m_{igA} - m_{igB})] \quad (7)$$

ground-corrected with the results from the baseline process B. More accurate results are obtained from determining % recoveries for each sampling cycle rather than calculating the recoveries from time-weighted averages of each stream, since the background levels and the baseline signals may not be constant over time.

To demonstrate the utility of the MEMS technique and the importance of analyzing process influent streams, two aqueous streams—one of which was continuously spiked with nonpolar organic compounds—were analyzed. The streams were a complex matrix of chemical wastewater containing solids and trace level organic contaminants. The diagram in Figure 2 shows the syringe and mixing jar configuration for spiking the aqueous stream with the organic compounds. These compounds, their concentration in the acetone dispersant, the mass/charge ratios (m/z) of the ions used for quantitation, and their mg/L-based response factors are listed in Table I. Each spike set contained two of the compounds of interest. The membrane extractor used to interface the sample streams with the mass spectrometer is shown in Figure 3. The second wastewater stream, which was not spiked, was analyzed in the same manner to obtain a baseline for calculating the spike contribution. An advantage of using hol-

Table II. Spike Concentrations (mg/L) in the Influent Wastewater

	calcd	measd
toluene	3.57	2.35
dichloromethane	3.57	3.40
ethylbenzene	3.47	0.49
chloroform	3.47	2.66
benzene	3.54	3.71
carbon tetrachloride	3.61	3.61
styrene	5.78	5.39
1,1,2-trichloroethane	5.81	5.81
chlorobenzene	3.43	4.69
tetrachloroethene	3.36	3.75
bromoform	5.95	2.98
1,1,1-trichloroethane	5.95	3.78

low-fiber membranes for the direct analysis of such complex samples is that fouling of the membrane by solids is inhibited by the high linear sample flows which continuously sweep the membrane surface.

Difficulty was encountered in spiking the aqueous stream—a problem that underscores the importance of analyzing the process influent streams. The measurements of some of the spiked compounds in the stream exiting the mixing jar were initially as low as 5% of the calculated levels. The aromatic compounds in particular showed very poor dissolution into the aqueous stream. Apparently, as the spike solution approached the exit tip of the $1/16$ -in. stainless steel syringe tubing, the acetone dissolved in the water stream, and the more insoluble organic compounds either precipitated in the bottom of the mixing jar or dissolved back into the acetone solution in the syringe. This problem was not observed when standards were prepared by quickly injecting 20- μ L aliquots of the spike solutions into a 1-L jar of water. These results suggest that if the linear velocity of the spike solution was increased sufficiently, more complete mixing of the spiked organic liquids into the aqueous phase would occur. The syringe was modified such that a 4-cm length of 50 μ m i.d. fused-silica tubing was epoxied into the tip of the syringe needle, through which the spike solution flowed into the influent stream. The modified syringe provided a calculated 400-fold increase in linear velocity for the spike solution, and the spiking efficiency, for the most part, improved dramatically.

The calculated concentrations based upon the amount of compound spiked and the actual measured concentrations of the compounds in the wastewater are listed in Table II. In spite of the improvements in the spiking technique, ethylbenzene continued to exhibit poor spiking efficiencies, possibly due to a combination of the low solubility for ethylbenzene in water (lowest among the compounds studied) and ethylbenzene's affinity for solids, as noted by Hanna and co-workers (15). During the study of the wastewater treatment process discussed below, the water exiting the mixing jars was used as the liquid influent streams for the bioreactors. The measured influent values—not the calculated values—were used in the bioreactor mass balance determinations, thus minimizing the errors that may result from the false assumption that the spikes were 100% efficient.

Application to a Biological Wastewater Treatment Process. The analyses of volatile organic compounds in wastewater and air are most commonly performed off-line after first extracting and concentrating the organic compounds from the matrix (16, 17). These procedures are often laborious and time-consuming and require sample manipulation. With MEMS, the on-line extraction, concentration, and analysis of the influent liquid and the effluent liquid and gas streams from the process shown in Figure 4 were performed nearly simultaneously. The influent air streams were analyzed for

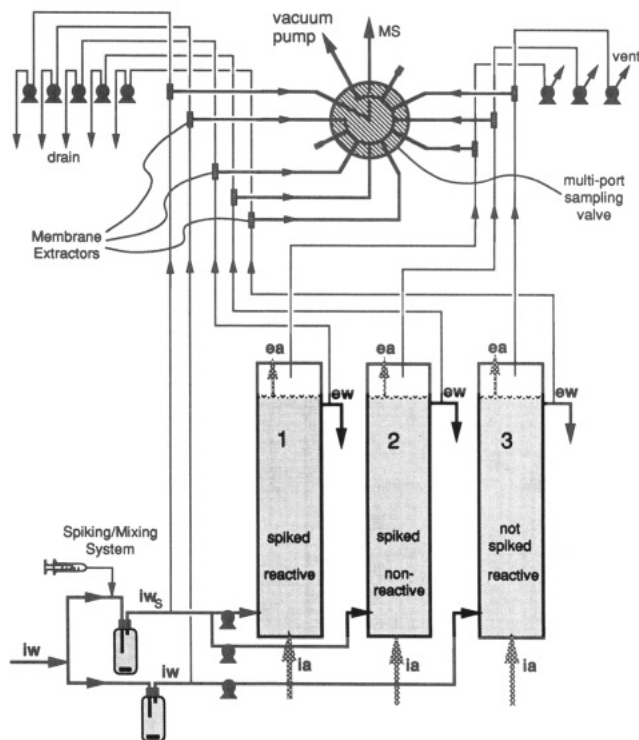


Figure 5. Process flow diagram illustrating the spiking and on-line sampling of three wastewater treatment bioreactors: iw = influent wastewater stream, iw_s = spiked influent wastewater stream, ia = influent air stream, ew = effluent water stream, ea = effluent air stream.

purity by MEMS prior to the on-line analyses but were not continuously monitored.

The process for the removal of volatile organic compounds from the wastewater mainly occurs via two mechanisms in a bioreactor: biodegradation and air-stripping. In many cases, these appear to be rate-competitive processes such that biodegradation of many compounds is improved when their residence time in the "biomass" is increased, i.e., when air-stripping is reduced. However, for aerobic biodegradation, aeration of the biomass is required, implying that some air-stripping is inevitable. The process shown in Figure 4 was studied by performing mass balance determinations for the organic priority pollutants listed in Table I. With the multi-gas/liquid-stream analysis capability, the process mass flow rates were determined for three different reactors. As shown in Figure 5, each reactor was prepared differently: In reactors 1 and 2, the influent wastewater was continuously spiked to 3–6 mg/L with the target compounds. Reactor 3, serving as the analytical blank or reference, was not spiked. Reactor 2, the analytical test sample, was spiked but its biomass was rendered nonreactive by maintaining the contents at pH less than 2.

The aqueous streams were analyzed with the flow-through silicone hollow-fiber membrane extractor shown in Figure 2, with a 0.147 cm i.d., 0.196 cm o.d. hollow-fiber membrane. A Reynolds number value of approximately 160 was achieved for the 10 cm³/min sample flows from the wastewater influent and effluent streams. By minimizing the effects of boundary layers, Reynolds numbers approaching 800 have been shown to improve the membrane extraction efficiency for many compounds (8). Reynolds number values of 800 were achieved with a 10 cm³/min wastewater flow by utilizing a 0.0305 cm i.d. hollow-fiber membrane, but plugging with solids and sludge resulted. A sample flow of 50 cm³/min in the larger hollow fiber would be required to attain these Reynolds numbers, but due to limits on sample consumption, 10 cm³/min was chosen as the maximum flow rate. Zero sample

Table III. Concentrations (mg/L) Detected in the Effluent Water and the Effluent Air Streams in the Reactive Process^a

	effluent water	effluent air
dichloromethane	0.41	0.003
chloroform	0.32	0.044
carbon tetrachloride	0.07	0.046
1,1,1-trichloroethane	0.30	0.073
1,1,2-trichloroethane	2.09	0.076
tetrachloroethene	0.15	0.065
bromoform	1.58	0.026
benzene	0.07	0.005
toluene	0.31	0.012
ethylbenzene	0.01	0.005
styrene	ND	0.003
chlorobenzene	ND	0.003

^a Styrene and chlorobenzene are not detected (ND) in the effluent water above the baseline.

Table IV. Percent Recoveries for the Spiked Organic Compounds

	reactive process	nonreactive process
dichloromethane	15 ± 1	100 ± 4
chloroform	64 ± 3	92 ± 5
carbon tetrachloride	42 ± 1	72 ± 3
1,1,1-trichloroethane	69 ± 4	85 ± 6
1,1,2-trichloroethane	77 ± 7	87 ± 8
tetrachloroethene	59 ± 7	103 ± 4
bromoform	80 ± 14	105 ± 12
benzene	6 ± 4	88 ± 4
toluene	29 ± 2	100 ± 6
ethylbenzene	34 ± 33	113 ± 20
styrene	2 ± 1	75 ± 6
chlorobenzene	2 ± 1	96 ± 3

consumption could have been achieved by recycling the sample streams back into the process; however this was not done in this study. In any case, the sensitivities were sufficient with the larger diameter membrane. The effluent air samples were pumped through the 0.0305 cm i.d. hollow fiber at a rate of 60 cm³/min. Convective mixing of the air streams is not as important since the diffusion of organic vapors in air is much more rapid than permeation through the membrane.

The mass flow rates were determined from the mass spectrometric steady-state process data and eq 4. Pure air was used for the influent gas; therefore $m_{ig} = 0$ for the organic compounds. Table III lists the steady state concentrations in milligrams per liter for the compounds in the effluent water and air streams in the reactive process (with the background signal from reactor 3 subtracted). These data demonstrate the capability of the technique to provide sensitive on-line analyses of the physically and chemically complex multiphase process. Mass flow rate vs time plots are displayed in Figures 6 and 7 for carbon tetrachloride and benzene, respectively, from the three reactors. Carbon tetrachloride was observed to be much more inert to the action of the biodegradation process than was benzene, as discussed in more detail below. As demonstrated by these plots, mass flow rate determinations can be more meaningful than concentration values when defining a chemical process.

The % recoveries for reactor 1 were calculated from eq 7, with reactor 3 providing the background values. The % recoveries for reactor 2 were calculated from the steady-state mass flow rates by using eq 4. A fourth reactor, not spiked and containing nonreactive biomass, would provide baseline data for reactor 2 but was not available for this study. For these calculations, it was assumed that the signal was due entirely to the compound of interest. The % recoveries for

Table V. Percent Recoveries in the Effluent Water Streams

	reactive process	nonreactive process
dichloromethane	12 ± 1	30 ± 2
chloroform	12 ± 2	18 ± 1
carbon tetrachloride	2 ± 1	11 ± 1
1,1,1-trichloroethane	8 ± 2	10 ± 1
1,1,2-trichloroethane	36 ± 4	41 ± 4
tetrachloroethene	4 ± 1	9 ± 1
bromoform	53 ± 11	74 ± 11
benzene	2 ± 1	24 ± 1
toluene	13 ± 1	21 ± 2
ethylbenzene	1 ± 1	19 ± 1
styrene	0 ± 1	18 ± 1
chlorobenzene	0 ± 1	17 ± 1

Table VI. Percent Recoveries in the Effluent Air Streams

	reactive process	nonreactive process
dichloromethane	3 ± 1	70 ± 2
chloroform	52 ± 3	75 ± 4
carbon tetrachloride	40 ± 1	61 ± 3
1,1,1-trichloroethane	61 ± 4	75 ± 5
1,1,2-trichloroethane	41 ± 3	46 ± 4
tetrachloroethene	55 ± 7	94 ± 4
bromoform	27 ± 3	31 ± 3
benzene	4 ± 3	64 ± 2
toluene	16 ± 1	79 ± 5
ethylbenzene	33 ± 33	94 ± 20
styrene	2 ± 1	58 ± 5
chlorobenzene	2 ± 1	79 ± 3

each compound in reactors 1 and 2 are summarized in Table IV. Had the amount of spiked compound added to the reactor influent been assumed to be correct and not measured, serious errors in the mass balance determinations would have resulted. The data in Table IV demonstrate the ability of the on-line analytical system to determine the relative inertness of different organic materials to a reactive process, where the substances exhibiting higher % recoveries are more inert to the process.

The ability to determine the relative air-stripping process efficiencies for the different compounds is also demonstrated. The fractions of the organic compounds remaining in the effluent water and removed from the water by the air-stripping process were calculated by using eq 6 and are given in Tables V and VI, respectively. Again, the results for reactor 1 are baseline-corrected.

The background-corrected fraction of organic material removed due to uptake by the biomass in reactor 1 was calculated from eq 5. This biouptake term represents the uncovered fraction of material and may be a combination of biological fermentation and absorption. The actual % removal due to the biomass may be affected by other factors. Deviations from 100% recoveries in the nonreactive process in reactor 2 are presumed to be due to experimental error as well as the presence of solids. These deviations are assumed to be consistent for the three reactors. Therefore, given the ability to monitor all of the reactors, the recoveries from reactor 2 could be used as correction factors in calculating corrected biouptake values:

$$\% \text{ Biouptake}_1 (\text{corrected}) = 100\% [1 - (\% \text{ Rec}_1 / \% \text{ Rec}_2)] \quad (8)$$

Both the uncorrected and corrected (given in parentheses) values for the biouptake are listed in Table VII, along with values reported in the literature from off-line analyses (18–23). The ability to demonstrate the relative reactivity of the dif-

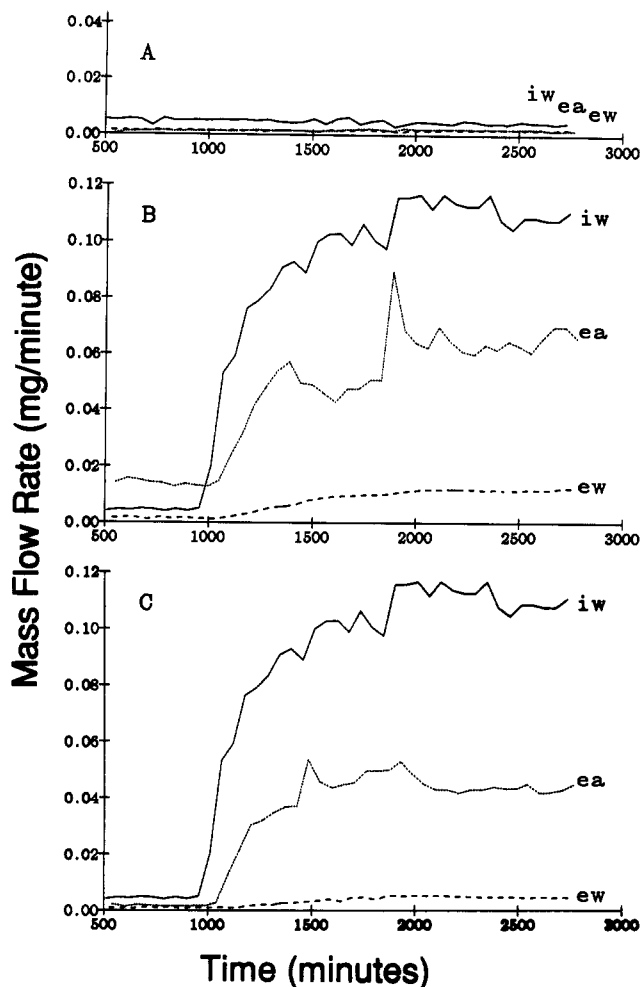


Figure 6. Mass flow rate plots for carbon tetrachloride in the influent wastewater (iw) stream, the effluent water (ew) stream, and the effluent air (ea) stream in (A) reactor 3 (reactive, not spiked), (B) reactor 2 (nonreactive, spiked), and (C) reactor 1 (reactive, spiked). The spike was started at about the 950-min mark.

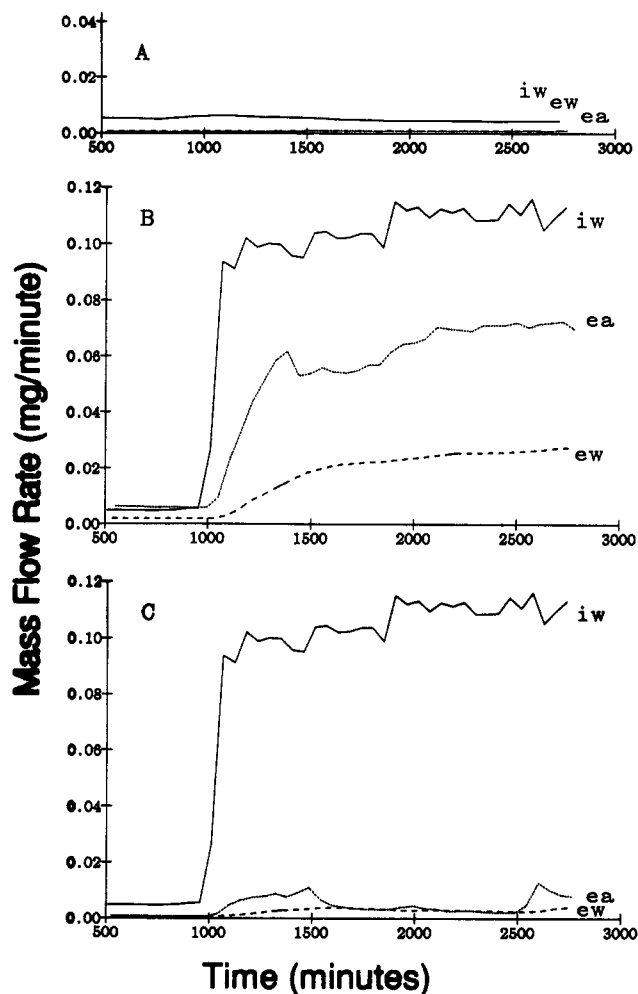


Figure 7. Mass flow rate plots for benzene in the influent wastewater (iw) stream, the effluent water (ew) stream, and the effluent air (ea) stream in (A) reactor 3 (reactive, not spiked), (B) reactor 2 (nonreactive, spiked), and (C) reactor 1 (reactive, spiked). The spike was started at about the 950-min mark.

Table VII. Percent Biouptake^a

	exptl	lit.
dichloromethane	85 ± 1 (85 ± 1)	50–95, ^c 100, ^e 96 ^f
chloroform	37 ± 3 (31 ± 4)	50–95, ^c 0 ^b
carbon tetrachloride	58 ± 1 (41 ± 4)	50–95 ^c
1,1,1-trichloroethane	31 ± 4 (19 ± 4)	5, ^c 0 ^b
1,1,2-trichloroethane	23 ± 7 (12 ± 2)	
tetrachloroethene	41 ± 7 (42 ± 7)	0 ^b
bromoform	20 ± 14 (24 ± 7)	
benzene	94 ± 4 (94 ± 4)	50–95, ^c 85–88 ^g
toluene	71 ± 2 (71 ± 1)	50–95, ^c 84–88, ^g 40–79 ^d
ethylbenzene	66 ± 33 (70 ± 28)	50–95, ^c 85–97 ^g
styrene	98 ± 1 (97 ± 1)	
chlorobenzene	98 ± 1 (98 ± 1)	91, ^b 79–93 ^d

^a Experimental values corrected for the recoveries in the analytical test reactor (reactor 2) are given in parentheses. ^b Reference 18. ^c Reference 19. ^d Reference 20. ^e Reference 21. ^f Reference 22. ^g Reference 23.

ferent compounds in biological wastewater treatment processes is provided by these analyses.

In most cases, the % biouptake results from this study are consistent with the % biodegradation values reported in the literature. The greatest disparity is observed for 1,1,1-trichloroethane and perchloroethylene, where essentially no biodegradation was reported in one literature reference (18), although biouptakes of 19% and 42%, respectively, were

observed in this study. As with any process, biodegradation is highly dependent upon the reaction conditions. The age and species of biomass, organic influent concentration, mineral nutrient content, process flow rate (retention time), oxygen concentration, temperature, pH, and other factors influence the biodegradation process. As is apparent from the comparison of literature values, the results can vary widely depending upon these process conditions. For example, one study (18) showed no biodegradation of chloroform (as well as 1,1,1-trichloroethylene and perchloroethylene), while another (19) reported the biodegradation of chloroform to be in a range of 50–95%. A corrected value of 31% biouptake for chloroform was observed in this study.

In spite of the use of filters, the flow of sludges and small particulates was constantly observed in the influent wastewater. The concentration of solids was not constant and could not be predicted. The influent water was sometimes clear one day and turbid with solids the next day. These solids apparently were road dirt (earth moving vehicles were working in the area), tars, and sludge from aggregated biomass. Extracting the organic compounds from this physically complex wastewater matrix was a crucial step in these experiments, since sample matrix effects can lead to large errors in trace analyses (24). Even small errors in a stream analysis may result in large errors in the mass balance determinations.

Frequently, the presence of solids affected the process when the solid levels became particularly high in the influent wastewater, causing the recoveries to become significantly

depressed. For example, when high turbidity was observed during one process analysis, mass balance determinations for dichloromethane and toluene around the nonreactive process (reactor 2) showed recoveries of only 39% and 32%, respectively. Large differences were still observed between the reactive and nonreactive processes for this experiment, where mass balance determinations around the reactive process (reactor 1) showed recoveries of only 1.6% for dichloromethane and 1.0% for toluene.

These results demonstrate the ability of the analytical system to monitor the effects of solids on the emissions of organic vapors from wastewater. However, the absorption of the organic compounds into the solids represented another process, thus introducing another uptake variable into the mass balance equation. This second uptake variable was difficult to separate from the biouptake variable and it was not within the scope of this study to do so. Therefore, when poor recoveries were observed from reactor 2, the experiment was repeated after the influent water became less turbid. As a result, the recoveries were sufficient for reactor 2 (mean % recovery = 93, σ = 12), considering the complexity and the concentration levels of the process streams. Relatively large standard deviations in the recoveries exhibited for ethylbenzene are likely due to its low influent concentration (0.49 mg/L), which increases the effects of random error and process baseline changes. Again, these results demonstrate the importance of analyzing the influent stream rather than relying on the calculated spike values.

When the process flows were interrupted for some reason (e.g., pump failure or plugging of the stainless steel sampling tubes) and solids dried on the membranes, the permeation characteristics changed. This happened occasionally and simply required replacement of the membranes. Following each study (every 3–4 days), the sample tubes and membranes for sampling the wastewater streams were flushed with clean tap water and allowed to sit for several hours to prevent the growth of anaerobic bacteria on the inside of the tubing. The membranes that were used to sample the gas streams showed no observable change in properties throughout these experiments.

CONCLUSIONS

It has been demonstrated that, with little or no sample preparation, membranes are used as an effective interface between complex and dirty matrices (gas and liquid) and a mass spectrometer. The use of a single technique and a single analyzer for the multiphase and multistream process minimizes experimental errors and simplifies calibration. The analytical system can be used to study, optimize, and potentially to help control and automate processes. In addition to the determination of the fate of organic compounds in waste treatment processes, other applications include the on-line study of fermentation, distillation, absorption, devolatilization, stripping, degassing, and membrane separation processes. The reliability of the continuous analysis of such processes depends upon (a) the general reliability of the analyzer, (b) the reliability of the sampling system, and (c) the reliability of the

process itself. Mass spectrometers for process monitoring are commercially available and have demonstrated reliability for specific applications. However, as stated above, sampling the process is generally the limiting factor such that the analyzer is only as good as the sample introduction system. Ultimately, the analysis depends upon routine maintenance and the continuous operation of the process at the range of conditions for which it—and the sampling system—was designed.

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Registry No. Water, 7732-18-5; dichloromethane, 75-09-2; chloroform, 67-66-3; carbon tetrachloride, 56-23-5; 1,1,1-trichloroethane, 71-55-6; 1,1,2-trichloroethane, 79-00-5; tetrachloroethene, 127-18-4; bromoform, 75-25-2; benzene, 71-43-2; toluene, 108-88-3; ethylbenzene, 100-41-4; styrene, 100-42-5; chlorobenzene, 108-90-7.

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