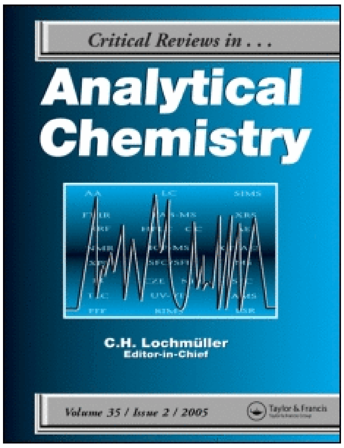

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

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To cite this Article Wilder, Darrel R.(1995) 'New Directions in Industrial Environmental Analytical Chemistry: Beyond Compliance Testing', Critical Reviews in Analytical Chemistry, 25: 2, 77 — 89

To link to this Article: DOI: 10.1080/10408349508050558

URL: http://dx.doi.org/10.1080/10408349508050558

Critical Reviews in Analytical Chemistry, 25(2):77–89 (1995)

New Directions In Industrial Environmental Analytical Chemistry: Beyond Compliance Testing

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ABSTRACT: The scope of industrial environmental analytical chemistry is being expanded increasingly to include measurement efforts that support voluntary pollution prevention and waste minimization projects. The new function supplements the routine regulatory compliance testing task. This additional priority naturally broadens and enriches the responsibility and the nature of the challenges of the environmental analytical chemist. This article presents a reveiw of selected strategies that hold particular promise for addressing the diverse measurement problems associated with pollution prevention and waste minimization projects.

KEY WORDS: environmental testing, waste minimization, on-line environmental analysis, waste load assessment, pollution prevention.

I. INTRODUCTION

The term "industrial environmental analytical chemistry" most typically suggests an image of prescriptive testing and sampling methodology, a redundancy of mandated standards and blanks, exhaustive QA/QC, and reams of documentation. Whether this testing is done by a contract laboratory for the industry or by an in-house environmental laboratory, the description is accurate when the term is meant to apply to the routine testing done for regulatory compliance. In a highly regulated industry like chemical manufacturing, compliance testing is a necessary and inescapable fact of business life.

Although compliance testing is clearly a very important and often scientifically challenging task, it is no longer the sole function of industrial environmental analytical chemistry. Increasingly, a proactive pollution prevention and waste minimization focus is supplementing, and in some cases supplanting, reactive compliance testing as a major focus in industrial environmental efforts. This has come about for several reasons. Recently, the U.S. Environmental Protection Agency (EPA) has realized that "end-of-the-pipe" command and control regulation has not been wholly effective in dealing with environmental discharges. As a result, the current emphasis of the agency is on pollution prevention, source reduction, and waste minimization — a new environmental focus that stresses a "front end" approach to pollution control.[1,2] Indeed, the agency has even included pollution prevention projects in enforcement agreements to further foster this policy.[3]

In addition to governmental initiatives, voluntary programs like those sponsored by the Chemical Manufacturers Association (CMA) have also stressed pollution preven-

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tion and waste minimization as a part of their Responsible Care Code. The CMA has set ambitious waste minimization goals and has reported excellent progress to date by the industry as a whole in attaining these voluntary goals.[4]

A final reason for an increased emphasis on pollution prevention and waste minimization is the financial benefits that accrue to companies that practice these programs. It makes good economic sense to try to capture all of a valuable chemical product or solvent for sale or reuse. This is especially true because the management of waste associated with chemical losses (often biosludge from an activated sludge treatment system) is becoming increasingly expensive and complicated. It is counterproductive to spend time and money to add value by building an increasingly complex chemical product through a multistep synthetic scheme, only to lose some of this product to a waste stream and treatment system and spend more time and money (in utility, testing, and biosludge disposal costs) to have microorganisms perform retro-reactions to convert the product to CO_2, water, and biosludge! A second less easily quantified economic benefit, but one that is becoming increasingly influential, is the importance to consumers and shareowners of dealing with an environmentally responsible company. Enlightened companies recognize the economic value of formulating corporate environmental strategies that go beyond mere regulatory compliance.[5,6]

The journey of the environmental analytical laboratory from solely providing a compliance data service toward pollution prevention typically follows an evolutionary process that moves progressively "upstream" (in the context of the plant's waste streams) in the manufacturing process. A common first step in this process involves establishing a measurement network that provides an early warning system to detect discharges upstream in plant effluent streams. The timely information received from the network drives control strategies developed for rapid mitigation of the effects of an accidental discharge through immediate termination of chemical processes, effluent flow diversion, etc. The next stage in the evolution progresses farther upstream to the source — to discrete chemical production units where waste load information from the process provides feedback to drive waste minimization projects. This step attacks the problem of pollution prevention by working on the source of potential discharges.

Providing analytical data to support pollution prevention, source reduction/elimination, and waste minimization projects (in addition to carrying out mandatory compliance testing) significantly broadens the scope of function of the industrial environmental analytical chemist. The job is expanded to involve not only the traditional oversight of prescribed testing protocol (with consequent rigorous attention to detail), but also demands creative solutions to difficult and unique measurement problems involving plant waste and process streams. As mentioned above, waste minimization projects entail an upstream movement of the testing and sampling function to provide information to sources, the specific chemical processes, and the losses of product, intermediates, solvents, and reagents to the waste stream. This is often best accomplished with at-line or online analyses to provide timely information. It is also, of necessity, a multidisciplinary effort, typically involving elements of process engineering, statistics, sensor design, as well as conventional laboratory analytical chemistry.

This article presents a review of selected examples of measurement technologies that have been applied to pollution prevention and waste minimization projects. The intention is not to perform an exhaustive review of all techniques and instrumentation used in environmental analysis. Recent application reviews have very satisfactorily fulfilled this function.[7,8] Rather, the review attempts to focus on methods and approaches that are unique examples relevant to measurement challenges in support of waste minimization. Because this review deals with a specific problem area rather than the comprehensive application of a defined discipline, the material included will span a range of topics pertinent to its purpose but not necessarily restricted to the mainstream analytical chemistry literature. For example, references relating to work on the process control of activated sludge wastewater treatment systems are included. Although the review primarily deals with measurements in aqueous media, a section on technology applicable to air emission waste minimization is also included. The sections conclude with a discussion of the shortcomings of currently practiced measurement technology when applied to waste minimization projects and propose a "wish list" of measurement improvements that would assist progress in this area.

II. DISCUSSION

Waste Load Concentration Measurement

A starting point for any waste minimization project involves gaining a knowledge of the waste load in plant effluent streams. Mass balance calculations for large-scale industrial chemical processes are often not precise enough to reliably stand alone as a guide to predict waste loads, so direct measurements of waste concentrations in aqueous streams are often required. Usually, the measurement of some nonspecific and easily measured screening parameter indicative of the total waste concentration is used. For inorganic constituents of the waste stream, the measurement of conductivity or pH is often an appropriate choice. For organics, total carbon (TC) or total organic carbon (TOC) is commonly measured. This is not to say that more selective, specialized tests for specific compounds are not also employed. The nonspecific analyzers, however, offer the advantage of providing reliable and robust screening tools to easily quantify waste loads. In addition, commercial on-line or at-line conductivity, pH, and TC analyzers are readily available and have a proven record of performance in the field.

Unfortunately, but inevitably, many waste streams offer a harsh and unforgiving environment for routine measurement. Some typical problems include streams that are highly corrosive, heavily concentrated with interfering constituents, exist as separate phases, are laden with solids, exhibit wide temperature extremes, or present safety hazards. An essential element of any waste stream monitoring system is a means for sample filtration and/or sample conditioning. There are several devices on the market that purport to satisfactorily perform this task. In field use in typical industrial waste streams, however, most single-system filtration devices are inadequate for routine operation. A common problem is the existence in the stream of solids of various forms and sizes — from pellets and metal chips to very finely divided solids, almost colloidal in nature, that agglomerate in aqueous streams and very quickly foul filters. At Eastman Chemical Company we use several different types of filtration devices — wire mesh screens, centrifugal in-line separators, and cartridge filters — in a train arrangement to produce the necessary sample cleanup prior to introduction of aqueous stream aliquots into our online analyzers. Even with the use of the filtration train, system elements must be back-washed, cleaned, or changed on a routine schedule.

On-line measurement of pH and conductivity has been practiced for many years and is generally reliable and straightforward. The on-line analysis of TC content of aqueous streams, however, is a relatively more recent methodology and can be more problematic. When organic constituents are to be measured, there are several considerations that need be taken into account to implement the most effective measurement strategy. If a total, generic assessment of carbon load is desired either TC or TOC measurements usually will suffice. TC offers the simplest, most rugged method to obtain this information but does not differentiate between inorganic carbon (e.g., carbonates) inherent to the water source and organic carbon. A TOC analyzer will discriminate between carbonate or bicarbonates and organic carbon, but the sparging cycle used in TOC analyzers to remove CO_2 emanating from acidified carbonates will cause the loss of volatile organics. Specialized modules or separate instruments[9] to overcome this problem are available but may result in an on-line system that is less reliable for routine unattended operation. A report by Henslee et al.[10] describes the field implementation of a TOC instrument and includes data on the effects of salt concentration, pH, and humic acid concentration on the operation and reliability of the instrument. The report also points out the need for a supplementary method — in this case, flow injection analysis and selective detection for aliphatic polyamines — to provide sufficiently timely data for the response to accidental discharges. A paper by Fabinski et al.[11] describes a new on-line instrument that measures not only TOC but also bonded nitrogen (TN) concentration as well.

Sometimes it is desirable to make a direct measurement of the effect that the biological or chemical decomposition of organic carbon waste has on the dissolved oxygen content of a receiving stream to supplement information on gross carbon load. On-line instruments have been developed that will measure total oxygen demand (TOD) and chemical oxygen demand (COD) in waste streams.[12] In particular, COD is often used as a rapid indicator of biochemical oxygen demand (BOD5), which is a common NPDES permit parameter but whose determination requires a 5-day incubation period. COD may also be a permit parameter as well. Several recent reports have described improved on-line COD monitors with emphasis on their use in the control of wastewater treatment systems,[13,14] but these devices might also be used to supplement TC or TOC data for waste load assessments.

Although much progress has been made in methods to reliably and quickly make waste stream concentration measurements, there are still enhancements that would be desirable. A reliable field instrument that would provide TOC measurements without the loss of volatile organics would be useful. Also the development of instrumentation to provide a rapid indication of permit compliance on currently lengthy analyses (e.g., BOD5), would be beneficial as well. Finally, the ultimate instrument for acquiring waste load concentrations would be a compact, portable, rugged on-line device that would allow the simultaneous acquisition of data on several pertinent parameters (e.g., pH, conductivity, TOC, and selected specific analytes). The instrument would be totally automated (i.e., self-calibrating and self-cleaning) and have redundant power (battery backup capability) and analytical measurement modules for uninterrupted data acquisition in all circumstances.

B. Flow Measurement

The preceding paragraphs have described one of the parameters — concentration of waste in the receiving stream — that must be measured to compute waste load. The second parameter necessary for calculating waste load is flow of the waste stream. The flow measurement is often the weakest data link in the waste load assessment calculation. Quite often the measurement is made on a makeshift basis in suboptimal locations and environments. Although the flow measuring devices are typically capable of good precision under ideal conditions, such conditions are seldom encountered in an industrial field environment and consequently data quality often suffers. A commonly used flow meter employs an electromagnetic sensor for the measurement of flow velocity as well as a differential pressure transducer as a depth indicator. When used in a weir or a Parshall flume, a specially designed chute for flow measurements, the meter generally produces good data. Unfortunately, it is not feasible to install Parshall flumes in all the locations where flow measurements are required, particularly when working upstream toward the chemical processes in a typically congested, existing plant facility. In these situations, portable flow meters are used in existing access points in the waste stream — often small diameter pipes with very variable flows. In addition, many of these upstream waste flows are highly concentrated in corrosive chemicals or heavily laden with materials that will coat the sensors and quickly degrade the quality of the flow data. Such conditions require very frequent cleaning and maintenance of the sensors. The conversion of these portable flow meters to true real time, on-line status through either a direct hardwired communication linkage to a control monitor or telemetric transfer of data to the control system is often a necessary enhancement for producing quality information.

Improved instrumentation for accurately measuring waste stream flows would significantly enhance waste minimization data. Specifically needed are rugged, chemically resistant, anti-fouling sensors that will deliver accurate measurement when faced with widely variable flow velocities and fluid levels. The flow meters should be compact, portable, and have the capability for ready remote transfer of information to a control center.

C. Specific Waste Component Detection

Very often there is a need for the analysis of specific waste components in addition to the general, nonspecific assessment of waste load described in the previous section. This is the kind of value-added analytical information that is required to provide specific guidance for waste minimization projects. Information may also be needed on specific components that must be excluded from a waste treatment system because of its toxicity to the microorganisms in the activated sludge system or on components that are biologically intractable and will pass through the treatment system undegraded.

Specific component analyses most fully utilize the creativity of the analytical chemist. He or she may be called on to devise sensitive and selective means for detecting and quantifying the component of interest rapidly and often in the presence of interferences. Often the only constraint is the ingenuity of the analyst in applying otherwise well-established and widely used methodologies to the rigors of a production environment. There is a wealth of recent literature on selective analyses in aqueous systems covering a wide variety of analytical techniques and environmental applications.[7,8] This article highlights a few selected examples of techniques that appear to offer particular promise in the specialized area of waste minimization and pollution prevention applications.

A report describing direct aqueous injection with gas chromatography/Fourier Transform infrared spectrometry (GC/FTIR) and gas chromatography/ion trap spectrometry (GC/ITS) for environmental analysis[15] is especially applicable to waste minimization measurement problems. Although the technique did not provide sufficient sensitivity for use without preconcentration to achieve EPA regulatory limits for compliance testing of volatiles in water, it would be an excellent tool for waste minimization measurements where concentrations of organic constituents of interest are sufficiently high for good detection and quantitation. The precision study indicated adequate ruggedness of the method and a linear range for GC/ITS of four orders of magnitude.

Membrane introduction mass spectrometry (MIMS) is another mass spectrometricbased technique that appears to be especially promising not only for providing rapid qualitative information on organic constituents of aqueous waste streams but also for its capability for low-level quantitation as well.[16–18] The method utilizes the process of pervaporation,[19] where an analyte is transferred from the solution on one side of a semipermeable membrane to the vapor phase on the opposite side. This type of membrane introduction device allows for direct contact with an aqueous phase containing volatile organics and selective transfer of the organics into the source of the mass spectrometer.

More conventional laboratory techniques may be used in conjunction with on-line TOC analyzers and automatic samplers to perform accelerated off-line analysis for quick identification of specific materials that are the cause of high carbon loads in a waste stream. Tennessee Eastman Division of Eastman Chemical Company uses such a system to reduce the potential for process sewer upsets at its activated sludge treatment plant.[20] The system entails the use of on-line TC analyzers in process sewer lines to initially detect high loads. The automatic sampler operation is actuated by high TC loads, and the grab samples are transported to the laboratory where organics are analyzed by ion trap GC/MS. A mass spectral library has been established involving compounds capable of being discharged to the sewer and waste treatment system.

A number of other methods in addition to mass spectrometry offer promise for specific detection in process streams, both to rapidly monitor upset conditions or to provide reliable quantitation for strategic waste reduction efforts. Electrospray ion mobility spectrometry has many attributes that recommend it as a viable means for on-line monitoring of waste streams. A report by Shumate and Hill[21] describes the use of ion mobility spectrometry in the flow injection, chromatographic, and continuous monitoring modes for the sensitive detection of alkylamines in aqueous samples. Systems employing process grade FTIR analyzers and specially designed sparging systems were used for the real-time monitoring of low levels of chlorocarbons in waste streams.[22,23] These systems may offer a rapid alternate to purge and trap GC analysis of other volatile organics as well. Fiber optic chemical sensors (optrodes) utilizing porous polymer or glass optical fibers present another means for selective and sensitive analysis in environmental samples. Sensors for the determination of pH, ammonia, ethylene, hydrazines, and aromatic fuel constituents (benzene, toluene, xylene) have been developed and demonstrated.[24] Flow injection analysis with biosensors has been applied to the determination of dimethylformamide in waste waters.[25] A system of this kind should be especially attractive for industrial bioprocess monitoring. Flow injection analysis in general has been applied to a whole range of environmental monitoring applications,[26] and the variety of sample introduction, sample conditioning, and detection modules available make this technique an attractive candidate for on-line selective component measurements to support waste minimization efforts.

Laser-induced fluorescence has been evaluated for use as a noninvasive real-time monitoring technique for raw sewage samples.[27] It is proposed that the information obtained may be correlated with BOD5 values and so offers a rapid alternative for obtaining an assessment of the carbon loading in sewage treatment plants. Synchronous fluorescence spectroscopy has also shown potential for the determination of carbon loading in waste waters as well as process control in activated sludge treatment systems.[28]

Future needs in the area of selective component analyzers involve the development of instrumentation that is rugged enough to survive the rigors of field installation and routine usage. The ideal equipment would also be straightforward in design and operation so that routine maintenance and calibration could be performed by plant operations personnel. The capability for data transfer to a remote control center for data analysis, such as use for control limit triggers and pattern recognition, is also desirable.

D. Strategically Designed Monitoring Network

The success of a real-time pollution prevention monitoring system depends on the establishment of an integrated network of monitors placed at strategic locations in the plant effluent lines. Considerations such as flow volume, mass loading, or potential hazards associated with a particular stream dictate monitor placement, as do such practical considerations as accessibility of the proposed site, safety issues, and cost. Historical data on the frequency of accidental discharges from particular point sources can serve as a useful guide in monitor placement. A pareto analysis of historical discharge frequency and severity data is a valuable interpretive aid for determining the locations that will benefit most from on-line monitors. Naturally, a high priority of the monitoring network is in providing real-time data so that appropriate actions may be taken as rapidly as possible to identify the precise location of a discharge and terminate it. This presupposes an analyzer duty cycle that will provide rapid data updates and a centralized data collection point, that is, a control room where communication concerning the discharge can be quickly disseminated to the discharging source location. A recent paper[29] describes a dynamic integrated monitoring system design used both to provide an alarm system to handle acute environmental incidents and to furnish longer-term data to point out trends in waste parameters that could lead to future compliance problems.

Real-time monitoring systems can offer advantages in waste minimization efforts too. Considerations similar to those used in the placement of accidental discharge monitors are operative in the placement of monitors and flow meters for waste minimization projects, but less emphasis need be placed on immediate intervention based on outlying results. The benefit of the real-time data in this case is to establish concentration and composition profiles as a function of time for streams where these parameters vary widely in the daily production cycle. Such a detailed profile will allow accurate pinpointing of sources that are primary candidates for waste load reduction efforts. The establishment of a need for real-time monitoring typically progresses through a series of grab-sampling campaigns that move upstream in the waste sewer lines until a particular source or process is implicated as a major waste load contributor. In many cases, periodic grab sampling over a period of several weeks or months is sufficient to satisfy the data needs for waste minimization work.

The analysis of the data generated from monitoring networks or periodic grab sampling for the purpose of establishing trends, correlations, causality, etc. can often be a complex undertaking. Very often there are large excursions in flow rates and in concentration data for waste stream components. This variability arises from short- and long-term production cycle periodicity as well as from measurement-related contributions like test and sampling variability and bias. There is frequently an abundance of data on hand; sometimes there is too much and there may be a wide range of data quality. The problem is in extracting useful information from the data and making valid interpretations from it. Advanced statistical treatments, such as pattern recognition and multivariate analysis techniques, can be of great assistance in making interpretations from bewildering data bases. Chemometric techniques have been applied with success to a range of environmental applications. The use of chemometric techniques for evaluating data quality in large environmental data bases, identifying discharge sources, and using an improved statistical protocol for analytical laboratory quality control, among other applications has been reported in a symposium series publication.[30]

E. Process Control of Activated Sludge Treatment Systems

Activated sludge treatment systems present an interesting paradox. Despite the fact that they themselves represent a means for "treating" chemical waste and hence play an important role in waste management, the disposal of the biological sludges from these plants is becoming an increasingly difficult and costly problem to industry. Some currently used disposal methods for biosludge, such as incineration or employment as a cofeed in boiler and industrial furnace units, are subject to strict regulations that are becoming ever more difficult to comply with.

There are three areas of emphasis for pollution prevention and waste minimization as it applies to activated sludge treatment systems. They involve optimization of operating parameters to ensure that the system is running in such a way that it will (1) produce effluent that complies with regulations, (2) make efficient utilization of utilities and consumables, and (3) produce biosludge with properties that facilitate easy removal from the system (flocculation) and subsequent treatment prior to disposal (dewatering). The knowledge of and measurement of the key parameters that influence the operation of activated sludge systems are well documented,[31] but the nature of the system itself — a dynamic, idiosyncratic biological system that is complex and difficult to satisfactorily characterize, much less precisely control — still leaves fertile ground for additional measurement development.

The major variables to be controlled in activated sludge systems are dissolved oxygen (DO) content (which is really only an indirect, and sometimes misleading, indicator of the physiological status of the microbiological system), nutrient balance (as expressed by the ratio of BOD/nitrogen/phosphorus), the ratio of influent "food" (TOC, BOD, or COD) for the microorganisms to resident biomass, and process configuration (plug flow, etc.). Of these parameters, the continuous monitoring of DO is deemed to be the most important for control of the activated sludge process. It has also been estimated that the major energy expenditure in the operation of an activated sludge treatment plant involves aeration to ensure adequate DO levels for proper aerobic degradation. Although the measurement of DO using commercially available electrochemical probes is a straightforward affair in the laboratory, there are nonetheless significant operational difficulties in field use of DO probes in a waste treatment plant. The probes are all too often plagued by problems with fouling and typically need correction for drift and calibration. Although recently more rugged DO probes have been developed and are in field service, alternative ways in which to obtain information on the status of the biological action of the system would be useful.

An interesting use of spectrophotometry to assess the degree of aerobic vs. anaerobic action in the microbial population by monitoring the change in the spectral characteristics of cytochromes in the biosludge has been reported.[32] The change in the spectrum of whole sludge between 500 to 650 nm was monitored to provide information analogous to an oxygen uptake rate (OUR) measurement, which is purported to better reflect the microbial metabolic status than data obtained from conventional DO measurements. Previously cited papers[27,28] on the use of fluorescence to characterize wastewater constituents also describe the application of this technique to obtain spectra from settled sewage sludge. Although the use of molecular fluorescence to probe the oxidation state of cytochromes or other biological molecules in sludge was not mentioned explicitly, this method may merit investigation to see if it provides information analogous to that described in the previously mentioned spectrophotometric papers in yielding information that correlates with OUR data.

A report by Kim et al.[33] describes the use of an on-line respiration meter for the determination of oxygen transfer coefficients. The knowledge of the oxygen transfer rate is a critical parameter in optimizing operation of an activated sludge process. The meter is unique in that it allows the actual respiration rate of activated sludge to be measured rather than the instantaneous respiration rate, which typically yields a lower value. On-line measurement of nutrient concentrations at a sewage treatment plant was accomplished and the values obtained for ammonium and nitrate nitrogen and phosphate phosphorus were compared with values obtained by conventional laboratory methods.[34] The on-line measurement of organic acids in a wastewater treatment system was also reported.[35] An especially novel approach for the assessment of the bioavailability of specific compounds in waste influent streams employs an optical biosensor that utilizes an immobilized bioluminescent catabolic reporter bacterium.[36] The method, based on a genetically engineered bioluminescent bacterium immobilized on the surface of an optical light guide, depends on the measurement of bioluminescence that results from the catabolism of selected compounds.

An expert system called the activated sludge advisor prototype (ASAP) was developed to assist wastewater treatment system operators in making difficult operational decisions.[37] The system, which uses the KnowledgePro expert system shell, contains the knowledge base of an experienced operator. The decision diagram allows operators to diagnose plant upset conditions from sensory observations, as well as from chemical testing data, and to take the necessary corrective actions. A report by Pilkington and Bridger[38] describes the problems involved in obtaining representative samples to characterize important operating parameters like influent TOC or nutrients when there are large diurnal variations in mass loading and flow. They describe a computer-controlled flow-proportional sampling system that alters the sampling frequency depending on flow to the system.[38]

There are substantive improvements that can be made in both monitoring methods and strategies in wastewater treatment systems. However, the real area of opportunity for increased performance and, hence, for efficient, waste-minimized operation lies in an improved understanding of the complicated microbial populations that comprise activated sludge systems. Because these are biological systems rather than chemical systems, they are often a source of extreme frustration for engineers and chemists who may be charged with control of their operation. The system can respond in seemingly perverse ways to adjustment of what were thought to be well-understood and straightforward parameters. Similarly, the system operation can become seriously degraded without a hint about the cause of the upset.

There has been ongoing innovative work to better understand and more completely characterize heterogeneous microbiological systems like activated sludge systems using chemical methods. One approach utilizes the chemical analysis of cellular components and metabolic byproducts to provide information on the mix of organisms in the system as well as on the physiological status of the population. For example, profiles of fatty acids from the phospholipid components of microbial cell membranes have been used not only to assess system biomass, but also to yield information on population diversity and nutritional status in numerous microbiological communities.[39–42] Some reports suggest an approach of this kind might be useful when applied to activated sludge treatment systems,[43,44] but detailed and unambiguous discrimination by this method when applied to such complex systems may not yet be possible.[45]

F. Air Emission Measurements for Pollution Prevention

Although the major thrust of this review centers on measurements made in aqueous streams, this is not meant to imply that the minimization of air emissions is unimportant. In fact, there is currently considerable time and energy expended on measurement and reduction of air emissions as mandated in the Clean Air Act Amendment of 1990. While the reduction of the emission of chemicals to the air is primarily driven by pollution prevention, it nonetheless clearly is a waste minimization activity also.

An aspect of the Clean Air Act Amendment that has a major impact on waste minimization as well as pollution prevention is the Leak Detection and Repair program. This initiative calls for the regulated community to identify sources of leaks of volatile chemicals from valves, flanges, fittings, to stop these leaks, and to set up a periodic monitoring schedule for each of the identified sources. Commonly used instruments for such leak detection and periodic monitoring employ detection systems analogous to GC detectors (e.g., flame ionization and photoionization detection). Analyzers used for monitoring for compliance purposes must meet U.S. EPA Method 21 performance criteria, but Method 21 does not specify the detector type. The available field monitors used to detect fugitive emissions are basically rugged, easy to calibrate, and capable of downloading emission data to a computer for the establishment of a fugitive emissions database. Unfortunately, the monitors suffer some of the same problems that these detection modes manifest in their GC applications; for example, a lack of sensitivity to some compounds and differing response factors.

Surface acoustic wave (SAW) chemical microsensors show promise for the sensing of fugitive chemical vapors.[46–49] The devices offer the advantages of being small, inexpensive, they have low power consumption, and are rugged enough to be used in the field. With the use of SAW sensor arrays utilizing individual sensors with different chemically specific coatings, there exists the capability for selective as well as sensitive detection.[50] Other chemical mass sensors, such as the quartz crystal microbalance (MCB) and flexural plate wave (FPW) devices, have been applied as chemical vapor sensors and may offer similar promise in the role of fugitive emission testing.[51,52]

Although extremely low-level detection is usually not required in fugitive emission testing, there may be specific applications involving particularly hazardous or valuable materials that require both specific and very sensitive methods. MIMS has been used recently to detect volatile organics in air at the trace levels.[53] A hollow fiber two-stage membrane interface was used with an ion trap mass spectrometer to detect toluene, carbon tetrachloride, trichloroethane, and benzene at the parts-per-trillion level.

Open-path optical remote sensing methods have been applied to a number of ambient air monitoring applications.[54] In particular, open-path FTIR spectroscopy has been especially promising as field instrumentation for measurement of emission to the air of volatile organics[55,56]. This technology has been capitalized on by several instrument suppliers and contract analytical testing firms to provide fenceline monitoring systems for industry. Such systems might similarly be useful for in-plant, smaller-scale assessments and speciation of fugitive volatiles for waste minimization projects.

An improved fugitive emission monitor would offer the simplicity and universality of the current detection modes while improving sensitivity and providing for the employment of optional selective detection when desired. The ideal monitor would also be compact, rugged, easy to calibrate and maintain, and inexpensive.

III. CONCLUSION

The opportunities to apply useful new approaches to the measurement challenges associated with waste minimization in the chemical industry are as varied as the scope of analytical chemistry. The constraints imposed in compliance testing do not apply to this internal self-directed effort so the range of measurement options is unlimited and left to the ingenuity of the analyst. Efforts of this kind have the beneficial effect of adding some diversity and creativity to the responsibilities of the environmental analytical chemist to offset the sometimes tedious routine of compliance testing. This activity can also contribute to reducing the future compliance testing burden as the sources of potential pollution are identified and eliminated.

ACKNOWLEDGMENT

I wish to thank Michael Bullard, Dr. Richard Grese, Craig Hoyme, Dr. Arthur Meyers, and Matthew Stevens for useful discussions and constructive suggestions for improvement of this paper.

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