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# Identification of Time-integrated Sampling and Measurement Techniques to Support Human Exposure Studies

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# Identification of Time-integrated Sampling and Measurement Techniques to Support Human Exposure Studies

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## Foreword

The mission of the National Exposure Research Laboratory (NERL) is to provide scientific understanding, information, and assessment tools that will quantify and reduce the uncertainty in EPA's exposure and risk assessments for environmental stressors. These stressors include chemicals, biologicals, radiation, and changes in climate, land use, and water use. The Laboratory's primary function is to measure, characterize, and predict human and ecological exposure to pollutants. Exposure assessments are integral elements in the risk assessment process used to identify populations and ecological resources at risk. The EPA relies increasingly on the results of quantitative risk assessments to support regulations, particularly of chemicals in the environment. In addition, decisions on research priorities are influenced increasingly by comparative risk assessment analysis. The utility of the risk-based approach, however, depends on accurate exposure information. Thus, the mission of NERL is to enhance the Agency's capability for evaluating exposure of both humans and ecosystems from a holistic perspective.

The National Exposure Research Laboratory focuses on four major research areas: predictive exposure modeling, exposure assessment, monitoring methods, and environmental characterization. Underlying the entire research and technical support program of the NERL is its continuing development of state-of-the-art modeling, monitoring, and quality assurance methods to assure the conduct of defensible exposure assessments with known certainty. The research program supports its traditional clients – Regional Offices, Regulatory Program Offices, ORD Offices, and Research Committees – and ORD's Core Research Program in the areas of health risk assessment, ecological risk assessment, and risk reduction.

**Gary J. Foley**  
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## Abstract

Accurate exposure classification tools are required to link exposure with health effects in epidemiological studies. Long-term, time-integrated exposure measures would be desirable to address the problem of developing appropriate residential childhood exposure classifications. Screening techniques are also of interest that could focus attention on the most highly exposed (to indicator compounds) populations for which costly multiroute, multimedia monitoring would be most informative. This report presents the results of a literature review that was designed to investigate and/or evaluate methods used in classifying exposure, both long-term, time-integrated and screening methods for assessing exposures to relatively short half-life contaminants

## CONTENTS

<u>Section</u>		<u>Page</u>
Glossary .....		vi
Acronyms .....		ix
1.0	INTRODUCTION .....	1-1
1.1	Background Information .....	1-1
1.2	Objectives .....	1-3
2.0	SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS .....	2-1
3.0	TECHNICAL APPROACH AND RESULTS .....	3-1
3.1	Search Routines and Approaches to Review of Current Literature Materials .....	3-1
3.2	Some Current Methods and Technologies .....	3-3
3.3	Emerging Technology Including Applications from Other Fields .....	3-5
4.0	REFERENCES .....	4-1
4.1	Air-Related .....	4-1
4.2	Water .....	4-4
4.3	Soil and Dust .....	4-5
4.4	Food .....	4-6
4.5	General .....	4-6

## LIST OF TABLES

<u>Number</u>		<u>Page</u>
1-1	Some Current Techniques for Time-Integrated Sampling and Analysis .....	1-4
3-1	Parameters for Major Searches .....	3-9
3-2	Summary Table of Some Method Papers by Group .....	3-11
3-3	Summary Table of Portable/Field-Ready Instruments from Gray Literature .....	3-53

## GLOSSARY

Active/passive sampling	active sampling depends on pumping or similar processes to collect the sample whereas passive sampling involves non-mechanical processes like diffusion
Activity pattern	individual activity associated with daily events
Acute/chronic effects	short-term versus longer-term effects
Aggregate exposure	total exposure from all routes for a particular time period
Ambient monitoring	monitoring of the local/microenvironment of an individual/population; generally refers to outdoor air monitoring
Chemical classes	VOCs, SVOCs, PAHs, metals, pesticides, herbicides, flame retardants
Chemical/physical	transformation within media-processes that lead to multiple forms/products of a given chemical to which one can be exposed
Composite sampling	combining of samples of similar types to get an overall reading of exposure, for example, combining different foods eaten at a meal
Continuous monitoring/ continuously direct reading	monitoring and displaying the concentration of a chemical or the magnitude of a condition as opposed to a periodic or cyclic monitoring process (also see discontinuous techniques)
Cumulative exposure	exposure over time that can lead to additive concentrations of chemicals
Diffusive sampler	one that depends on the process of diffusion to collect the sample
Discontinuous techniques	parts done at different times, such as collection of the sample in the field which is properly packaged and taken to the laboratory for analysis some time later (also see continuous monitoring/direct reading)
Environmental nervous system	term used to describe the wireless networking of lab-on-a-chip or sensors for continuous monitoring of some environment of interest
Epidemiological studies	the study of occurrence and distribution of disease
Exposure assessment	nature and extent of exposure
Exposure classification	characterization of exposure in various terms to permit grouping of individuals/populations in epidemiological and related studies
Grab sampling	designed to capture a pollutant sample at a specific point in time (often during "peak" exposure) for subsequent analysis
Half-life	time at which the rate of disappearance of a chemical in the environment leads to a 50% decrease in concentration
Halides	halogen (chlorine, bromine, etc.) anion
Headspace analysis	usually associated with the analysis of volatile chemicals in the defined headspace above a confined sample of water, food, etc.
High sensitivity/cost/ burden methods	methods usually more complex and costly that may be required for adequate sensitivity to characterize exposures for the general population (also see low sensitivity/cost/burden/methods)
Intensity/frequency of contact	variables which define the nature and extent of exposure
Lab-on-a-chip	understood to mean a small device integrating chemical reaction and analysis functionalities

Limit of detection	lowest detectable concentration for an analyte at a given signal/noise ratio
Long-term/time-integrated measures	approaches to sampling to collect the pollutants over a specified period of time
Low sensitivity/cost/burden methods	usually simpler and more cost effective; more suitable for screening (also see high sensitivity/cost/burden methods)
Media of exposure	air, water, dust, food, etc.
Metalloporphyrins	class of biomolecules with nearly planar/many electron structure used as sensitive layers in sensors
Method validation level	E, EPA approved/accepted; F, field validated; L, laboratory validated; P, proposed method
Microenvironmental	may be very specific and well-defined local environments such as in a shower stall, or more general, such as indoor
Oxyanions	common anions often associated with acidity like the sulfates, nitrates, etc.
Pathways of exposure	refers to specific ways an individual or population comes in contact with an environmental agent, e.g., hand to mouth contact
Pattern recognition	statistical models used to aid in analysis of response patterns for sensors
PB-PK	physiologically based pharmacokinetics
Personal monitoring	monitoring clearly associated with an individual; usually conducted by wearing a personal monitor
Portable instruments	usually means small or miniaturized for field used and may be operated remotely in some cases
Preconcentration/enrichment	some type of process usually designed to concentrate or enrich the target analyte(s) before analysis to minimize problems with interferences and improve detectability
Reactivity equivalents	used to describe chemicals of similar or ostensibly dissimilar structures that have similar chemical reactivity properties
Real-time method	gives instantaneous (or nearly so) information at the point of sampling
Remote operation	usually means to describe field instruments that can be operated from a distance
Route of exposure	inhalation, ingestion, and dermal adsorption
Scale of exposure	extent of populations/individuals exposed
Screening techniques	usually lower sensitivity/cost/burden methods to help in preclassifying sample components
Selectivity	ability to discriminate
Sensitivity	change in response (slope) as a function of incremental changes in analyte concentration
Sensors	understood to mean a device that contains a specific chemical recognition element for identifying a molecule or class of molecules and a means of signal transduction for quantifying the material
Sorbent material	activated charcoal, Carbotrap <sup>™</sup> , Carboxen <sup>™</sup> , Carboxen <sup>™</sup> , Carbopack <sup>™</sup> , Tenax <sup>™</sup>

Sorbent tubes	tubes containing some adsorbing/absorbing material for capturing and preconcentrating/enriching target analytes
Spatial/temporal concentration patterns	concentrations found over time and distance
Spike exposure	higher than normal exposure associated with some specific activity that occurs infrequently
Time of exposure	various aspects such as during certain stages of biological development, daily activities, time of day, etc

## ACRONYMS

AAS	atomic absorption spectroscopy
ECD	electron capture detector
FID	flame ionization detector
FPD	flame photometric detector
GC	gas chromatography
GC-AED	gas chromatograph with atomic emission detector
GC-MS	gas chromatograph coupled to mass spectrometer
GC-NPD	gas chromatograph with nitrogen/phosphorus detector
GFAAS	graphite furnace atomic absorption spectroscopy
HiVol PUF sampler	active sampling device containing polyurethane foam plugs
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectrometer
IR	infrared spectroscopy
ISE	ion selective electrode
LC-MS	liquid chromatography-mass spectrometer
LDPE	low density polyethylene
MIPs	molecularly imprinted polymers used for introducing molecular recognition in sensors
MOSES II	a commercially produced electronic nose equipped with two arrays of eight sensors
MOS	metal oxide semiconductor
MQL	method quantitative limit
NCI-MS	negative chemical ionization mass spectrometry
OP	organophosphate pesticides
PAHs	polynuclear aromatic hydrocarbons
PBDE	polybrominated diphenyl ethers
PCA	principle component analysis/computer routine used to aid in analysis of response patterns from sensors
PCBs	polychlorinated biphenyls
PID	photoionization detector
POPs	persistent organic pollutants
PRC	performance reference compounds
PVC	polyvinyl chloride
RSD	relative standard deviation
SAW	surface acoustic wave

SOP	sensorial odor perception; also used in good laboratory practice to mean standard operating procedure
SPMD	semipermeable membrane device
SVOCS	semivolatile organic chemicals
TCD	thermal conductivity detector
TDS	thermal desorption system
TLV	threshold limit value
UV	ultraviolet spectroscopy
VOCs	volatile organic chemicals
XRF	X-ray fluorescence spectroscopy

## SECTION 1.0

## INTRODUCTION

## 1.1.1 BACKGROUND INFORMATION

Human exposure to environmental chemicals can be defined as the condition which exists when both the person and the chemical(s) at “measurable concentrations” are present at the same time and location. The dimensions of exposure are generally expressed and specified in terms of the media of exposure, time, route, number of people, scale, microenvironment, and activity pattern. Assessing total exposure of an individual or population involves identifying the contaminant, contaminant sources, environmental media of exposure, transport through each medium, chemical and physical transformations, routes of entry into the body, intensity and frequency of contact, and spatial and temporal concentration patterns of the contaminant. The accuracy and precision of exposure assessments greatly influence the reliability of decisions that depend upon such assessments.

Accurate exposure classification tools are required to link exposure with health effects in epidemiological studies. Long-term, time-integrated exposure measures are needed to address the problem of developing appropriate residential childhood exposure classifications. Screening techniques are also of interest that could focus attention on the most highly exposed (to indicator compounds) populations for which costly multiroute, multimedia monitoring would be most informative. This project was designed to investigate and/or evaluate methods used in classifying exposure, both long-term, time-integrated and screening methods for assessing exposures to relatively short half-life contaminants. Focus on single chemicals by government regulatory agencies has limited advancement of methods designed to detect and quantitate classes or families of chemicals that may be of interest in environmental settings. However, this may change in the future since there is growing interest in assessing cumulative exposures to various chemicals. An important part of this task then is to also attempt to assess emerging

technologies and methods that have potential for developments for these purposes.

1.1.2 Indoor Pollutant Problem Area

The use of building materials, furniture, carpets, and various household products invariably releases pollutants to the air or surfaces. These pollutants may then be transferred to humans by inhalation, dermal contact or ingestion. Assessing an individual's exposure to such indoor pollutants is best done through personal monitoring methods which can also include assessments of daily activity patterns and the potential for exposure. However, active personal monitoring methods tend to place a high burden on the individual. Ambient monitoring designed to map microenvironments and the activity patterns of individuals are useful surrogates in assessing personal exposures.

A wide range of chemicals is of interest as indoor pollutants including physiochemical classes/families such as the VOCs, SVOCs, PAHs and metals. Use groupings like the pesticides, flame retardants and cleaning solvents are also of interest. Methods that permit detection of chemical classes and families in one collected sample can be helpful for human exposure screening and preclassification purposes. Real-time methods designed to detect specific prototype chemicals for the various classes are a possibility, but such approaches have received relatively little attention. However, real-time methods are not generally useful for media/samples like food and surfaces where it is difficult to quickly and effectively transfer target analytes to measuring devices or sensors. .

1.1.3 Brief Overview of Current Technology And State-of-the Art

Monitoring of environmental pollutants (organic and inorganic) represents an ongoing challenge for the environmental chemist. Since most environmental pollutants are present at low concentrations, highly sensitive detection methods as well as efficient separation methods are needed to quantify environmental samples.

Some current techniques that have been reviewed (see reference 120) for time integrated sampling and analysis are listed in Table 1-1. Continuously operating analytical devices offer a high time resolution, but often lack sufficient sensitivity and selectivity. Application of such devices for assessing the presence of classes or families of chemicals can be even more difficult since it is necessary to fine tune both qualitative and quantitative analytical parameters for multiple chemicals. Therefore, discontinuous techniques with a (pre)concentration step during or after the sample collection are still preferred, especially in the case of toxic substances where the ability to detect low concentrations is demanded. To evaluate exposures over time, various methods have included time-integrated approaches in which the sampled medium passes through an absorbing or adsorbing material that removes the desired pollutants during a specified period of time, grab sampling designed to permit one to measure pollutants at a specific point in time and evaluate "peak" exposures, and direct reading monitoring devices designed to collect and analyze samples continuously.

Most integrated sampling methods appear to use active sampling techniques in which the pollutants are collected by forced movement (e.g., use of a pump) through an appropriate collection device such as a sorbent tube, treated filter, or impinger containing a liquid media. The availability of an acceptably low burden active personal air exposure sampler for use by children that is also suitable for a wide range of chemical classes or families of interest in indoor environments is generally lacking. Passive sampling/monitoring devices appear to be the currently accepted technology where collection of sample is controlled by a physical process such as diffusion through a static air layer or permeation through a membrane without the active movement of the medium. A passive sampler can be used over a long sampling period, integrating the pollutant concentration over time. Since only a few analyses are possible over the sample-collection period, analytical costs (usually associated with expensive dynamic sample isolation and preconcentration techniques) can be substantially reduced. Because of their ease of

use, passive dosimeters (such as organic vapor monitors) are attractive alternatives to active samplers for monitoring personal exposures to air contaminants and are receiving more study (see references 40-41 for recent studies) for personal, indoor and outdoor air monitoring of VOCs in community and office environments with sampling times ranging from days to weeks. Because of the limited capacity and "breakthrough" problem of some of these badges, sequential sampling with several monitors may be necessary for time-integrated studies. Semipermeable membrane devices (SPMDs) have received some attention for indoor studies involving air, but the devices have received more detailed study in the context of water sampling and analysis.

In both cases (active and passive), the actual sample collection and analysis steps are usually discontinuous, although validated methods exist that have combined the two steps into a single method. Real-time methods with immediate results offer advantages, but have other limitations. For example, real-time methods are usually designed for a specific target analyte (such as may be present in an occupational setting) and are not generally useful for detecting classes or families of chemicals, an important consideration for environmental monitoring. However, there are exceptions to this such as the aerosol-based total PAH real-time monitor that has been in use for a number of years to measure indoor concentrations of PAHs (see for example reference 46). It may be possible to adapt monitors of this type to other classes of indoor pollutants that may be detected using photoelectric ionization instruments.

## 1.2 OBJECTIVES

The primary objective of this project is to identify the time-integrated sampling and analytical methods and technology that are currently available (or will be validated field-ready in the next two years) or that can reasonably be adapted from other applications to interrogate air, water, soil, and surfaces in indoor environments for target compounds/compound classes (VOCs, metals, pesticides, etc). Long-term time-integrated

exposure measures are needed in order to develop an appropriate exposure classification for a given individual which then can be linked to that same individual's health outcome data for epidemiological studies involving general population exposures. Health outcomes can be short-term, acute or more long-term, chronic in nature, so it is important to assess both short term and long term exposures. Most previous multimedia human exposure studies have made microenvironmental or personal pollutant measurements for only a brief duration (e.g., one day or one hour). These types of studies could easily miss a key exposure event (i.e., a short duration event with high microenvironmental concentrations) in a given individual's life because of the brief temporal monitoring regime. Missing such a key exposure event could lead to misclassification of an individual's exposure. In addition, since pollutant concentrations in the home are generally expected to be low with only occasional sporadic acute spikes, the merits of continuous-long-term or composite sampling methods should be considered. Therefore, long-term time-integrated monitoring techniques as well as techniques that will permit detection and recording of "spike" exposures must be identified to improve the accuracy of exposure classifications. Methods that may have potential for use as screening techniques (such as for chemical/structural classes and/or reactivity families) are also identified where possible.

In addition, selected sampling/analysis methods should have appropriate detection sensitivities and operate in a time frame consistent with study objectives. Methods should also be sufficiently rugged and transferable to provide comparable data for large numbers of samples, sufficiently selective to prevent misidentifications of chemicals and provide pollutant concentration data that meet a study's accuracy and precision objectives. Furthermore, the collection methods must place as small a burden as possible on the study population. Finally, because large numbers of samples must often be collected and analyzed, both the collection and analysis methods should be as efficient and cost effective as possible.

TABLE 1-1. SOME CURRENT TECHNIQUES FOR TIME INTEGRATED SAMPLING AND ANALYSIS

Sampling Techniques	
<p><b>Passive Devices</b></p> <ul style="list-style-type: none"> <li>● Collection by diffusion (for gases and vapors)           <ul style="list-style-type: none"> <li>▸ activated charcoal</li> <li>▸ silica gel</li> <li>▸ Tenax</li> <li>▸ Chromosorb<sup>tm</sup></li> <li>▸ Amberlite XAD<sup>tm</sup> resins</li> <li>▸ molecular imprinted polymers</li> <li>▸ SPMDs</li> </ul> </li> <li>● Collection by sediment (for aerosols)           <ul style="list-style-type: none"> <li>▸ weigh boats</li> </ul> </li> <li>● Collection by wiping           <ul style="list-style-type: none"> <li>▸ surface wipes</li> <li>▸ EL press</li> <li>▸ PUF roller</li> <li>▸ hand rinse</li> <li>▸ body dosimeter</li> </ul> </li> </ul> <p><b>Active Devices</b></p> <ul style="list-style-type: none"> <li>● Solid Sorbents           <ul style="list-style-type: none"> <li>▸ activated charcoal</li> <li>▸ silica gel</li> <li>▸ porous polymers</li> <li>▸ Tenax<sup>tm</sup></li> <li>▸ Porapak<sup>tm</sup></li> <li>▸ Chromosorb<sup>tm</sup></li> <li>▸ Amberlite XAD<sup>tm</sup> resins</li> </ul> </li> <li>● Chemically treated filters</li> <li>● Liquid absorbers</li> <li>● Sampling bags/evacuated rigid containers           <ul style="list-style-type: none"> <li>▸ Teflon<sup>tm</sup> bags, etc.</li> <li>▸ Summa<sup>tm</sup> canisters</li> </ul> </li> <li>● Sample size-selective sampling for aerosols           <ul style="list-style-type: none"> <li>▸ filters for aerosols</li> <li>▸ cyclone</li> <li>▸ impaction</li> </ul> </li> </ul> <p><b>Sensors/Emerging Technologies</b></p> <ul style="list-style-type: none"> <li>● Direct-reading instruments for gases and vapors           <ul style="list-style-type: none"> <li>▸ combustion gas detectors</li> <li>▸ colorimetric detectors</li> <li>▸ electrochemical sensors</li> <li>▸ infrared gas analyzers</li> </ul> </li> </ul>	<ul style="list-style-type: none"> <li>▸ metal oxide sensors</li> <li>▸ thermal conductivity sensors</li> <li>▸ portable instruments, (i.e., GC, GC-MS, XRF, etc.)</li> </ul> <ul style="list-style-type: none"> <li>● Techniques for aerosols           <ul style="list-style-type: none"> <li>▸ light-scattering photometers</li> <li>▸ light-scattering particle counters</li> <li>▸ condensation nucleus counters</li> <li>▸ single particle aerosol mass monitors</li> <li>▸ piezoelectric crystal microbalance</li> <li>▸ trapped element oscillating microbalance</li> </ul> </li> <li>● Biosensors           <ul style="list-style-type: none"> <li>▸ immunosensors</li> <li>▸ enzymatic biosensors</li> <li>▸ molecular probe</li> </ul> </li> <li>● Other           <ul style="list-style-type: none"> <li>▸ fiber optic sensors</li> <li>▸ affinity sensors/molecular imprinted polymers</li> </ul> </li> </ul>

TABLE 1-1. (Continued)

Analytical Techniques		
Conventional		Emerging
Organic	Metals	Mostly organic
<ul style="list-style-type: none"> <li>▶ GC-MS</li> <li>▶ GC-ECD</li> <li>▶ LC-MS</li> <li>▶ GC-AED</li> </ul>	<ul style="list-style-type: none"> <li>▶ ICP-MS</li> <li>▶ ICP-AES</li> <li>▶ XRF</li> <li>▶ AAS</li> <li>▶ ISE</li> <li>▶ ASV</li> </ul>	<ul style="list-style-type: none"> <li>▶ immunoassays</li> <li>▶ MIP-based sensors</li> <li>▶ MOS-based sensors</li> <li>▶ electronic nose</li> <li>▶ electronic tongue</li> <li>▶ lab-on-a-chip</li> <li>▶ remote operated portable instruments</li> </ul>

## SECTION 2.0

### SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Several approaches were used to identify publications/materials relevant to meeting the project objectives including scientific literature, gray literature (gray literature is a term used for articles in trade publications that have not undergone the peer-review process used by scientific journals), and internet resources, some outside the traditional chemical and environmental subject areas. Important works were grouped primarily according to methods/technologies that are currently in use, to those that will be ready in 2-3 years, to promising technologies that are further from commercialization. Recent developments in some of the emerging technologies are also discussed. Information is also provided on some of the more promising portable instruments that were found in the gray literature. Unfortunately, none of these systems/methods clearly meet the objectives of this task in all respects. Limited information was available on promising new approaches that might be useful for personal monitoring in indoor environments.

In general, air and water samples are more amenable to the application of long-term, time-integrated approaches to sampling and analysis, and these matrices have been emphasized in this report. Application to dust/surfaces and food samples is more problematic, and the biggest problem area is the preparation required to put such samples into a form amenable to periodic or continuous analysis. Dust/surface samples may still require wiping/vacuuming approaches with subsequent labor-intensive extraction and clean-up procedures prior to analysis. Validated methods are available for such purposes.

It is recommended that EPA consider funding further developments in the areas of passive monitors (especially the SPMDs and sorbent tube type) for their own specific applications. It would probably also be worthwhile to follow new developments with novel passive samplers for long-term

monitoring, such as described in reference 47, since these appear to avoid the need for laborious recovery of analytes from the samplers (or sampling medium) after exposure by solvent extraction or dialysis and the need for expensive cleanup of the extracts before chromatographic analysis. Also recent work (see abstract 37.01 from meeting, 12<sup>th</sup> Conference of the ISEA/14th Conference of the ISEE, August 11-15, 2002, Vancouver, BC, Canada, describes the development of a passive sampler consisting of a denuder made from sections of a multi-capillary GC column which permits sampling rates about 100 times higher (increased surface area) than the traditional badge and tube-type diffusive samplers. Recent applications (see, for example, reference 122) of commercially available solid-phase microextraction devices (SPMEs) as a diffusive sampler for time-weighted average sampling of volatiles and semivolatiles might also be of interest.

Although most of the emerging research on sensors is well into the future in terms of real application potential, it may be worth considering their use for preclassifying pilot studies before using the more expensive methods. This might be particularly appropriate for sensors that can be designed and applied to detect a range/window of chemicals within chemical classes/families of interest. Recent developments using metalloporphyrins as sensitive layers in electronic noses/tongues appear to hold promise for such purposes since there is considerable opportunity to design in chemical class selectivity and sensitivity through synthetic manipulations of the macrocyclic ring and its peripheral groups and the metal center. It might also be worthwhile to follow developments in "lab-on-a-chip" technology, a term understood to mean a device integrating chemical reaction and analysis functionalities. Since chemicals having similar structures usually means similar reactivity and mechanisms of toxic action, "lab-on-a-chip" approaches might be useful for developing a kind of "reactivity equivalents measure" that could potentially provide an amplified signal (for a specific kind of reactivity underlying a specific

toxic effect) for use in exposure studies. A recent perspective (reference 123; also see recent reviews 124-125) on analytic chemistry published in *Science* indicated that such miniaturized chemical analysis systems have the potential to revolutionize analytical chemistry and that the uses for these systems could be numerous with application to airborne contaminants being one of the more promising. It is further recommended that new developments in portable GC and MS instruments, especially those with preconcentration devices at the front end, be given serious consideration for certain applications.

VOCs, PAHs, pesticides and other SVOCs continue to receive attention as target analytes in various long-term monitoring studies. Metals have received less attention, probably as a result of the increased complexity of sample collection and analysis problems associated with their study. Brominated flame retardants (for a review see reference 121) are receiving increased attention since they are used in a variety of applications to reduce flammability of computers and other electronic devices, upholstered furniture, and other products. Among the widely used brominated flame retardants are the polybrominated diphenyl ethers (PBDE) which are of concern because of evidence for potential neurodevelopmental toxicity and endocrine disruption. Commercial technical PBDE mixtures generally contain less than 10 congeners, while technical PCBs are mixtures of about 80 congeners. Although the PBDEs are less stable than their chlorinated counterparts, degradation should be less of a problem in indoor environments. Thus, their analysis by highly sensitive techniques such as negative chemical ionization-mass spectrometry (NCI-MS) is promising. Very few methods have been developed for air samples, although some work with indoor air particles has been reported (see reference 121 for discussion). Another important class of brominated flame retardants that has received less attention is tetrabromobisphenol A. Other chemicals/classes that have been detected in recent residential

indoor studies (see abstracts 16.21, 53.19 and 41.02 for example) from the Vancouver Conference involving air and dust measures include the phthalates, alkylphenols, herbicides and aldehydes. The indoor aldehyde work described in abstract 41.02 is also an example of an effort to address a structurally related class of contaminants using a sampling and analysis approach common to all members of the class. Other abstracts from this recent conference that may be of interest include 21.04 (Repeated personal monitoring versus microenvironmental monitoring for assessing exposures to airborne chemicals), 37.01 (Development of a sensitive diffusion sampler for the measurement and assessment of personal exposure to PAHs in air), 53.22 (Polycyclic aromatic hydrocarbon (PAH) levels in house dust from homes with infants in relation to maternal smoking behavior), and 44.28 (Brominated flame retardants: Policy implications of the emerging science).

Finally, there is currently considerable interest and effort to develop rapid detection/monitoring systems for chemical and biological warfare agents not only for use by the military in the field but also for monitoring environments occupied by the general population including indoor settings. Since for security reasons not all of these developments are readily accessible and/or can be found in the public domain, it may be necessary for EPA to take other measures to gain access to components of this work that might have a bearing on the objectives of this task.

SECTION 3.0  
TECHNICAL APPROACH AND RESULTS

3.1 SEARCH ROUTINES AND  
APPROACHES TO REVIEW OF  
CURRENT LITERATURE

Several approaches were used to identify publications/materials relevant to meeting the project objectives. Published literature (scientific and trade), gray literature, and internet resources were searched to identify promising technologies and methods. Both fee-based databases and free internet sources were searched. These resources included databases such as Chemical Abstracts as well as databases outside the traditional chemical and environmental subject areas such as MEDLINE. Both topic-specific and multi-disciplinary databases and web links were searched to ensure that a broad range of resources were used to uncover relevant technologies and methods across a variety of disciplines. Table 2-1 provides a list of key parameters/descriptors for major searches performed in this task.

A broad based MEDLINE search to identify references on the analysis of organic and inorganic compounds, including pollutants, noxae, and pesticides was performed. This search specifically identified continuous and time integrated sampling/monitoring techniques as well as techniques using sensors/microsensors. The searched resulted in 371 records, including a subset of 54 records referencing time integrated techniques. Continuous monitoring techniques were also identified in the ScienceDirect database including 58 initial references. Another 149 references were found on electronic nose/tongue technologies using the following databases: MEDLINE, ScienceDirect, NTIS, LC MARC, and NLM LOCATORplus. References identified in ScienceDirect from the journals Sensors and Actuators (Part A & B) and Biosensors and Bioelectronics have proven particularly useful. Over 20 patents relating to continuous and real-time monitoring were also identified from the U.S. Patent and Trademark

database. Using standard web search engines like Google [<http://www.google.com>], potentially useful analytical methods-related web sites including those at NIOSH [<http://www.cdc.gov/niosh/nmam/nmammenu.html>], ASTM [<http://www.astm.org/cgi-bin/SoftCart.exe/STORE/productsearch.htm?E+mystore>], and OSHA [<http://www.osha-slc.gov/dts/sltc/methods/index.html>] were identified. Other useful web sites identified include a comprehensive sensor site at the NSF supported Long Term Ecological Research Network [<http://lternet.edu/technology/sensors/index.html>]. Over 25 key authors were identified and other relevant papers by these authors were sought using the databases Ingenta and ScienceDirect, among others.

A search of fee-based engineering, technology, health, and environmental/pollution databases for references on real-time monitoring and on SPMDs was performed. The search resulted in 54 relevant citations. A larger search of this same database set, along with a search of the EPA and Library of Congress online catalogs was performed with an emphasis on long-term monitoring as well as conventional sampling/analytical techniques. This search resulted in 73 relevant citations. These searches have also included a database that indexes conference papers from all scientific disciplines, as well as a food science database and an engineering database, along with the above mentioned Library of Congress database. The use of these resources broadened the search to include references from outside the chemistry/environmental literature. In addition to searching by keywords, over 50 relevant papers were identified from searching 19 authors considered prominent in this field. A search of Chemical Abstracts and Analytical Abstracts for predominantly review articles identified 39 references. State-of-the-art research and applicable research from outside the chemistry/environmental disciplines was examined by searching over 15 web sites identified by the TOPO. These sites include trade journals [some examples are Chemical

Equipment [<http://www.chemequipmag.com>] and Hazardous Materials Management [<http://www.hazmatmag.com>] and gray literature indexes such as the GrayLIT Network [<http://www.osti.gov/graylit>].

A search of technology, health, environmental/pollution and multi-disciplinary databases for references on flame retardants in indoor environments was also performed. This search resulted in the identification of 10 relevant citations. Two searches were made of the Dissertation Abstracts database, an index of international doctoral dissertations and masters' theses. The first search concentrated on references in the field of chemistry and environmental science. This resulted in 41 relevant citations. A second search of Dissertation Abstracts concentrated on disciplines outside of the chemical and environmental sciences. This search produced 46 relevant citations. Fourteen multi-disciplinary trade magazine/trade magazine publisher web sites [See Above] were searched and 24 relevant citations were identified. Additionally, the GrayLIT Network [<http://www.osti.gov/graylit>], a web portal to Federal gray literature from the Department of Energy's Office of Scientific and Technical Information, was searched and 8 key references were identified. An additional 14 notable references were identified from databases covering the fields of aerospace, agriculture, biotechnology, energy, safety, pharmacology, materials science, and electrical engineering. Reference 121 provides a brief overview of the analytical methodology used for the determination of brominated flame retardants in environmental samples and concentrations found in the samples.

A search for information on the topic of "lab-on-chip" was also conducted. This resulted in 21 relevant references, including a web information portal on the subject at [<http://www.lab-on-a-chip.com/home/index.html>]. Special attention was given to coverage of the gray literature, instrumentation/equipment supplier application notes, etc. In considering efforts toward the

development of autonomous environmental monitoring systems, the concept of total analysis systems or Lab-on-a-Chip, which is based on the twin strategies of integration and miniaturization that have been so successful in the electronics industry, was also considered. A recent paper (M Sequeira et al., Talanta 2002, 56, 355-363) may be of interest. The article looks at the materials issues, particularly with respect to new polymeric materials that are becoming available, and strategies for integrating optical (colorimetric) detection. It is indicated that for environmental monitoring, the further integration of wireless communications with micro-dimensioned analytical instruments and sensors will become the driving force for new developments in the field, and that the emergence of these compact, self-sustaining, networked instruments will have enormous impact on all field-based environmental measurements. It is further indicated that the ultimate manifestation of this concept is to develop an 'environmental nervous system' through the distribution of a multitude of devices in waterways, airways, etc. However, these systems, as promising as they appear to be, are still in the future.

In trying to address the objectives of identifying methods/equipment that are either currently in use or will be validated field ready within the next two years, developments reported in the gray literature, supplier application notes, etc. have received some attention. Using a freely available search engine [[www.google.com](http://www.google.com)] and the keywords "air monitoring" provided a large number of links, many of them interesting, and perhaps 5% of them yielding some information relevant to this task. The general impression from study of the material from this search was that analytical instruments are changing fast, and peer-reviewed journals are not keeping up. The trend is toward portable instruments that are more suited for process control and hazardous waste remediation than scientific research directed at exposure assessment, so the use of these instruments is less likely to be reported in peer-reviewed journals. Some examples include

portable GC-MSs, GCs (some handheld) with various detectors including TCD, PID, ECD, surface acoustic wave, photoacoustic IR, etc. An important aspect of some of these systems is their ability to be operated remotely. Not all of these instruments are appropriate for personal exposure monitoring, but they are interesting as examples of technological improvements that will ultimately lead to more sensitive/selective and more portable analytical devices. A website [<http://fate.clu-in.org>], run by EPA, was also found that provides an online encyclopedia containing information about technologies that can be used in the field to characterize contaminants in soil and ground water, and to monitor the progress of remedial efforts, and in some cases, to confirm by analysis that the site is ready for close out. The website also provides information here on new instruments that have been field tested. It appears that technological advances over the past decade have created specifically designed tools to improve site clean-up and long-term monitoring.

A solicitation from DOE/PNWL to companies interested in obtaining license rights to commercialize, manufacture and market a prototype exposure-to-risk monitor (E2RM) was also recently encountered on the web [[technology@pnl.gov](mailto:technology@pnl.gov)]. The E2RM developed at DOE/PNWL is intended to monitor exposure of workers who work with or around hazardous chemicals (notably VOCs) by determining the amounts of chemicals in the worker's breath. The system combines a breath inlet device with an ion trap mass spectrometer that is controlled by a PC with appropriate software. A physiologically-based pharmacokinetic model (PB-PK) is then used to relate exposure concentrations to the amount of internal dose received and thus, the resulting health risk, immediately following the worker's exposure. VOCs studied include trichloroethylene, carbon tetrachloride, benzene, toluene, and others. This interesting approach to personal exposure monitoring/assessment might be useful in a non-occupational setting as well. However, this approach is subject to all the uncertainties normally associated with the use of animal-

based PB-PK models when extrapolated to humans. Although this is an attractive and promising technology, special care will need to be exercised in using and interpreting the data/results obtained from the use of such monitors.

### 3.2 SOME CURRENT METHODS AND TECHNOLOGIES

Although many papers were found which appeared to be of sufficient interest to warrant review, only a small percent of the overall search material obtained had a direct bearing on the goals of this project. References (grouped according to sample matrix/type) for some of the more relevant and important scientific publications in the recent literature identified from the above search efforts are shown in the Reference Section. References in the general category are of general interest/reviews and/or more research and development in nature. Hard copies of most of these articles have been obtained. A number of the recently published papers emphasizing both organic and inorganic analytes in different media (with an emphasis on air) using current and/or emerging methods and approaches have been reviewed in more detail to identify performance characteristics for both the sampling and measurement components of the method to the extent possible. These papers have been organized into six groups including:

- (1) conventional time-integrated/continuous/real-time methods
- (2) recent developments and applications of SPMDs,
- (3) new high-speed/portable/sensor based approaches to ambient/personal monitoring of VOCs in indoor air and breath,
- (4) recent developments and applications of molecular imprinted polymer based sensors for various organics in water environments,

- (5) recent developments and applications of sensors for various inorganics (metals, oxyanions, halides, etc),
- (6) recent developments and applications of the electronic nose and tongue.

A summary table of the groups by matrix, type, chemicals and timeframe is provided in Table 3-2 emphasizing air and water as sample matrix, and showing a range of old, new and improved method types, range of chemicals/classes of target analytes, and various monitoring timeframes. This is followed (p 3-21) by more detailed descriptive material for each method within each group to the extent it was possible to extract it from the reference. In some cases, review or more general interest papers are included which are useful in understanding emerging technologies and potential applications. In moving from Group 1 to Group 6, the methods/technologies tend to proceed from currently in use, to will be ready in 2-3 years, to promising technologies that are well into the future (more than five years out).

Group 1 includes some attractive, amply validated methods for long-term sampling (4 to 12 weeks) of ambient indoor air for a range of VOCs. For example, the sampling tube method described by Uchiyama and Hasegawa is ready to use, and a hand-packed tube of carbotrap/carboxen material with a drying tube placed in front is used to collect the sample by pumping and the tubes are thermally desorbed directly onto GC-MS. A passive (diffusive) sampler method described by Mabilia et al., based on activated charcoal with solvent extraction and GC analysis would appear to be ideal for long-term indoor air use. The method might have potential for application to a wide range of VOCs for even longer time periods (up to 8 months). Other papers are included from the same group headed by Bertoni. A conventional PUF air sampling method described by Carlsson et al., for organophosphate ester flame retardants in indoor air is also

included with reported mean levels in schools, daycare and office buildings. The paper does not mention organophosphate pesticides, which are presumably amenable to this method.

Group 2 includes papers describing some new developments for the application of SPMDs as time-integrated passive samplers. Of particular interest are two papers describing their use for very long-term (2 years) sampling of outdoor air for PCBs which are considered prototypes for nonpolar analytes. One paper presents data showing good agreement between SPMD and HiVol PUF samplers at two sites with widely different mean ambient temperatures. The primary advantage of this approach is that it allows for long-term (2-24 months), unattended, time-integrated sampling, and low limits of detection. Also new developments on the use of low density polyethylene (LDPE) lay-flat tubing instead of lipid-filled SPMDs are described that show much potential, but the testing presented does not appear to be rigorous enough to support deployment at this time. Novel integrative passive samplers of this type for long-term monitoring of SVOCs in air have been described in the very recent literature (see reference 47). They consist of poly(dimethylsiloxane) (PDMS)-coated stir bars or silicone tubing, acting as a solid receiving medium, enclosed in a heat-sealed LDPE membrane. In addition, accumulated analytes are analyzed by thermo-desorption GC-MS to avoid the use of solvents and costly sample preparation and clean-up steps.

Group 3 includes three recent papers from one of the more active industrial hygiene based groups (ET Zellers et al.) working on acoustic wave sensing systems for indoor air applications to VOCs and SVOCs. One paper describes a promising approach to indoor air measurements using a high-speed analysis of complex indoor VOC mixtures by vacuum-outlet GC with air carrier gas and programmable retention. This would appear to be useful for a broad range of VOCs and SVOCs using a portable, in-home instrument with no gas supply

tanks. However, there is apparently not a prototype ready for deployment at this time.

Group 4 includes several recent papers on promising developments and applications of molecular imprinted polymer (MIP) sensors for a range of different analytes, viz., pesticides, herbicides, nerve gases, organophosphate flame retardants, and metal ions. MIPs are a very promising technology, but routine field use will probably have to wait until an instrument manufacturer starts producing the sensors. However, the potential for designing MIPs for detecting families of similar chemicals such as organophosphate pesticides and triazene herbicides is already evident. Similarly, group 5 includes several sensor/multisensor-based approaches for determination of inorganic analytes (metals, oxyanions, halides, etc) in aqueous environments, including soil pore water. Although such methods are attractive for possible field work, most, if not all, suffer from serious matrix effects that will require sample pretreatment. Group 6 includes several recent papers on developments and applications of electronic nose/tongue sensors to air, water and food samples with some attention given to VOCs and sensorial odor perception. However, the use of such devices for exposure monitoring could be limited by their inability to identify individual contaminants at low concentrations in complex matrices.

Groups 1-3 include methods that could possibly be adapted for quantitative, time-integrated studies of some target chemicals in indoor environments. Methods described in Groups 4-6 are generally not currently suitable for such indoor studies but might be useful in pilot studies aimed at screening and preclassifying samples for further study using other methods and approaches.

### 3.3 EMERGING TECHNOLOGY INCLUDING APPLICATIONS FROM OTHER FIELDS

#### 3.3.1 SPMDs as Passive Samplers

Membrane-based passive samplers such as the semi-permeable membrane devices

(SPMDs) seem to be a promising tool for time-integrated monitoring of hydrophobic pollutants in both water and air media. Despite earlier promising results and the numerous attractive qualities, i.e., their long-term stability, low cost, and ease of deployment, there are only limited published data pertaining to their use as passive sampling tools in air monitoring. It is recommended that the low density polyethylene usually used as membrane material be preextracted prior to use to remove impurities (shown to contain many PAHs). Recent studies present results from side-by-side comparison of SPMDs and conventional HiVol systems in the field. Excellent agreement was found between air concentrations (of PCBs as prototype persistent organic pollutants/POPs) calculated from the SPMDs and the active samplers suggesting the potential of these devices for time-integrated passive atmospheric sampling of gas-phase POPs. Furthermore, the use of SPMDs in indoor environments might be useful for shedding considerable light on the dynamics of POPs at the air-water interface. There are also recent studies (see for example reference 77) suggesting that there are no technical barriers to the use of performance reference compound (PRC) data to estimate site-specific sampling rates of POPs and improve the accuracy of sample concentration estimates while reducing the amount of calibration data required for the use of SPMDs and passive sampling devices (PSDs). However, SPMDs require rather labor-intensive extraction and clean-up procedures to prepare samples for analysis by conventional methods.

#### 3.3.2 Sensors as Real-time Devices

A means to produce sensors for any specific chemical or chemical class that requires quantitation would be ideal. Chemical sensors must fulfill two goals: 1) the development of a specific chemical recognition element that allows a molecule, or class of molecules, to be identified, and 2) a means of signal transduction in which the presence of the molecule causes a measurable change in a physical property of the material. Recent promising developments in the

area of chemical (both organic and inorganic) sensor research are using the technique of molecular imprinting to provide the desired chemical recognition element required, and chemical sensing using optical fibers and luminescence spectroscopy or acoustic wave detection. Their use for monitoring indoor pollutants remains a goal for the future, and the current view is that such sensor-based approaches generally can not yet replace laboratory analysis but are very useful to guide the sampling process, to delineate contaminated areas, or to preclassify samples. Although chemical sensor research has been more directed toward specific target analytes (such as might be needed in an occupational setting), recent development using double/multiple imprinting and the principles of supramolecular host-guest chemistry are permitting more flexibility in the design and fine tuning of layers sensitive to specific chemicals used for molecular recognition. For example, it seems reasonable that one could design a chemical sensor that is the equivalent of the biological receptor for dioxin in terms of its ability to screen for the presence of the broad class of dioxin-like compounds. Progress is also being made in linking sensor arrays to portable instruments such as the system under development by Zellers, et al. (reference 14) for high-speed analysis of complex indoor VOC mixtures by vacuum-outlet GC with air carrier gas and a dual-preconcentrator, a separation-column ensemble with tunable and programmable retention.

### 3.3.3 Electronic Nose/Tongue as Biomimetic Sample Quality Sensors

Gas sensor arrays, i.e., electronic noses or odor/smell sensors, have received far more study than their wet chemical counterparts, i.e., electronic tongues or taste sensors. Behind these somewhat misleading terms, one finds an array of bio-or chemical-sensors, the response pattern of which are analyzed with pattern recognition routines and/or chemometrical methods. These sensor combinations behave in a biomimetic way when they are used, e.g., for quality control

and/or classification of water, food, air, clinical samples, etc. The sensor array in these systems produces signals which are not necessarily specific for any particular species in the environment, in the water, etc., but are components of a signal pattern which can be related to certain features or qualities of the sample. These qualities can be determined by a computer trained to recognize the class of response patterns related to the sample environment under study. This is similar (biomimetic) to the way the human sense organs produce signal patterns to be qualitatively interpreted by the brain. Electronic nose and tongue techniques are normally used to give some qualitative answers about the sample under study and only in special cases are they used to estimate concentration of individual species in the sample. So in terms of drinking water, the electronic system provides a way to classify the water but not generally to determine if it is drinkable or undrinkable. These systems will most likely find applications in environmental monitoring. Several of the technologies and applications are not yet fully developed. Sensor drift, for example, is a problem that has to be solved if sensor arrays are to be implemented for routine monitoring purposes. It is anticipated that combinations of sensors based on different technologies may give even more useful information. Attention is also being given to metallo-porphyrins as a class of molecules for use as sensitive layers in these sensors. The important point to remember is that these systems often predict a quality of a sample but do not provide hard data in terms of composition and concentration.

### 3.3.4 Portable/Field-Ready Instruments from the Gray Literature

As indicated previously, the trend in instrumentation development in the gray literature is toward very portable instruments that are more suited for process control and site remediation than for scientific research. It appears that technological advances over the past decade have created a whole new set of tools to assess site clean-up and long-term monitoring following clean-up. Descriptions of

some of the better GC and MS portables found in the gray literature are included here and summarized in Table 2-3 (p 2-61). The portable GC manufactured by Photovac, Inc. uses a photoionization (PID) or electron capture detector (ECD), making it much more sensitive (and more suitable for environmental use) than instruments using thermal conductivity detectors (TCD) or standing acoustic wave (SAW) detectors. A new field portable, high speed GC/time-of-flight-MS (described on the web) is manufactured by Sygen Technology, Inc. [[www.sygen.com](http://www.sygen.com)]. A new gas chromatography system based on the use of a water electrolyzer as its only source of gases has also been developed (not shown in the descriptive tables, but see reference 117 for details). Other systems appropriate for organic analytes were not considered further since they had various problems associated with their use, i.e., the hand-held PID was mostly for non-specific gas detection, the photoacoustic IR had poor LOD, the FTIR generally required a long pathlength to achieve low LOD, odor meters have selectivity/analyte identification problems, and so on. Also references 118 and 119 are recent reviews describing new developments in gas chromatography and miniature mass analyzers including portable systems.

Unfortunately, none of these systems/methods clearly meet the objectives of this project for identifying methods/equipment that are either currently in use or will be validated and field-ready in 2 - 3 years nor do they meet the criteria that the collection and analytical methods be integrated or combined into a single method and which can be used with a minimum of evaluation for assessing time-integrated indoor exposures. As indicated earlier, these systems/methods are generally not designed for such purposes and would need to be adapted. However, some of the very portable instruments described in the gray literature have considerable promise for continuous, periodic (and possibly long -term) monitoring of indoor environments. Such real time, autonomous monitoring has some distinct advantages over conventional grab-sampling techniques.

However, field validation of such autonomous systems appears to be generally lacking. The portable MS system produced by Intelligent Ion, Inc. was clearly the most advanced, well documented, and best marketed portable instrument. Numerous publications about this portable MS system are available on the web site.

In addition to conventional literature searches, an attempt was made to go through the 2002 Pittcon vendors list to find methods that could be used (currently or in the near future) for the time-integrated determination of metals in air, dust, food, and water. The biggest obstacle to such trace-element determinations is the preparation required to put samples in a form amenable to analysis. Sample preparation, invariably the bottleneck for most trace metal determinations, would be difficult to complete in the field. This would make real-time on-site exposure measurements for these analytes and samples more difficult. Sample preparation would be especially critical for many of the analytical techniques described in the other papers reviewed. For example, electrochemical methods are vulnerable to matrix interferences which is a restriction on the utility of these measurements.

With this in mind, attention was given to gray-literature searches for techniques that would require minimal sample preparation and could readily make field measurements of the chemical classes of interest. One potentially useful technique is X-Ray Fluorescence (XRF). Several instrument manufacturers have portable systems that are available for immediate purchase and use. Niton is marketing a hand-held product for the determination of Pb in air filter samples [[www.niton.com/airfilt.html](http://www.niton.com/airfilt.html)]. An application note for this product can be found at: <http://www.niton.com/7702.pdf>. Dust wipe samples could be analyzed using a similar approach. Other manufacturers (Spectro, Cianflone, etc.) offer similar portable products that could probably be adapted to such an application. A description of Spectro's smallest XRF instrument can be found at [[www.spectro-ai.com/pages/e/p010501.html](http://www.spectro-ai.com/pages/e/p010501.html)] while Cianflone's

can be found at

[\[www.cianflone.com/model2501bt.html\]](http://www.cianflone.com/model2501bt.html).

Detection limits for XRF instruments are generally higher than those for other trace-element techniques (ICP-MS, GFAAS, etc.).

Since the technique is non-destructive, samples could be screened/analyzed in the field and then sent to a laboratory for further study.

Instruments are also currently available for time-integrated mercury vapor measurements in air. A description of a Tekran, Inc. mercury vapor analyzer is available at:

[\[http://216.36.224.163/2537/2537A.pdf\]](http://216.36.224.163/2537/2537A.pdf). This system does require a preconcentration step, the length of which varies with the level of Hg in air that you wish to measure. If airborne elemental Hg is of interest, this approach may be suitable.

TABLE 3-1. PARAMETERS FOR MAJOR SEARCHES

Keywords (* indicates truncation)	Databases	Language	Time Period
(organic chemicals/analysis or inorganic chemicals/analysis or environmental pollutants, noxae, and pesticides/analysis) and (time integrated or continuous sampling or continuous monitor* or time factor* or biosensing techniques) or (sensor* or biosensor* or microsensor* and air or soil or water or surface not blood or urine or biomarker* or biological marker*)	MEDLINE	no restriction	1966-present
time integrated or continuous sampling or continuous monitor* or sensor* or biosensor* or microsensor*	ScienceDirect (chemistry, engineering, and environmental sections), USPTO Patent Database	no restriction	1980's-present
electronic nose or electronic tongue	MEDLINE, NLM LOCATORplus, NTIS, ScienceDirect, LC MARC	no restriction	1980's-present
(real-time monitoring or realtime monitoring or spmd* or semipermeable membrane device*) and (indoor or sampling or analy* or measurement* or collection or determination or detection or identification) and (method* or technique*) and (air or water or soil or surface*) or (spmd or semipermeable membrane device*) and (continuous monitoring or time integrated)	MEDLINE, Environmental Bibliography, Enviroline, Water Resources Abstracts, Biosis, Food Science and Technology Abstracts, Pollution Abstracts, Aquatic Sciences and Fisheries Abstracts, Abstracts in New Technologies and Engineering, Conference Papers Index, Ei Compendex, NTIS	no restriction	1960's-present
(time integrated or attic dust or window* of exposure or badge*) and (monitoring or sampling or analy* or measurement or collection) or (automated monitoring or repetitive monitoring or long term monitoring or passive monitoring) and (time integrated or indoor or environmental or review* or technique* or pollutant* or device* or gated)	MEDLINE, Environmental Bibliography, Enviroline, Water Resources Abstracts, Biosis, Food Science and Technology Abstracts, Pollution Abstracts, Aquatic Sciences and Fisheries Abstracts, Abstracts in New Technologies and Engineering, Conference Papers Index, Ei Compendex, NTIS, EPA Catalog, LC MARC	no restriction	1960's-present
(long term monitoring or continuous monitoring or continuous sampling or repetitive sampling) or indoor and (sampling or collection or analy* or measurement*) and (air or water or soil* or surface*) or time integrated	Analytical Abstracts, Chemical Abstracts	no restriction	1960's-present

Keywords (* indicates truncation)	Databases	Language	Time Period
flame retardant* and indoor	MEDLINE, NTIS, Toxline, ScienceDirect, Environmental Sciences and Pollution Database, SciSearch	no restriction	1960's-present
lab-on-a-chip	Google, ScienceDirect, Ei Compendex, Environmental Sciences and Pollution Database, SciSearch, NTIS, Academic Search Elite, MasterFILE Premier	no restriction	1990's-present
time integrated or continuous monitoring or continuous sampling or long term monitoring	Dissertation Abstracts	no restriction	1980's-present
real time and PAH or PAHs or polycyclic aromatic hydrocarbon* or polynuclear aromatic hydrocarbons)	Google, SciSearch, Environmental Sciences and Pollution Database	no restriction	1990's-present
time integrated or continuous monitoring or continuous sampling or long term monitoring	GrayLIT Network	no restriction	1970's-present
(time integrated or real time or realtime or continuous) and monitoring or (long term monitoring and indoor or passive or active or sensor* or biosensor* or spmd* or semipermeable membrane*)	Occupational Safety and Health, Aerospace Database, Agricola, Current Biotechnology Abstracts, Energy SciTec, Engineering Materials Database, Geobase, INSPEC, International Pharmaceutical Abstracts	no restriction	1970's-present
3M organic vapor monitor*	Google, ScienceDirect, SciSearch, Environmental Sciences and Pollution Database	no restriction	1990's-present

TABLE 3-2. SUMMARY TABLE OF SOME METHOD PAPERS BY GROUP

Group 1. Conventional Time-integrated/Continuous/Real-time Methods

Matrix	Type	Chemicals	Time Frame
Air	Air Sampling (pump), carbotrap/carboxen	VOCs	Up to 4 weeks
Air	Passive sampler/diffusive device charcoal	Benzene/alkyl benzene	Continuous 4-12 weeks
Air	Passive(diffusive) sampler/charcoal	Benzene/Xylenes	Up to 8 months
Air	Passive(diffusive) sampler/carbopack	PAHs	2 months
Air	Passive(diffusive) sampler/Tenax	Acetone,benzene, alkyl benzene, alkanes	1-14 days
Air	Passive (diffusive) membrane/charcoal	Alkyl benzene, chloro-alkanes	8 hours
Air	Wet effluent diffusive	Alcohols/Acetone	Continuous up to 24 hours plus
Air	Conventional PUF air sampler	Flame retardant/alkyl phosphate	Approximately 12 hours
Water	On-line membrane extraction	Semivolatiles	Real time/HPLC
Water	Diffusive sampling based photo-acoustic cell	Benzene/toluene	Continuous

Group 2. Recent Developments and Applications of SPMDs

Matrix	Type	Chemicals	Time Frame
Air	Passive/SPMD	PCBs	2-24 months
Air	SPMD/HiVol PUF comparison	PCBs	2-24 months
Water	SPMD	Chrysene/DDT/SVOC	2-24 months
Water	SPMD	PAHs	14days
Water	SPMD	Pesticides/PCBs	Various
Water	SPMD	Hydrophobic	Various

Group 3. High-speed/Portable/Sensor Based Approaches to Ambient/Personal Monitoring of VOCs

Matrix	Type	Chemicals	Time Frame
Air	Portable GC instrument/air carrier gas	VOCs/SVOCs	Periodic/few days
Air and breath	Portable/preconcentrator/pump/SAW detector	VOCs	Continuous/5 min cycle/long-term potential
Air	Personal monitor/sorbent preconcentrator pump/SAW detector	VOCs	Periodic/few days

Group 4. Molecularly Imprinted Polymer (MIP) Based Sensors for Organics in Water

Matrix	Type	Chemicals	Time Frame
Water	MIP based sensor	Pesticides/OPs	Real-time with cycle
Water	MIP based sensor	Herbicides/atrazine family	Periodic/10 min cycle
Water	MIP based sensor	Nerve gases/related to OPs	Periodic/10 min cycle
Water	MIP based sensor/general interest	cAMP/related to OPs	Periodic/cyclic
Water Hexane	MIP based sensor/preconcentration	Divalent lead	Periodic/ISE analysis
—	MIP based extraction/preconcentration	OP flame retardant	---

Group 5. Sensors for Various Inorganics in Water

Matrix	Type	Chemicals	Time Frame
Water	Multisensor array/artificial neural network	Various ions, cation and anions	Real-time aqueous monitor
Water	Multisensor/thin film sensors	Metal ions/Divalent lead, cadmium, zinc, and Iron	Real-time aqueous monitor
Water	Sensor head/laser excitation with fluorescence emission	Heavy metals	Real-time approximately 30 minute cycle
Water	Various methods for real-time determination of trace metals/marine surface water	Trace metals	Various real-time
Water	Membrane potentiometric sensor based on crown ether	Lead	Periodic/ 40 second cycle
Water	Synchronous fluorescence/sensor	Hexavalent chromium	Instrument development/emerging work
Soil Columns	Tracer compound in soil column	Nitrate as tracer	Near real-time potential

Group 6. Recent Developments and Applications of Electronic Nose and Tongue (EN/ET)

Matrix	Type	Chemicals	Time Frame
Air	Electronic nose/porphyrin based	Volatile compounds	Real-time
Water	Electronic tongue/sensor array	Review/general	Real-time
Water	Electronic nose	Pesticides/pyrethroids	Periodic/real time potential
Water	Electronic nose	VOCs/wastewater	Continuous monitoring potential
Water	Electronic nose/multiple sensor	Cyanobacteria	Potential for long-term continuous monitoring
Urine Milk	Electronic nose/tongue/based on metalloporphyrins	Headspace Volatiles	Real-time

## Group 1

Authors	Shigehisa Uchiyama and Shuji Hasegawa		
Title	Investigation of a long-term sampling period for monitoring volatile organic compounds in ambient air		
Citation	<i>Environ. Sci. Technol.</i> 34:4656-4661 (2000)		
Matrix	air		
Method Type	air sampling tube		
Method Description Sample Collection Sample Preparation Analysis	Sampling tube (150 x 4 mm) packed with Carbotrap C (250 mg), Carbotrap B (120 mg), and Carboxen 1000 (200 mg). Magnesium perchlorate (2 g) drying tube used in front of sampling tube. Pump flow was 0.5 mL/min for 4-week period. Tubes were thermally desorbed onto GC-MS. 24 hour samples collected for comparison. Paper gives data to show good agreement between mean 24 hour samples and 4-week samples. Sampling pump and flow controller are off-the-shelf components. Styrene was low in 4-week samples because of ozonolysis.		
Monitoring Time Frame	Integrating, up to 4-week		
Method Performance Precision Bias	Precision: 1 to 5% for 21 of 26 VOCs. All < 9%. Bias: given with respect to 24 hour samples, < 9%.		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
26 VOCs:	not applicable	0.01 to 0.04 µg/m <sup>3</sup>	single laboratory
Other Chemicals:	most VOCs with -29°C < bp < +174°C		
Participant Burden	not applicable (mass flow controller + pump required)		
Field Burden	pumps could be left unattended in field		
Analytical Costs	\$100 to \$300 (GC-MS)		
Comments	***** Highly recommended. This method is ready to use with a sampling period of 4 weeks. This paper gives ample validation data. Tubes must be packed by hand, but all other components are readily available.		
Other References	None		

Authors	R. Mabilia, G. Bertoni, R. Tappa, A. Cecinato		
Title	Long-term assessment of benzene concentration in air by passive sampling: a suitable approach to evaluate the risk to human health		
Citation	<i>Analytical Letters</i> . 34(6): 903-912 (2001)		
Matrix	air		
Method Type	passive sampler		
Method Description Sample Collection Sample Preparation Analysis	Sampler is a glass tube with a diffusion device and activated charcoal. Sampler is placed in field and retrieved 4 to 12 weeks later. Charcoal is then extracted with solvent, and the solvent analyzed by GC. Data is presented showing agreement ( $\pm 6\%$ ) with BTX monitors (field-based GC system) for benzene, toluene, ethylbenzene, and xylenes for a 4 week exposure. Additional data indicates agreement for benzene over a 12 week exposure.		
Monitoring Time Frame	continuous, 4 to 12 weeks		
Method Performance Precision Bias	precision: $\sim 5\%$ bias: $\pm 6\%$ compared with field-based GC system.		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Target Chemicals:	not tested	not stated	
Other Chemicals:	probably useful for VOCs with bp > benzene		
Participant Burden	unknown		
Field Burden	low (deploy and retrieve passive device)		
Analytical Costs	\$100 to \$300 (GC-FID or GC-MS)		
Comments	Paper does not give a good description or diagram of sampling device. This sampling method might be applicable to a wide range of VOCs. If so, this would be ideal for long-term IAQ use. Authors have applied for a patent for sampling device.		
Other References	Assessment of a new passive device for the monitoring of benzene and other volatile aromatic compounds in the atmosphere. Bertoni, G., Tappa, R., Allegrini, I., <i>Annali di Chimica</i> . 90:249-263		

Authors	G. Bertoni, R. Tappa, A. Cecinato		
Title	The Internal Consistency of the 'Analyst' Diffusive Sampler - A Long-Term Field Test		
Citation	<i>Chromatographia</i> 54, 653 - 657 (2001)		
Matrix	air		
Method Type	passive (diffusive) sampler		
Method Description Sample Collection Sample Preparation Analysis	Sampler consists of a tube or vial, closed at one end. Charcoal sorbent is packed in a layer against the closed end, and held in place with a screen. Another screen covers the open end of the tube to control eddy currents. The sampler is placed on location in the field, then retrieved up to 8 months later. The charcoal is extracted with 1.5 mL benzyl alcohol. The extract is then analyzed by GC-FID.		
Monitoring Time Frame	up to 8 months		
Method Performance Precision Bias	duplicates within +/- 10% accuracy not tested		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
benzene		0.3 µg/sampler	not given
xylenes		0.03 µg/sampler	not given
Participant Burden	not applicable to personal monitoring		
Field Burden	low – no pumps needed		
Analytical Costs	\$50 -- \$200 (quick extraction, then GC-FID)		
Comments	presumably, a modification of this method would be applicable to a wider range of VOCs. This seems like the kind of cost-effective long-term sampling technique that this Task calls for.		
Other References	Bertoni, G.; Tappa, R; Allegrini, I; <i>Annali de Chimica</i> 2000, 90, 249		

Authors	G. Bertoni, R. Tappa, A. Cecinato		
Title	Environmental Monitoring of Semi-Volatile Polycyclic Aromatic Hydrocarbons by Means of Diffusive Sampling Devices and GC-MS Analysis		
Citation	<i>Chromatographia</i> 53, Suppl, S-312--S-316 (2001)		
Matrix	air		
Method Type	passive (diffusion) sampler		
Method Description Sample Collection Sample Preparation Analysis	Sampler consists of a glass tube, open on both ends, with a sorbent disk held in place in the middle of the tube between two screens. Sorbent was 400 mg Carbopack C. Samplers are exposed for 2 months, then extracted with 1.5 mL toluene. Extract is analyzed by GC-MS. Authors calculate an uptake rate for PAHs of 18.5 mL/min by comparison with co-located active samplers.		
Monitoring Time Frame	2 months		
Method Performance Precision Bias	spike recovery: 72 to 100% for naphthalene, phenanthrene, and fluoranthene; chrysene 59% (?). Accuracy ~ 10%.		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
PAHs:		~ 5 ng/m <sup>3</sup>	no data
Participant Burden	not applicable to personal monitoring		
Field Burden	low – no pumps needed		
Analytical Costs	\$200 – \$300 (quick extraction, then GC-MS)		
Comments	method needs a little work to expand scope to heavier PAHs. Note also that this method does not measure PAHs bound to particles.		
Other References	None		

Authors	Nicholas M. Bradshaw and James A. Ballantine		
Title	Confirming the Limitations of Diffusive Sampling Using Tenax TA During Long Term Monitoring of the Environment		
Citation	Environmental Technology, Vol. 16. pp 433-444 (1995)		
Matrix	Air		
Method Type	High sensitivity/cost/burden method		
Method Description	Target analytes diffuse at a known rate and are adsorbed onto Tenax TA.		
Sample Collection	None.		
Sample Preparation	Analytes are thermally desorbed onto a GC column where they are separated by		
Analysis	gas-liquid chromatography and detected using FID.		
Monitoring Time Frame	1 to 14 day intervals		
Method Performance			
Precision	Not determined		
Bias	Not determined		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Target Chemicals: Acetone Hexane Benzene Toluene m/p-Xylene Nonane Decane Undecane		Approx. 1 ng each on-cartridge (FID) <sup>1</sup>	F
Other Chemical:			
Participant Burden	Low		
Field Burden	Low		
Analytical Costs	Approx. \$300.00 per sample for mass spectrometry confirmation		
Comments	Approach should be considered for the determination of volatile organic compounds in ambient air over long sampling periods. <sup>1</sup> Method quantitation limits will be based on diffusion rates of individual compounds and exposure times.		
Other References	None		

Authors	Mannino, D.M., J. Schreiber, K. Aldous, D. Ashley, R. Moolenaar, D. Almaguer		
Title	Human exposure to volatile organic compounds: a comparison of organic vapor monitoring badge levels with blood levels		
Citation	Int Arch Occup Environ Health (1995) 67:59-64		
Matrix	Air		
Method Type	High sensitivity/cost/burden method		
Method Description			
Sample Collection	Target analytes diffuse through a permeable membrane at a known rate and are adsorbed onto a charcoal pad.		
Sample Preparation Analysis	Analytes are extracted from the charcoal pad with carbon disulfide. Extraction solvent is analyzed by GC/FID or GC/ECD		
Monitoring Time Frame	8 hours		
Method Performance			
Precision	Not addressed in this study. However, organic vapor monitors are used routinely to determine workplace exposures. Precision data is available in the literature.		
Bias	Not determined by direct comparison to known reference standards. There was a high correlation between air concentrations of gasoline components determined by the organic vapor monitor and levels found in blood assays.		
Applicable Chemicals	Method QL		Level of Validation <sup>1</sup>
	Personal	Microenvironmental or ambient	
Target Chemicals:			
Toluene	8 µg/m <sup>3</sup>		F
Ethyl benzene	8 µg/m <sup>3</sup>		F
m/p-Xylene	8 µg/m <sup>3</sup>		F
1,1,1-Trichloroethane	2 µg/m <sup>3</sup>		F
Tetrachloroethane	2 µg/m <sup>3</sup>		F
Participant Burden	Low		
Field Burden	Low		
Analytical Costs	Approx. \$100.00 per sample		
Comments	The use of organic vapor monitors is not a novel approach. These devices have been used extensively to determine personal exposures. <sup>1</sup> Not validated in this particular study. Other validations have been performed.		
Other References	None		

Authors	Jana Peskova, Petr Parizek, Zbynek Vecera
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Title	Wet effluent diffusion denuder technique and determination of volatile organic compounds in air		
Citation	<i>Journal of Chromatography A</i> , 2001; 918: 153-158		
Matrix	air		
Method Type	sampler/concentrator device		
Method Description Sample Collection Sample Preparation Analysis	A thin film of water traverses the inside of a glass tube (40 x 1.1 cm) at a flow rate of 0.5 mL/min. The air being sampled is pulled through the tube at a constant flow rate. Alcohols and ketones are thereby stripped from the air and concentrated in the water stream. The analyst collects 5 µL of water from the tube exit, and analyzes by GC-FID. The tube operates continuously. This setup could easily be automated. The method is limited to analytes with high water solubility.		
Monitoring Time Frame	probably up to 24 hours or more; continuous sampling		
Method Performance Precision Bias	collection efficiencies reported: methanol 98%, ethanol 83%, 2-propanol 73%, ... , acetone 31%, MEK 30% @ 20 °C		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Tested analytes		0.24 µ (GC-FID)	needs work
		1 ng/L (GC-MS)	not given
Potential analytes	method could apply to alcohols and other water soluble analytes		
Participant Burden	see comments		
Field Burden	see comments		
Analytical Costs	sampling~ \$10/day; GCMS analysis~ \$100 to \$200/sample		
Comments	This method was intended for industrial hygiene use, and requires operator intervention in order to take a sample. Although this method could be automated, the device lacks ruggedness, and the method is only applicable for alcohols and ketones.		
Other References	None		

Authors	Håkan Carlsson, Ulrika Nilsson, Gerhard Becker, and Conny Östman		
Title	Organophosphate ester flame retardants and plasticizers in the indoor environment: analytical methodology and occurrence		
Citation	<i>Environ. Sci. Technol.</i> 31:2931-2936 (1997)		
Matrix	Air		
Method Type	conventional PUF air sampler/GC-NPD, GC-AED or GC-MS		
Method Description Sample Collection Sample Preparation Analysis	Indoor air is sampled at 3 and 17 L/min for 700 minutes using sampling tubes consisting of borosilicate fiber filters with cellulose backing pads and PUF plugs. Battery-powered pumps used. Filters and PUF extracted with dichloromethane by sonication, concentrated and analyzed by GC-NPD, GC-AED (atomic emission) and GC-MS. Authors report mean levels of alkyl phosphates in schools, daycare, and office building as 1 to 250 ng/m <sup>3</sup>		
Monitoring Time Frame	700 minutes (~12 hours)		
Method Performance Precision Bias	precision ~ 10% (when comparing co-located samplers) recoveries from spiked filters/PUF: >95% accuracy not reported		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Tri(2-chloroethyl)phosphate	not given	0.5 ng/m <sup>3</sup>	field study
other alkyl phosphates	not given	0.5 ng/m <sup>3</sup>	field study
Participant Burden	moderate (loud pump in home, two visits in the same day)		
Field Burden	moderate (12 hour sample requires field staff to be diligent)		
Analytical Costs	\$200 to \$400 (GC-AED or GC-MS)		
Comments	Conventional sampling and analysis techniques used. This is an excellent paper, both for the detailed description of the analysis, and for important data on this class of compounds. Paper does not mention phosphate pesticides, which are presumably amenable to this method.		
Other References	<i>Plastics Additives, Stabilizers, Processing Aids, Plasticizers, Fillers, Reinforcements, Colorants for Thermoplastics, 4<sup>th</sup> ed.</i> , Gächter, R. Müller, H., Eds.; Hanser/Gardner Publications, Inc., Cincinnati, OH, 1993.		

Authors	Guo, X. and S. Mitra		
Title	On-line Membrane Extraction Liquid Chromatography for Monitoring Semi-Volatile Organics in Aqueous Matrices		
Citation	Journal of Chromatography A		
Matrix	Water		
Method Type	High sensitivity/cost/burden		
Method Description			
Sample Collection	Not addressed. Semi-volatile organic compounds (SVOCs) are extracted from water on-line. Parameters associated with the collection of water samples for exposure monitoring that may affect extraction efficiency such as pH and temperature have not been studied.		
Sample Preparation	Extraction method is optimized for removal efficiencies. Parameters studied include flow rate, flow direction and extraction solvent.		
Analysis	Extraction solvent flow is sampled periodically using a six-port liquid sample valve. Aliquots are analyzed by HPLC.		
Monitoring Time Frame	Real-time		
Method Performance			
Precision	RSD less than 1 percent at nominal stream concentration of 1 ppm.		
Bias	Not determined. Linear relationship between SVOC concentration in water and detector response was assessed.		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
SVOCs		Nominal 10 µg/L	None
Participant Burden	High (if sample analysis is performed in the field)		
Field Burden	High		
Analytical Costs	Not determined.		
Comments	Applicability of method to concentration of SVOCs found in typical drinking water is questionable.		
Other References	None		

Authors	A. Mohacsi, Z. Bozoki, R. Niessner		
Title	Direct diffusion sampling-based photo acoustic cell for in situ and on-line monitoring of benzene and toluene concentrations in water		
Citation	<i>Sensors and Actuators B</i> 79:127-131 (2001)		
Matrix	water		
Method Type	sensor, photoacoustic		
Method Description Sample Collection Sample Preparation Analysis	R&D of photoacoustic (PA) cell intended for remote monitoring benzene, toluene and xylene in ground water. Benzene in water diffuses across PTFE membrane into air-filled PA cell. Diode laser (1 mW, 1668 nm) pulsed at 3300 Hz. Note: water vapor in PA cell also absorbs near 1668 nm, causing high background and poor sensitivity. Cell tested at 1 - 5 mg/L concentration level in lab. Sensitivity must be improved by a factor of >1000 before it is suitable for the stated purpose.		
Monitoring Time Frame	continuous		
Method Performance Precision Bias	not given		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
benzene	not applicable	1.5 mg/L	none
toluene	not applicable	1.5 mg/L	none
Participant Burden	not applicable		
Field Burden	requires installation		
Analytical Costs	unknown. Sensor probably \$5k to 20k; \$0 marginal cost per sample.		
Comments	It is unlikely that this cell design will ever meet the desired sensitivity (< 1 µg/L for potable water).		
Other References	None		

Group 2

Authors	Wendy A. Ockenden, Harry F. Prest, Gareth O. Thomas, Andrew J. Sweetman, and Kevin C. Jones		
Title	Passive air sampling of PCBs: field calculation of atmospheric sampling rates by triolene-containing semipermeable membrane devices		
Citation	Environ. Sci Technol. 1998, 32: 1538-1543		
Matrix	Air		
Method Type	SPMD passive sampler / GC-MS		
Method Description Sample Collection Sample Preparation Analysis	<p>Passive sampler (SPMD) deployed 2-4 months Extract with hexane, cleanup on silica gel, followed by GPC, followed by second silica gel fractionation. GC-MS determination.</p> <p>This paper gives sampling rates (diffusion of PCBs -&gt; SPMD) for 43 PCB congeners at two temperature ranges, and shows that air concentrations calculated from SPMDs closely matches concentrations measured by conventional PUF Hi-Vol samplers.</p>		
Monitoring Time Frame	2-24 months, time-integrating, unattended.		
Method Performance Precision Bias	<p>Accuracy: ~ ±50% agreement with PUF sampler Precision: ~ 20% from duplicate SPMDs</p>		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Tested analytes:		PCBs (43 congeners) < 0.1 pg/m <sup>3</sup>	single field test
Potential Analytes:	nonpolar SVOCs		none
Participant Burden	not applicable		
Field Burden	not applicable		
Analytical Costs	probably ~ \$300 - 600		
Comments	<p>The primary advantage to this method is that it allows for long-term (2-24 mo.) unattended time-integrated sampling, and low limits of detection. This method is ready to use (PCBs only). Cleanup of SPMD extracts is labor-intensive.</p> <p>Interesting note:</p> <ul style="list-style-type: none"> <li>• in air, SPMD sampling rate increases with decreasing temp</li> <li>• in water, SPMD sampling rate decreases with decreasing temp</li> </ul>		
Other References	None		

Authors	Wendy A. Ockenden, Andrew J. Sweetman, Harry F. Prest, Eiliv Steinnes, and Kevin C. Jones		
Title	Toward an understanding of the global atmospheric distribution of persistent organic pollutants: the use of semipermeable membrane devices as time-integrated passive samplers		
Citation	<i>Environ. Sci. Technol.</i> , 1998, 32: 2795-2803		
Matrix	Air		
Method Type	SPME (time-integrated passive samplers)		
Method Description Sample Collection Sample Preparation Analysis	<p>SPMD (semipermeable membrane device) is hung in screened box outdoors for <math>\geq 2</math> mo. then analyzed by soaking in hexane 2 x 24 hr. Extracts concentrated and analyzed by GC/MS and GC/ECD.</p> <p>USGS SPMDs were deployed for 2 years at 11 locations in western Europe at varying latitudes from north Norway to south UK. SPMDs were then analyzed for PCBs. Air concentrations were calculated from diffusion rates previously reported by this group (see ref. at bottom of this review sheet). Authors provide data indicating that these rates are applicable to a wide range of climate (temperature). Data is presented showing good agreement between SPMD and HiVol PUF samplers at 2 sites with widely different mean temperatures.</p>		
Monitoring Time Frame	2 - 24 months; time-integrated passive sampler		
Method Performance Precision Bias	precision ~ 25% (duplicate SPMEs) accuracy ~ 25% (compared with HiVol PUF)		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental	
Tested analytes		PCBs (43 congeners) QL < 1 pg/m <sup>3</sup>	field tested
Potential analytes	nonpolar SVOCs		not tested
Participant Burden	not applicable		
Field Burden	low		
Analytical Costs	about \$300 to \$600 per sample		
Comments	<p>This is a good method for PCBs in outdoor air when a low QL is needed, and a very long sampling time (2 years) can be tolerated.</p> <p>SPMDs can probably be used for a wide range on non-polar analytes, although the diffusion rates must first be determined for each analyte. Reference given below describes how rates were determined for PCBs.</p>		
Other References	<u>Major ref.</u> : Ockenden, W. A.; Prest, H. F.; Thomas, G.O.; Sweetman, A.; Jones, K. C. <i>Environ. Sci. Technol.</i> 1998, 32, 1538-1543 (we have this).		

Authors	Branislav Vrana, Albrecht Paschke, Peter Popp, and Gerrit Schuurman		
Title	Use of semipermeable membrane devices		
Citation	<i>Environ Sci. &amp; Pollut Res.</i> , 2001; 8(1): 27-34		
Matrix	water		
Method Type	integrating, passive sampler		
Method Description	SPMD consists of a flat polyethylene tube containing 1 mL of triolene (C <sub>57</sub> H <sub>104</sub> O <sub>6</sub> ). PE tube is 2.54 x 91.4 cm, 75-90 um wall thickness. Tube was placed horizontally in water, tethered to stream bed for 43 days. Tube is analyzed by soaking in hexane 24 hr x 3. Extracts are combined and concentrated. A portion is blown to dryness and reconstituted in acetonitrile for HPLC-Flourescence. The other portion is concentrated to 1 mL and analyzed by GC-ECD. Results are reported as ng/SPMD. A method is cited and used to converting/SPMD to ng/L (aq), although the accuracy of these calculations is uncertain; for example, there is no term in any of these calculations for temperature.		
Sample Collection			
Sample Preparation			
Analysis			
Monitoring Time Frame	2 to 24 months, integrating		
Method Performance	precision (duplicate SPMD): 24%		
Precision	Bias: unknown (measures "bioavailable" concentration)		
Bias			
Applicable Chemicals	Method QL		Level of Validation
	50 ng/SPMD chrysene	0.4 ng/L chrysene	needs work
Tested analytes	3 ng/SPMD DDT	10 pg/L DDT	
Potential analytes	nonpolar SVOCs		see other papers
Participant Burden	not applicable		
Field Burden	low		
Analytical Costs	probably ~ \$300 - 600		
Comments	Very low MQL. Excellent method for integrated time monitoring of a stream, especially over a long time period (here, 43 days). However, calculating water concentrations from SPMD results involves several approximations and assumptions.		
Other References	Petty, J. D.; Huckins, J. N.; Zajicek, J. L. Application of semipermeable membrane devices (SPMD) as passive air samplers. <i>Chemosphere</i> , 1993; 27: 1609-1624		

Authors	Crunkilton, R.L., W.M. DeVita		
Title	Determination of Aqueous Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in an Urban Stream		
Citation	Chemosphere, Vol. 35, No. 7, pp. 1447-1463, 1997		
Matrix	Water		
Method Type	High sensitivity/cost/burden		
Method Description			
Sample Collection	A lipid filled semipermeable membrane device (SPMD) is exposed to a continuous water stream. PAHs below a certain molecular size diffuse through a low density polyethylene tube and concentrate in the neutral lipid triolein.		
Sample Preparation	SPMDs are returned to the lab and cleaned with DI water, acetone, and hexane prior to dialysis. Sample are then dialyzed for 2 hours with hexane. The dialysates are concentrated to 1 mL by Kuderna-Danish under nitrogen. The lipid is removed from the concentrated dialysate by gel permeation chromatography.		
Analysis	Final volumes are analyzed by gas chromatography/ion trap mass spectrometry.		
Monitoring Time Frame	14 days		
Method Performance			
Precision	Replicate measurements were made, but not reported		
Bias	Estimates of concentrations compare favorably with standard techniques.		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
PAHs (below 1.0 nm)		14 day average reported at nominal 0.01 µg/L for most PAHs	
Participant Burden	High		
Field Burden	High		
Analytical Costs	Not determined. Expected to be high due to sample recovery and analysis costs (GC/MS)		
Comments	Time-integrated average measurement. Based on concentrations of environmental contaminants expected in exposure monitoring tasks, field deployment could require weeks of exposure to collect enough sample to satisfy instrumental detection limits.		
Other References	None		

Authors	Chris S. Hofelt and Damian Shea		
Title	Accumulation of Organochlorine pesticides and PCBs by semipermeable membrane devices and <i>Mytilus edulis</i> in New Bedford harbor		
Citation	<i>Environ. Sci. Technol.</i> <b>31</b> : (1) 154-159 (reprinted in dissertation as chapter 1)		
Matrix	Water		
Method Type	SPMD passive sampler		
Method Description Sample Collection Sample Preparation Analysis	<p>Using SPMDs with greater surface area and thinner LDPE walls, SPMD reaches equilibrium with the surrounding water in &lt; 30 days for most compounds. The resulting data show better agreement with concentrations measured in mussels. This method avoids the problems with traditional SPMD stemming from the assumption of linear uptake of analytes over the sampling period.</p> <p>Standard SPMD: 2.54 x 91.4 cm, 75-90 um wall thickness. Thin SPMD (here): 5 x 90 cm, 25 um wall thickness</p>		
Monitoring Time Frame	time-integrating		
Method Performance Precision Bias	<p>Correlation with levels found in mussels:</p> <p>pesticides: <math>r^2 = 0.80</math> PCBs: <math>r^2 = 0.90</math></p>		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Pesticides/PCBs	not applicable	0.1 mg/Kg in lipid	not given
Potential Analytes:	not applicable	Other nonpolar semivolatile organics	
Participant Burden	not applicable		
Field Burden	low (place/retrieve SPMD in field)		
Analytical Costs	\$300 - \$600 (extensive cleanup procedure)		
Comments	<p>This was reproduced as chapter 2 in Hofelt's dissertation (NCSU 1998). This is a useful alteration of the standard SPMD method (see reference below). It makes sense to let the SPMD reach equilibrium with respect to aqueous concentrations, and thereby eliminate one (of many) source of errors in this technique.</p>		
Other References	<p>J. N. Huckins, M. W. Tubergen, G. K. Manuweera. Semipermeable membrane devices containing model lipid: a new approach to monitoring the bioavailability of lipophilic contaminants and estimating their bioconcentration potential. <i>Chemosphere</i> <b>20</b>: 533-552 (1990). [original pub. on SPMD]</p>		

Authors	Christopher Scott Hofelt	
Title	Use of artificial substrates to monitor organic contaminants in the aquatic environment.	
Citation	Dissertation, North Carolina State University Department of Toxicology, Raleigh 1998	
Matrix	Water	
Method Type	SPMD passive sampler	
Method Description Sample Collection Sample Preparation Analysis	<p>Chapter 3: Measurement of sampling rates of SPMDs and LDPE strips. They suspend strips in jars of water with triolene (spiked with analytes) floating on top. Although the rates they calculate are suspect (two adjustment factors), LDPE strips appear to work as well as SPMDs.</p> <p>Chapter 4. Field test of LDPE strips in streams, alongside SPMDs. They report levels found in LDPE strips against levels found in fish and sediment, but not in SPMDs. Calculations are fuzzy, and hard data is thin in this work, but LDPE strips (without lipids) are worth looking into.</p>	
Monitoring Time Frame	time-integrating	
Method Performance Precision Bias	<p>Precision: factor of 2 at best</p> <p>Bias: yes, probably greater than factor of 2.</p>	
Applicable Chemicals	Method QL	Level of Validation
DDT, DDE...	QL (LDPE) ~ QL (SPMD) = 0.01 ng/L in water	
Potential Analytes:	hydrophobic molecules not much larger than pyrene	
Participant Burden	not applicable	
Field Burden	low (deploy and retrieve)	
Analytical Costs	~ \$ 200 - 400 (GC-ECD). LDPE cheaper than SPMD – less effort in cleanup	
Comments	<p>The use of strips of LDPE lay-flat tubing instead of lipid-filed SPMDs has much potential, but the testing presented here is not rigorous enough to support deployment. In this work, the LDPE strips are presumed to have reached equilibrium with the water. With SPMDs, the opposite is presumed. LDPE is presented here as a screening method, and as a substitute for catching a fish for analysis.</p>	
Other References	<p>J. N. Huckins, M. W. Tubergen, G. K. Manuweera. Semipermeable membrane devices containing model lipid: a new approach to monitoring the bioavailability of lipophilic contaminants and estimating their bioconcentration potential. <i>Chemosphere</i> <b>20</b>: 533-552 (1990). [original pub. on SPMD]</p>	

## Group 3

Authors	Andrew J. Grall, Edward T. Zellers, and Richard D. Sacks		
Title	High-speed analysis of complex indoor VOC mixtures by vacuum-outlet GC with air carrier gas and programable retention		
Citation	Environ. Sci. Technol., 2001; 35: 163-169		
Matrix	air / VOCs		
Method Type	portable instrument		
Method Description	Paper describes on-going development towards a portable (field) GC system for determination of 42 VOCs and SVOCs in air at indoor air concentrations. System consists of two short GC columns (4.5 m DB-1, and 7.5 m trifluoropropyl methyl) joined with a variable pressure junction. Inlet is at atmospheric pressure. Detector end of column is connected to vacuum pump. SAW array detector is promised for eventual field use, but is not discussed in this paper. Sample is collected on sorbent beds, then thermally-desorbed onto column. Bulk of paper discusses optimization of separations through pressure programming of the column junction. No working prototype is discussed.		
Sample Collection			
Sample Preparation			
Analysis			
Monitoring Time Frame	periodic, 30% duty cycle, could perhaps operate for a few days		
Method Performance	Not Tested		
Precision			
Bias			
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Tested analytes		not given	none
Potential analytes	Potential for use for a broad range of VOCs and SVOCs		
Participant Burden	instrument in home		
Field Burden	portable instrument - no tanks		
Analytical Costs	about \$20/24 hour sample		
Comments	This is promising for indoor air VOCs. However, the authors do not have a prototype as of this paper.  Look for more recently published reports from this group		
Other References	Refer to papers on SAW: Park, J.; Groves, W. A.; Zellers, E. T. <u>Anal Chem</u> <b>71</b> , 3877		

Authors	William A. Groves and Edward T. Zellers		
Title	Analysis of solvent vapors in breath and ambient air with a surface acoustic wave sensor array		
Citation	<i>Ann Occup Hyg.</i> , 2001; 45(8): 609-623		
Matrix	air, breath		
Method Type	portable monitor, 0.6 to 37 mg/m <sup>3</sup> for VOCs		
Method Description Sample Collection Sample Preparation Analysis	<p>Prototype monitor evaluated. Uses internal thermally-desorbed preconcentrator, pump, and four acoustic wave sensors. Sensor frequency output must be acquired in real time by external computer.</p> <p>Unit distinguishes between 16 VOCs and simple mixtures by the relative response of the four sensors using principal components regression or neural network software.</p>		
Monitoring Time Frame	potentially long term (months?); continuous (5 min cycle)		
Method Performance Precision Bias	precision ~ 10% bias - not given		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Tested analytes:	16 VOCs ~ 0.6 to 37 mg/m <sup>3</sup>	16 VOCs ~ 0.6 to 37 mg/m <sup>3</sup>	none
Potential analytes	Potentially applicable to all VOCs		
Participant Burden	not applicable		
Field Burden	not applicable		
Analytical Costs	probably \$20 for 24 hour sample		
Comments	This prototype is not ready for deployment — see later papers from this group		
Other References	None		

Authors	Jeongim Park, Guo-Zhen Zhang, Edward T. Zellers		
Title	Personal monitoring instrument for the selective measurement of multiple organic vapors		
Citation	AIHAJ, 2000; 61: 192-204		
Matrix	Air		
Method Type	Personal Monitor		
Method Description	Development and testing of a small, personal monitor for occupational exposure to 16 VOCs. Monitor uses polymer sorbent preconcentrator, pump, and surface-acoustic-wave (SAW) detector. Monitor operates on a 5.5 minute cycle: sampling, thermal desorption/analysis, then recycling. Monitor stores raw data which is later uploaded to computer for analysis. Authors present results of lab testing of six SAW chips, each coated with a different polymer. By analyzing desorption curves and varying response of solvents on different chips, authors are able to distinguish among 16 individual VOCs, and several binary and ternary mixtures. LODs are mostly ~ 0.1 x TLV or higher.		
Sample Collection			
Sample Preparation			
Analysis			
Monitoring Time Frame	periodic, 30% duty cycle, could perhaps operate for a few days		
Method Performance	data given for recognition rate and precision at ~ 10 to 300 ppm		
Precision	selectivity given as recognition matrix		
Bias			
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Tested analytes:	16 VOCs ~ 10 ppm		preliminary
Potential analytes;	Potentially applicable to all VOCs		
Participant Burden	low		
Field Burden	low		
Analytical Costs	about \$20/24 hour sample		
Comments	Monitor not useful at concentrations below 0.1 x TLV Paper gives good discussion of SAW calibration		
Other References	None		

Group 4

Authors	Jenkins, A.L., R. Yin, and J.L. Jenson		
Title	Molecularly Imprinted Polymer Sensors for Pesticide and Insecticide Detection in Water		
Citation	Analyst. The Royal Society of Chemistry 2001.		
Matrix	Water		
Method Type	High sensitivity/cost/burden		
Method Description			
Sample Collection	Sample collection not addressed. For exposure monitoring, it is assumed that water could be collected directly from the tap and shipped to the laboratory for analysis.		
Sample Preparation	Preparation of real-world samples not addressed. Water samples generated in the laboratory were adjusted to pH = 10.5 with sodium hydroxide and analyzed.		
Analysis	A fiber optic probe coated with a 200 µm film of molecularly imprinted polymer (MIP) is exposed to the water sample for 12 to 15 minutes. The MIP is excited to a wavelength of 465.8 nm with an argon ion laser for detection.		
Monitoring Time Frame	Snap-shot		
Method Performance			
Precision	Not determined.		
Bias	Not determined. Linear relationship between pesticide concentration in water (nominal 5 ppt to 100 ppm) and detector response was assessed.		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Pesticide		Nominal 5 ppt	None
Participant Burden	Low		
Field Burden	Low		
Analytical Costs	Not determined.		
Comments	Method is in early stages of development. No method validation performed. Future work to involve miniaturization of detector, which may lead to a portable monitor for field use.		
Other References	None		

Authors	T. A. Sergeyeva, S. A. Piletsky, A. A. Brovko, E. A. Slinchenko, L. M. Sergeeva, A. V. El'skaya	
Title	Selective recognition of atrazine by molecularly imprinted polymer membranes. Development of conductometric sensor for herbicides detection	
Citation	<i>Analytica Chimica Acta</i> . 1999, 392: 105-111	
Matrix	water	
Method Type	electrochemical sensor / MIP	
Method Description Sample Collection Sample Preparation Analysis	<p>Grab sample, adjust pH to 7.5, dip sensor in sample, read in 6-10 minutes. Could possibly be used as a continuous monitor if water stream is pH <math>\geq</math> 6.</p> <p>Molecular imprinted polymer (MIP) membrane must be prepared in lab by skilled personnel. This paper gives sufficient information for MIP production. Low-frequency waveform generator applies 60 mV across membrane; conductivity is measured with nanovolt meter across a resistor connected from one electrode to ground. This equipment could be miniaturized, but at substantial cost.</p>	
Monitoring Time Frame	periodic (10 min) / possibly continuous	
Method Performance Precision Bias	<p>Accuracy: not tested</p> <p>Precision: not tested</p> <p>Selectivity: <math>\geq</math> 7x compared with simazine, triazine, prometryn</p>	
Applicable Chemicals	Method QL	Level of Validation
Tested analytes	atrazine: 5 nM ~ 1 ng/mL	laboratory calibration
Potential analytes	extensive development required to make applicable to other analytes	
Participant Burden	not applicable	
Field Burden	low (grab sample) / possible use as a portable instrument	
Analytical Costs	unknown (cost of membrane production/no. of samples over lifetime) If commercialized could be \$5/sample.	
Comments	<p>MIPs are a very promising technology. However, routine field use will probably have to wait until an instrument manufacturer starts producing the sensors. A sensor like this is ideally suited to agricultural applications where the analyst already knows that atrazine is in use. The use of a MIP in a conductivity cell could probably be extended to other polar pesticides such as 2,4-D or glyphosate.</p> <p>This paper gives an excellent treatment of MIP production and "tuning." Discusses use of oligourethane acrylate to make MIP flexible.</p>	
Other References	None	

Authors	Bradley A. Arnold, Alex C. Euler, Amanda L. Jenkins, O. Manuel Uy, and George M. Murray		
Title	Progress in the development of molecularly imprinted polymer sensors		
Citation	<i>Johns Hopkins APL Technical Digest</i> , 1999, 20(2): 190-197		
Matrix	Water		
Method Type	MIP/Fiber Optic Luminescence		
Method Description Sample Collection Sample Preparation Analysis	Nerve agent (soman) sensor described, but may be applicable to phosphate pesticides. MIP is created by complexing Eu <sup>3+</sup> with phosphate analyte, then deposited on end of optical fiber in divinyl benzene / styrene copolymer. Argon laser/monochromator-CCD detector used to stimulate and detect luminescence. At 1000 ppm level, phosphate pesticides are spectrally resolved from nerve agent. This method should be optimized for pesticides before deployment.		
Monitoring Time Frame	grab sample; dip sensor, read in 6 minutes		
Method Performance Precision Bias	Accuracy not given. Bias stated in terms of selectivity for nerve agent.		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Tested analytes:		soman: 0.7 ppb	not given
Potential analytes:	possibly OP pesticides		
Participant Burden	not applicable		
Field Burden	low if modified for portability, high if table-top laser used		
Analytical Costs	probably < \$5/sample if optimized for field use		
Comments	<p>Like all MIP methods, this would require the fabrication and testing of specific MIPs for our analytes. However, this method, using Eu<sup>3+</sup> as a chromaphor that complexes with the phosphonate ion, is already geared towards phosphate pesticides. Ar laser could be replaced with a blue LED for better portability.</p> <p>Paper mentions previous work in which authors developed a MIP method for lead in water. See reference below.</p>		
Other References	Murray, G. M., Jenkins, A. L., Bzhelyansky, A., and Uy, O. M., "Molecularly imprinted polymers for the selective sequestering and sensing of ions, <i>Johns Hopkins APL Tech. Dig.</i> , 1997, 18(4): 464-472.		

Authors	Petra Turkewitsch, Barbara Wandelt, Graham D. Darling, and William S. Powell		
Title	Fluorescent functional recognition sites through molecular imprinting. A polymer-based fluorescent chemosensor for aqueous cAMP		
Citation	<i>Anal. Chem.</i> 1998, 70: 2025-2030		
Matrix	water		
Method Type	unfinished; MIP		
Method Description	<p>Paper reports fabrication of a molecular imprinted polymer (MIP) for cyclic adenosine monophosphate (cAMP). A dye molecule (with an olefin chain) is incorporated into the polymer while bound to cAMP. After polymerization and rinsing, the MIP contains 'imprinted' sites containing the dye as a functional unit. 150 mg of the finished granular MIP is incubated with an aqueous solution of cAMP. The MIP granules are analyzed by fluorescence as an aqueous suspension in a quartz cell. As it turns out, cAMP quenches the fluorescence of the dye rather than shifting or enhancing the band as the authors expected. By measuring the degree of quenching, [cAMP] can be determined in the range 10-100 nM.</p> <p>Interesting work, but useful to us only as a starting point for designing MIPs.</p>		
Sample Collection			
Sample Preparation			
Analysis			
Monitoring Time Frame	grab sample		
Method Performance	not applicable (method development not complete)		
Precision			
Bias			
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Tested analytes:		cAMP 0.1 $\mu$ M	incomplete
Potential analytes:	requires extensive development to extend to other analytes		
Participant Burden	not applicable		
Field Burden	not applicable		
Analytical Costs	not known		
Comments	<p>General interest paper only.</p> <p>“Until recently, organic solvents have been used exclusively as the media for studies on the binding of ligands to MIPs.” ... “substitution of water for organic solvents dramatically alters the relative importance of polar and hydrophobic interactions”</p>		
Other References	None		

Authors	G.M. Murray, et al.		
Title	Molecularly Imprinted Polymers for the Selective Sequestering and Sensing of Ions		
Citation	<i>Johns Hopkins Apl. Technical Digest</i> , 1997, <b>18(4)</b> , 464-472		
Matrix	Various: seawater, organic solvents.		
Method Type	Lower sensitivity; Potential for analysis in field.		
Method Description Sample Collection Sample Preparation	Several ion exchange materials were used to preconcentrate Pb in seawater prior to analysis with fabricated ion selective electrode (ISE). Calibration standards for determination of Pb with fabricated optical sensor prepared in hexane.		
Analysis	Paper described potential uses of imprinted polymers. For example, an ISE based on vinylbenzoic acid for Pb <sup>2+</sup> determination in seawater, an imprinted optical sensor for Pb <sup>2+</sup> determination in hexane standards, and an imprinted polymer detector for the hydrolysis byproducts of nerve agents.		
Monitoring Time Frame	Single "grab" for ISE, optical sensor work.		
Method Performance Precision Bias	For Pb <sup>2+</sup> ISE, linear range 100 µg/L to 2,000 µg/L in aqueous solutions. Preconcentration would lower detection limit. No precision/bias data presented. Results for analyzed sample confirmed with ICP-AES. For Pb <sup>2+</sup> optical sensor, linear range 70 µg/L to 70,000 µg/L in hexane.		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
	Pb <sup>2+</sup> in seawater (ISE)	< 100 µg/L	P
	Pb <sup>2+</sup> in hexane (optical)	50 µg/L (in hexane)	P
Participant Burden	Very low (water collection).		
Field Burden	Low (water sample collection).		
Analytical Costs	Fabrication/imprinting procedures labor intensive. Once completed (i.e. for a Pb <sup>2+</sup> ISE) analyses appear to be simple and inexpensive..		
Comments	<ol style="list-style-type: none"> <li>1. Authors describe fabrication of several polymers imprinted with desired analyte. A vinylbenzoic acid resin imprinted with Pb<sup>2+</sup> was used to selectively measure this ion in seawater. Imprinted polymers were also employed to develop an optical sensor for Pb<sup>2+</sup>, an ISE for the uranyl ion, and a detector for the hydrolysis products of nerve agents.</li> <li>2. Resins may be vulnerable to acidic pH's, limiting potential utility.</li> <li>3. Small linear range for Pb ISE results from low exchange capacity of imprinted resins (many exchange sites not accessible to ions).</li> <li>4. Imprinting intended to make polymers analyte specific. Other cations common in environmental samples may present interferences.</li> <li>5. Optical sensor based on imprinted polymer not readily adapted for field studies. Laboratory use only. Calibration curve in hexane reported.</li> </ol>		
Other References	None		

Authors	K. Möller, U. Nilsson, C. Crescenzi		
Title	Synthesis and evaluation of molecularly imprinted polymers for extracting hydrolysis products of organophosphate flame retardants		
Citation	<i>Journal of Chromatography A</i> , 938:121-130 (2001)		
Matrix	none (R&D)		
Method Type	cleanup of biological fluids		
Method Description Sample Collection Sample Preparation Analysis	R&D towards a cleanup method for determination of diphenyl phosphate and other metabolites of flame retardants in urine. Authors synthesize and test MIP stationary phase for use in SPE (solid phase extraction) columns. Work not complete.		
Monitoring Time Frame	not applicable		
Method Performance Precision Bias	not applicable		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Target Chemicals:	not applicable	not applicable	
Other Chemicals:	not applicable	not applicable	
Participant Burden	not applicable		
Field Burden	not applicable		
Analytical Costs	not available (probably prohibitive)		
Comments	Work is geared towards the analysis of urine. If commercially produced columns become available in the future, this technology could greatly simplify sample cleanup. I suspect that these will be available in 10 years or so, but probably only for analytes with a strong commercial demand, i.e. drug metabolites.		
Other References	None		

Authors	A. Rudnitskaya, et al.
Title	Multisensor System on the Basis of an Array of Non-Specific Chemical Sensors and Artificial Neural Networks for Determination of Inorganic Pollutants in a Model Groundwater
Citation	<i>Talanta</i> , 2001, <b>55</b> , 425-431
Matrix	Synthetic aqueous solutions.
Method Type	Lower sensitivity, potential for analysis in field.
Method Description	
Sample Collection	Not applicable (synthetic aqueous solutions).
Sample Preparation	None.
Analysis	Use of sensor array for simultaneous determination of several ion species: Cu <sup>2+</sup> , Mg <sup>2+</sup> , Na <sup>+</sup> , Cl <sup>-</sup> , Mn (II), Fe(III), Ca <sup>2+</sup> , Zn <sup>2+</sup> , SO <sub>4</sub> <sup>2-</sup> in model water solutions. Artificial neural network used to process complex analytical signals from non-specific electrode detectors. Two sets of synthetic aqueous solutions prepared to test array.
Monitoring Time Frame	Potential use for single “grab” or real-time aqueous sample monitoring.
Method Performance	
Precision	For samples with same background ion content as calibration standards: accuracy within ≈ 1% for Cl <sup>-</sup> , Cu <sup>2+</sup> , Fe(III), Ca <sup>2+</sup> , SO <sub>4</sub> <sup>2-</sup> ≈ 5% for Na <sup>+</sup> , Mg <sup>2+</sup> , Zn <sup>2+</sup> ; ≈ 17% for Mn (II).
Bias	For samples with ion background different than calibration standards: accuracy within ≈ 5% for Cu <sup>2+</sup> ; ≈ 10% for Ca <sup>2+</sup> , Mg <sup>2+</sup> , SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> , Na <sup>+</sup> ; ≈ 60% for Zn <sup>2+</sup> ; ≈ 25% for Mn (II).
	%RSD generally ≤ 10% for Cu <sup>2+</sup> Zn <sup>2+</sup> Mn (II) Fe(III) regardless of background ion content; % RSD generally ≤ 10% for Cl <sup>-</sup> , Ca <sup>2+</sup> , SO <sub>4</sub> <sup>2-</sup> , Na <sup>+</sup> , Mg <sup>2+</sup> when background matches calibration standards, ≤ 25% when background is variable.

## Group 5 (continued)

Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Cu <sup>2+</sup>		0.003 µg/mL (low cal. standard)	P
Mg <sup>2+</sup>		1.2 µg/mL (low cal. standard)	P
Na <sup>+</sup>		4.6 µg/mL (low cal. standard)	P
Cl <sup>-</sup>		10.6 µg/mL (low cal. standard)	P
Mn (II)		0.055 µg/mL (low cal. standard)	P
Fe(III)		0.280 µg/mL (low cal. standard)	P
Ca <sup>2+</sup>		4 µg/mL (low cal. standard)	P
Zn <sup>2+</sup>		0.007 µg/mL (low cal. standard)	P
SO <sub>4</sub> <sup>2-</sup>		9.6 µg/mL (low cal. standard)	P
Participant Burden	Very low (potential water collection).		
Field Burden	Sample collection/preparation inexpensive. Electrode component and data processing equipment are commercially available.		
Analytical Costs	Potentially expensive to assemble array and “train” electrodes, inexpensive sample collection, preparation, and in-field monitoring.		
Comments	<ol style="list-style-type: none"> <li>1. Authors describe development of array of non-specific detectors (both solid-state and PVC) for simultaneous determination of metal ions in aqueous samples.</li> <li>2. Best results for majority of ions obtained when using entire array (not just solid state or PVC electrodes).</li> <li>3. Reported accuracy for ion species often varied significantly when array challenged with variable “background” ion content from other species. For example, zinc accuracy in test solution was within ≈5% while accuracy in test solutions with different background was within ≈60%.</li> <li>4. Potential application: “real-time” water monitoring.</li> </ol>		
Other References	None		

Authors	Y. G. Mourzina, et al.		
Title	Development of Multisensor Systems Based on Chalcogenide Thin Film Chemical Sensors for the Simultaneous Multicomponent Analysis of Metal Ions in Complex Solutions		
Citation	<i>Electrochimica Acta</i> , 2001, <b>47</b> , 251-258		
Matrix	Synthetic aqueous solutions.		
Method Type	Lower sensitivity, potential for analysis in field.		
Method Description	Not applicable (synthetic aqueous solutions)		
Sample Collection	None.		
Sample Preparation	Use of laboratory fabricated microsensor array for simultaneous determination of heavy metal ion species (Pb <sup>2+</sup> , Cd <sup>2+</sup> , Zn <sup>2+</sup> , and Fe <sup>3+</sup> ). Only solid state sensors (n = 7) were used to construct array. The multidimensional sensor array response is processed by means of an artificial neural network		
Analysis			
Monitoring Time Frame	Potential use for single “grab” or real-time aqueous sample monitoring.		
Method Performance	For replicate analyses of metal ions present at µg/mL levels in synthetic aqueous solutions, RSD for Pb <sup>2+</sup> ranged from 12 - 21%, Cd <sup>2+</sup> from 14 - 23%, Zn <sup>2+</sup> from 15 - 26%, Fe <sup>3+</sup> from 15 - 31%. Reported average accuracy within ± 15 - 30% when array of seven solid state sensors was used to determine Pb <sup>2+</sup> , Zn <sup>2+</sup> , and Cd <sup>2+</sup> . Error exceeded 30% for Zn <sup>2+</sup> , Fe <sup>3+</sup> for system when additional macrosensors added to array. Authors suspect presence of iron in mixtures adversely impacting accuracy.		
Precision			
Bias			
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Pb <sup>2+</sup>			
Cd <sup>2+</sup>		4.14 µg/mL (lowest sample conc. measured)	P
Zn <sup>2+</sup>		3.36 µg/mL (lowest sample conc. measured)	P
Fe <sup>3+</sup>		0.655 µg/mL (lowest sample conc. measured)	P
		2.79 µg/mL (lowest sample conc. measured)	P
Participant Burden	Very low (potential water collection).		
Field Burden	Low (sample collection). Moderate if analysis done in field.		
Analytical Costs	Potentially expensive to assemble array and “train” electrodes, inexpensive sample collection, preparation, and in-field monitoring.		
Comments	<ol style="list-style-type: none"> <li>1. Authors describe multidimensional array comprised of novel thin film solid state sensors (n = 7) for simultaneous determination of metal ions in aqueous matrix. It was necessary to add additional “macrosensors” to the array to determine Fe<sup>3+</sup>. Response processed by means of an artificial neural network.</li> <li>2. Much of the article deals with the analytical performance of individual solid state sensors in single-ion solutions as a means of selecting the best candidate sensors for the array. Eventually films with Cu, Pb, Cd, and Tl primary ions were selected for incorporation into the array.</li> </ol>		
Other References	None		

Authors	H. Prestel, et al.		
Title	Detection of Heavy Metals in Water by Fluorescence Spectroscopy: On the Way to a Suitable Sensor System		
Citation	<i>Fresenius J. Anal. Chem.</i> , 2000, <b>368</b> , 182-191		
Matrix	Water (ground, surface).		
Method Type	Lower sensitivity; adaptable for field measurements.		
Method Description	Not applicable. Sensor head is lowered directly into water to be tested.		
Sample Collection	None.		
Sample Preparation	Fiber optic bundle transmits N <sub>2</sub> laser excitation energy to sample and the resulting fluorescence emission radiation back to CCD array detector. Sensor head can be equipped w/ modules for simultaneous multielement determinations. Several fluorescing compounds were used to chelate metals.		
Analysis			
Monitoring Time Frame	Approximately 30 minutes required between quantitative measurements.		
Method Performance	Not described.		
Precision			
Bias			
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Cd <sup>2+</sup>		3 µg/L (low cal. standard)	P
Hg <sup>2+</sup>		300 µg/L (low cal. standard)	P
Ni <sup>2+</sup>		20 µg/L (low cal. standard)	P
Cu <sup>2+</sup>		200 µg/L (low cal. standard)	P
Be <sup>2+</sup>		5 µg/L (low cal. standard)	P
Participant Burden	Very low (water collection).		
Field Burden	High. Described system is designed for larger scale field operations (rivers, lakes, effluents) not so much for residential applications.		
Analytical Costs	Moderate to high.		
Comments	<ol style="list-style-type: none"> <li>1. Authors describe inert sensor head (consisting of 5 modules) which can be lowered into water sample for multielement determinations. Sample water is introduced into module where it is separated from fluorescent complexing agent by a membrane. 2. When metal complexes form, the fluorescence emission behavior of the complexing agent changes (wavelength shift, enhancement, or suppression of signal). These changes can be used to identify different complexes (Ni<sup>2+</sup>, Cu<sup>2+</sup>, etc.).</li> <li>2. Metal/complexing agent reaction rate is limited by diffusion through membrane. System requires approximately 30 minutes between quantitative measurements.</li> <li>3. Multielement calibration calculations are described for several metals as there are competing complexation reactions which can alter measurements. Other potential matrix effects include organic acids and chloride.</li> </ol>		
Other References	None		

Authors	E.P. Achterberg		
Title	Automated Techniques for Real-Time Shipboard Determination of Dissolved Trace Metals in Marine Surface Waters (Review Paper)		
Citation	Int. J. Environment and Pollution, 2000, <b>13(1-6)</b> , 249-261		
Matrix	Seawater.		
Method Type	Several techniques for field measurements of seawater reviewed.		
Method Description	Two major modes of shipboard collection described: 1-Discrete mode, using pump and weighted hose, and 2-“underway pumping”, where hose attached to pump is secured to torpedo structure and held at fixed distance/depth from the ship. Water continuously sampled while ship moves.		
Sample Collection	Two major modes of shipboard collection described: 1-Discrete mode, using pump and weighted hose, and 2-“underway pumping”, where hose attached to pump is secured to torpedo structure and held at fixed distance/depth from the ship. Water continuously sampled while ship moves.		
Sample Preparation	Varied with the mode of analysis reviewed (voltammetric, chemiluminescence, and colorimetric methods). Generally involved combination of preconcentration, filtration, and matrix removal steps.		
Analysis (3 modes reviewed)	<p>Colorimetric: Analyte reacts w/ reagent and color change is monitored. Generally low sensitivity for metals.</p> <p>Chemiluminescence: Analyte reacts w/ reagent and electromagnetic radiation is monitored. Higher sensitivity. Requires matrix treatment.</p> <p>Voltammetric: Analyte collected on electrode, voltammetric scan applied and current measured. Differential pulse voltammetry (anodic/cathodic stripping) using hanging Hg drop electrode is most popular form. Matrix treatment required, no preconcentration step.</p>		
Monitoring Time Frame	All modes can be equipped for real-time measurements.		
Method Performance	Review paper, specifics not provided.		
Precision	Review paper, specifics not provided.		
Bias	Review paper, specifics not provided.		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Participant Burden	Very low (water collection).		
Field Burden	Moderate if laboratory analysis, higher if field analysis.		
Analytical Costs	Inexpensive instrumentation and analysis procedures reviewed.		
Comments	<ol style="list-style-type: none"> <li>Review paper focusing on modes of shipboard metal determinations. Three modes of analysis were reviewed: colorimetric, chemiluminescence, and voltammetric. All utilize small, inexpensive instrumentation adaptable to residential field work (less so for voltammetric methods using dropping Hg electrodes).</li> <li>All three of the reviewed analysis modes can suffer from serious matrix effects. As a result, water samples containing potential interferences (dissolved organic material, interfering ions, etc.) often require sample pretreatment. Sample preconcentration may be needed if lower detection limits are desirable for colorimetric and chemiluminescence.</li> </ol>		
Other References	None		

Authors	Shamsipur, et al.		
Title	Lead-Selective Membrane Potentiometric Sensor Based on an 18-Membered Thiocrown Derivative		
Citation	<i>Analytical Sciences</i> , 2001, <b>17</b> , 935-938		
Matrix	Water		
Method Type	Lower sensitivity; Potential for analysis in field.		
Method Description	Not described.		
Sample Collection	None.		
Sample Preparation			
Analysis	Use of laboratory fabricated Pb selective membrane sensor. Potential use in field		
Monitoring Time Frame	Single “grab” described. Stabilization time between samples is 40 s.		
Method Performance			
Precision	For one field water sample measured in quadruplicate, 1.4% RSD.		
Bias	<5% (at pH of 2.0 - 5.0).		
Applicable Chemicals	Method QL		Level of Validation
Pb <sup>2+</sup>	Personal	Microenvironmental or ambient	
		Approx. 200 µg/L	
Participant Burden	Very low (water collection).		
Field Burden	Low (sample collection). Moderate if analysis done in field.		
Analytical Costs	Sample collection/preparation inexpensive. Fabrication of Pb selective PVC membrane labor intensive, not automated.		
Comments	<ol style="list-style-type: none"> <li>1. Authors describe development and optimization of Pb-selective membrane sensor, with less emphasis on application of sensor.</li> <li>2. Electrode is Pb<sup>2+</sup> selective, but suffers from potential interferences from other ionic species (mostly Hg<sup>2+</sup>, other species to lesser extent).</li> <li>3. Bias expected at alkaline pH. Response appears to be linear from pH range of 2 - 5, but drops at pH of 6 and above.</li> <li>4. Field water sample was collected from a lead mine and had measured level (22.1 ± 0.3 ppm) in agreement with collected AAS data (22.3 ± 0.2 ppm).</li> </ol>		
Other References	None		

Authors	Xiao, et al.			
Title	Synchronous Fluorescence and Absorbance Dynamic Liquid Drop Sensor for Cr(VI) Determination at the Femtomole Level			
Citation	<i>Analyst</i> , 2001, <b>126</b> , 1387-1392			
Matrix	Water			
Method Type	Low or high sensitivity; laboratory analysis required.			
Method Description Sample Collection Sample Preparation Analysis	<p>Not described. Wastewater samples (n=4) were filtered prior to analysis.</p> <p>Synchronous fluorescence and absorbance detection on dynamic liquid drop. Collected signals from both measurements are used to determine Cr(VI). Instrumentation would require laboratory setting.</p>			
Monitoring Time Frame	Single “grab”.			
Method Performance Precision/Bias	<p>&lt; 5% at 50 µg/L. &lt; 10% in absence of potentially interfering species.</p>			
Applicable Chemicals	Method QL		Level of Validation	
Cr(VI)	Personal	Microenvironmental or ambient		
		Approx. 1 µg/L		P
Participant Burden	Very low (water collection).			
Field Burden	Low (batch water collection); analysis in laboratory.			
Analytical Costs	Sample collection and preparation inexpensive. Instrument operation expected to be labor intensive.			
Comments	<ol style="list-style-type: none"> <li>1. Authors describe dynamic drop system for quantifying µg/L levels of Cr(VI) in water samples with minimal pretreatment. System collects both fluorescence and absorbance data to determine Cr(VI). Article focus is instrumentation development - not application.</li> <li>2. Reagent (TMB-d) strong fluorescence emitter at acidic pH. Reaction with Cr(VI) results in fluorescence quenching and increase in absorbance of reaction product.</li> <li>3. Other species can react with reagent and cause interferences. Mn(VI) an Fe(III) are of particular concern.</li> <li>4. Cr(VI) recoveries for fortified water samples (n=3) range from 98.9% to 99.5% Cr(VI); concentrations in field water samples (n=4) within ± 3% of data collected from spectrophotometric analysis of same samples.</li> </ol>			
Other References	None			
Authors	M. Chendorain, et al.			

Title	Real Time Continuous Sampling and Analysis of Solutes in Soil Columns		
Citation	<i>Soil Sci. Soc. Am. J.</i> , 1999, <b>63(May-June)</b> , 464-471		
Matrix	Soil columns.		
Method Type	Measurement of tracer compound through soil column (transient signal)		
Method Description			
Sample Collection	Not applicable (preparation of laboratory soil columns).		
Sample Preparation	Soil columns (n = 3) of varying composition were packed uniformly and were saturated with a CaCl <sub>2</sub> solution.		
Analysis	Small tube sampler (STS) inserted at various points in soil column and interfaced with pump. Pore solution pumped to a UV absorbance detector where the concentration of tracer compound (nitrate) was determined. Measured concentrations were used to generate breakthrough curves for the tracer as it passed through the columns.		
Monitoring Time Frame	Potential for near “real-time” integrated measurements (1 - 2 min. delay).		
Method Performance			
Precision	Not described.		
Bias			
Applicable Chemicals	Method QL		Level of Validation
<i>No metals listed</i>	Personal	Microenvironmental or ambient	
Participant Burden	Moderate (real-time soil monitoring).		
Field Burden	High (potential for field measurements).		
Analytical Costs	Highly variable (depends on mode of detection interfaced with STS).		
Comments	<ol style="list-style-type: none"> <li>1. Authors describe sampling device for analysis of pore water during displacement studies. The small tube sampler (STS) is stainless steel tube with a grid at the entrance to prevent clogging. The STS is interfaced to pump and pore water is transported to detector w/ 1-2 min. delay.</li> <li>2. Nitrate used as tracer. Mode of detection could be varied depending on analyte list (electrochemical detection, etc.).</li> <li>3. Soil must be saturated for this sampling mode to function.</li> <li>4. Potential utility for sampling real-time effluent flows of desirable compounds?</li> </ol>		
Other References	None		

Group 6

Authors	Corrado Di Natale, D. Salimbeni, R. Paolesse, A. Macagnamo, A. D'Amico
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Title	Porphyrins-based opto-electronic nose for volatile compounds detection		
Citation	Sensors and Actuators B 65 (2000) 220-226		
Matrix	Air		
Method Type	Low sensitivity/cost/burden method		
Method Description	<p>Sample Collection Not addressed. Assuming instrument can be deployed in the field, air sample would simply be injected through the inlet port of an 18 mL Plexiglass chamber.</p> <p>Sample Preparation None</p> <p>Analysis Air sample is passed through a Plexiglass chamber coated with various metalloporphyrins. Each porphyrin layer lies on a different optical path creating an optical multisensor (opto-electronic nose). UV visible spectrophotometer is used to detect changes in the optical spectra (blue region) of solid state films of porphyrins in the presence of volatile analytes.</p>		
Monitoring Time Frame	Real-time		
Method Performance	<p>Precision Not determined</p> <p>Bias Not determined</p>		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Target Chemicals: Hexane Propanol Methanol and Ethanol Acetone Triethylamine		Not determined	None
Other Chemicals: Acetic acid		Not determined	None
Participant Burden	Low		
Field Burden	Low		
Analytical Costs	Unknown		
Comments	Not practical for ambient air monitoring because of lack of sensitivity. Concentration ranges studied were between 70 and 4000 ppm.		
Other References	None		

Authors	Krantz-Rulcker, C., M. Stenborg, F. Winqvist, I. Lundstrom		
Title	Electronic Tongues for Environmental Monitoring Based on Sensor Arrays and Pattern Recognition: A Review		
Citation	Analytica Chimica Acta, 426 (2000) 217-226		
Matrix	Water		
Method Type	Low sensitivity/cost/burden		
Method Description			
Sample Collection	On-line monitoring.		
Sample Preparation	Not addressed.		
Analysis	Electronic tongue based on voltammetry. Water samples from a drinking water production plant were analyzed with a voltammetric sensor array based on four electrodes (gold, iridium, platinum, and rhodium). An increasing potential is applied sequentially across each electrode and measurements are collected in cycles. Pattern recognition routines are used to distinguish changes in the on-line stream.		
Monitoring Time Frame	Real-time monitoring		
Method Performance			
Precision	Not addressed.		
Bias	Not addressed.		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
None	Not applicable.	Not applicable.	Not applicable.
Participant Burden	Low		
Field Burden	Low		
Analytical Costs	Unknown		
Comments	Paper indicates that technology is not applicable to determining composition of sample, but rather may be useful in process control or quality control applications		
Other References	None.		

Authors	Baby, R.E., M. Cabezas, E.N. Walsoe de Reca		
Title	Electronic Noses: A Useful Tool for Monitoring Environmental Contamination		
Citation	Sensors and Actuators B 69 (2000) 214-218		
Matrix	Water		
Method Type	Low sensitivity/cost/burden		
Method Description	<p>Sample Collection: Not addressed.</p> <p>Sample Preparation: Not addressed.</p> <p>Analysis: An electronic nose, MOSES II, equipped with two arrays of eight (tin oxide and quartz microbalance) sensors is used to detect differences in the concentration of lindane in water. The tin oxide sensors respond to changes in the resistivity in relation to the oxidating and reducing properties of the gas in the headspace above the solution. Differences in the concentration of nitrobenzene in water have also been determined by this technique. In addition, the electronic nose has been used to distinguish mixtures of three synthetic pyrethroids in 1) a dry powder mixture, 2) a solution of acetone, and 3) individual pyrethroids prepared in an inert powder (alumina) and in water at various concentrations.</p>		
Monitoring Time Frame	Snap-shot		
Method Performance	<p>Precision: Not addressed.</p> <p>Bias: Not addressed. Linear relationship between Lindane concentration in water (nominal 1 ppm to 4 ppm) and detector response was assessed.</p>		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Lindane		1 ppm in water	None
Nitrobenzene		1 ppm in water	None
Permethrin		Not determined	None
Deltamethrin		Not determined	None
Cypermethrin		Not determined	None
Participant Burden	Low		
Field Burden	Low		
Analytical Costs	Not determined.		
Comments	Electronic noses are normally used to determine food quality and may have other uses in process control applications. The use of these devices for exposure monitoring could be limited by their inability to identify individual contaminants at low concentrations in complex matrices.		
Other References	None		

Authors	T. Dewettinck, K. Van Hege, W. Verstraete		
Title	The electronic nose as a rapid sensor for volatile compounds in treated domestic wastewater		
Citation	<i>Wat. Res.</i> , 2000; 35(10): 2475-2483		
Matrix	Water		
Method Type	grab sample, non-compound-specific.		
Method Description	Paper describes the use of a commercially available instrument (FOX 3000 electronic nose, Alpha M.O.S., Toulouse, France) to test potable treated (regenerated) wastewater for unidentified VOCs. Results are given in units of sensorial odor perception (SOP). No data are given for calibration with respect to concentrations of VOCs.		
Sample Collection			
Sample Preparation	2 liter sample collected, transported to lab, and analyzed without sample preparation.		
Analysis			
Monitoring Time Frame	grab sample; potential for continuous monitoring (1 day to ? weeks)		
Method Performance	none given (instrument not calibrated)		
Precision			
Bias			
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Tested analytes	none	[odor]	none
Potential analytes	May be applicable to VOCs at the ppm level		
Participant Burden	not applicable		
Field Burden	low (grab sample)		
Analytical Costs	\$10/grab sample; \$10/day continuous		
Comments	The commercial instrument described in this paper may be useful for human exposure studies, however, this paper is of little help. Manufacturer of instrument claims sensitivity of about 1 ppm.		
Other References	Kress-Rogers E. (ed.) <i>Handbook of Biosensors and Electronic Noses</i> . CRC Press, Boca Raton, FL. (1997)		

Authors	Julian W. Gardner, Hyun Woo Shin, Evor L, Hines, Crawford S. Dow		
Title	An electronic nose system for monitoring the quality of potable water		
Citation	<i>Sensors and Actuators B</i> . 2000, 69: 336-341		
Matrix	potable water		
Method Type	gas sensor array		
Method Description Sample Collection Sample Preparation Analysis	<p>Grab sample, stick sensor in neck of bottle for 1-2 min, analyze signals on computer.</p> <p>Authors use 6 sensor (MOS, metal oxide semiconductor) electronic nose to identify presence and type of cyanobacteria (blue-green algae) in potable water. Principal components analysis (PCA) clearly distinguishes between toxic and non-toxic algae. No information is given that would indicate the usefulness of MOS detectors for VOCs in indoor air, although one might consider it a possibility.</p>		
Monitoring Time Frame	grab; potential for continuous, long term monitoring		
Method Performance Precision Bias	No quantitative results given, good selectivity		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Tested analytes		not given	not given
Potential analytes	System has undeveloped potential for VOC analysis		
Participant Burden	not applicable		
Field Burden	grab sample, potential for portable field instrument		
Analytical Costs	about \$5 per sample		
Comments	Method is not applicable to personal exposure studies. However, this technology has potential for VOC analysis. Unlike MIPs, these sensors can be software-calibrated for multiple analytes. QL is a big question.		
Other References	<u>Major reference:</u> J. W. Gardner, P. N. Bartlett, <i>Electronic Noses: Principles and Applications</i> , Oxford Univ. Press, 1999		

Authors	Corrado Di Natale, R. Paolesse, A. Macagnamo, A. Mantini, A. D'Amico, A Legin, L. Lvova, A Rudnitskaya, Y. Vlasov		
Title	Electronic nose and electronic tongue integration for improved classification of clinical and food samples		
Citation	<i>Sensors and Actuators B</i> 64 (2000) 15-21		
Matrix	Urine and milk		
Method Type	Low sensitivity/cost/burden method		
Method Description			
Sample Collection	Urine collected from 0 to 13 year old children. Pasturized and ultrahigh temperature milk obtained from commercial sources.		
Sample Preparation	Whole urine and milk samples were equilibrated in sealed vials for 30 minutes at 30 C.		
Analysis	Volumes of headspace were injected into 35 mL quartz chambers coated with eight metalloporphyrins (electronic noses). Electronic tongue measurements made by immersing seven porphyrin electrodes directly into the sample. Readings were taken after 15 minutes.		
Monitoring Time Frame	Real-time		
Method Performance			
Precision	Not determined		
Bias	Not determined		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Target Chemicals:			
Other Chemicals: pH Specific weight Blood cell content	Not determined	Not determined	None
Participant Burden	Low		
Field Burden	Low		
Analytical Costs	Unknown		
Comments	Target parameters (analytes) not applicable to exposure monitoring.		
Other References	None		

TABLE 3-3. SUMMARY TABLE OF PORTABLE/FIELD-READY INSTRUMENTS  
FROM GRAY LITERATURE

Company	Instrument Type	Matrix
Intelligent Ion, Inc.	miniature MS	air
Agilent	portable micro GC	air/water
Varian	portable GC/TCD	air
Electronic Sensor Technology	portable/handheld GC/SAW	air
Photovac	portable GC	air
Monitoring Instruments.com	portable MS	air
Moorfield Associates	portable MS/TDS	air

Authors	Intelligent Ion, Inc. 2815 Eastlake Avenue E Suite 300 Seattle, WA 98102 tel 206.336.5608 fax 206.336.5558
Title	Miniature Mass Spectrometry Breakthrough
Citation	<a href="http://www.intelligention.com">www.intelligention.com</a>
Matrix	air
Method Type	portable mass spectrometer
Monitoring Time Frame	continuous, long term (~ several months unattended?)
Working Principle	Mattauch-Herzog design with permanent magnets and micro-channel plate based position sensitive ion detector
Mass Range	1-300 amu standard, optional 200-2000 range for medical, genomic and biotech applications, 1-100 amu lower cost model retaining high sensitivity and other attributes
Resolution	1 amu standard, 2 amu over extended mass range
Ionizer	Electron impact, closed, thermionic source
Detector	Position sensitive micro-channel based electro optical ion detector
Duty cycle	100%, non-scanning instrument
Read-out speed	0.02 sec or less
Sensitivity	Prototype 10-ppb benzene demonstrated in alpha prototype, expected sensitivity is 5 ppb with new designed (closed) ionizer and dual MCP layout
Trace analysis	Part per trillion with enrichment peripheral
Linearity	3 orders of magnitude demonstrated, 4-5 orders of magnitude expected
Long term stability	Superb long-term stability demonstrated with the existing prototypes This long-term stability results from the use of DC voltages and permanent magnets
Front-end	Modular and easily adapted to customer need. Default (a) direct coupled GC, or high-speed GC, including by-pass valve for direct gas inlet via flow restriction, or (b) continuously open and heated quartz capillary
Total Weight	35 lbs (159 kg)
Footprint	8.5" x 20" x 11" (21.6 x 50.8 x 28 cm)
GC interface	Uniquely suited for direct-coupled, modern high-speed GC interface due to high read-out speed and 100% duty cycle
Applicable Chemicals	VOCs/SVOCs
Participant Burden	small, quiet instrument, operated remotely
Field Burden	low (?)
Analytical Costs	capital cost (?)
Comments	This is clearly the most advanced, well documented, and best marketed portable instrument out there. Numerous publications available on web site.
Other References	Resolving power enhancement of a discrete detector (array) by single event detection, .P. Sinha , D.P. Langstaff , D.J. Narayan , K. Birkinshawb, <i>International Journal of Mass Spectrometry</i> 176 (1998) 99-102

Authors	Agilent		
Title	the power is in your hands. Agilent 3000 Micro GC		
Citation	<a href="http://www.agilent.com/chem/microgc">www.agilent.com/chem/microgc</a>		
Matrix	air/water		
Method Type	portable micro GC		
Method Description Sample Collection Sample Preparation Analysis	Agilent is presently selling a line of portable micro instruments that house two or four micro-machined GC modules. Each module is about 2x4x5" and contains injector, column, GC oven, and detector. Modules can operate simultaneously and under different conditions. The two module instrument is about 4x9x12". Agilent claims that it can be operated continuously, and controlled remotely. Detector is not described. Carrier gas source not described, but it does not use external tanks. Injector system not described. Custom configurations are available.		
Monitoring Time Frame	continuous/periodic, remote control		
Method Performance Precision Bias	no performance data on web site		
Applicable Chemicals	Method QL		Level of Validation
	Personal	Microenvironmental or ambient	
Target Chemicals:	n/a		
Other Chemicals:	n/a		
Participant Burden	low?		
Field Burden	portable instrument		
Analytical Costs	capital cost: probably > \$10k per instrument		
Comments	need to find out what detectors are available		
Other References	None		

Authors	Varian
Title	Varian CP-4900 Micro-GC
Citation	<a href="http://www.varianinc.com/cgi-bin/nav?varinc/docs/csb/microgc/">http://www.varianinc.com/cgi-bin/nav?varinc/docs/csb/microgc/</a>
Matrix	Air
Method Type	portable GC/TCD
Monitoring Time Frame	up to 20 days (?) until carrier gas runs out
Manufacturer's Specifications:	
Injector	Micro-machined injector with moving parts
Injection volume:	1 $\mu$ L to 10 $\mu$ L, software selectable
Optional heated injector:	30 °C -- 110 °C, including heated transfer line
Column Oven	Temperature range: 30 °C to 180 °C, isothermal Optional backflush capability
Detector	Micro-machined Thermal Conductivity Detector (TCD)
Detection Limits	WCOT columns: 1 ppm; micro-packed columns: 10 ppm
Operating Range	Linear dynamic range: 10 <sup>6</sup>
Carrier Gas	He, H <sub>2</sub> , N <sub>2</sub> or Ar: 550 $\pm$ 10 kPa (80 $\pm$ 1.5 psig) input
Dimensions and Weight	Two-channel system: 28 cm (h) x 15 cm (w) x 30 cm (d) Four-channel system: 28 cm (h) x 15 cm (w) x 55 cm (d)
	Weight: minimum of 5.2 kg
Gas containers:	one or two 300 mL gas containers with maximum pressure of 12,000 kPa (1740 psig)
Rechargeable battery packs:	two
Applicable Chemicals	all VOCs, some SVOCs
Participant Burden	portable GC with internal gas tanks (small, quiet)
Field Burden	internal gas tanks – restrict duration of sampling
Analytical Costs	capital costs (?)
Comments	TCD has poor LOD. SAW would be better for environmental work. Carrier gas should last: $300\text{mL} * (1740\text{psi}/15\text{psi}) / (1\text{ml}/\text{min}) = 34,800 \text{ min} = 24 \text{ days}$
Other References	web site.

Authors	Electronic Sensor Technology 1077 Business Center Circle Newbury Park • CA • 91320 Ph. (805) 480-1994 • Fax (805) 480-1984
Title	4100 Portable Handheld Gas Chromatograph
Citation	<a href="http://www.estcal.com/Specs/4100Spec.pdf">http://www.estcal.com/Specs/4100Spec.pdf</a>
Matrix	Air
Method Type	portable GC/SAW

Manufacturer's Specifications:

Size:	20" W x 14" D x 10" H
Weight:	35 lbs
Power:	120-240 VAC at 250 watts MAX, 50 watts typical
Detector:	Surface Acoustic Wave quartz microbalance Dynamic Range - 2x10 <sup>5</sup>
Detector Temperature:	0°C to 125°C, programmable
System Controller:	Intel Pentium or higher processor Minimum 16MB RAM – 1GB Hard Drive Windows 95 or 98 Software Included: MS Office Standard, Winzip, PCAnywhere and EST System Software
Communications:	RS-232 between controller and 4100
Sampling:	30-40 cc/m sampling flow from internal pump
Sample Introduction:	Time programmable from 1-60 seconds Internal Tenax trap
Inlet Connection:	Stainless Steel LUER inlet port
Inlet temperature:	50°C to 200°C
Carrier Gas:	Helium, HP – 12-24 hours depending on usage
Column Limits:	35°C to 200°C
Column Ramping:	Isothermal or ramped from 1-18°C/second
Compound Identification:	Automatic with user calibration
Analysis Time:	10 – 60 seconds
Recycle Time:	30 seconds minimum
Precision:	5% RSD
Accuracy:	10%
Sensitivity:	Low ppb level for most compounds
Applicable Chemicals	All VOCs
Participant Burden	carrier gas must be replenished every 24 hours .
Field Burden	(above) Instrument can be operated remotely
Analytical Costs	capital cost (?)
Comments	Specs look good. A portable GC with an internal hydrogen generator for carrier gas would enhance its utility.
Other References	None

Authors	Photovac, Inc. 176 Second Avenue, Waltham, MA 02451 USA Phone: 781-290-0777
Title	Voyager Portable Gas Chromatograph
Citation	<a href="http://www.photovac.com/products/products_Voygr.html">http://www.photovac.com/products/products_Voygr.html</a>
Matrix	air
Method Type	portable GC
Manufacturer's Specifications	
Size	15.4" ( 39 cm ) long, 10.6" ( 27 cm ) wide, 5.9" ( 15 cm ) high
Weight	15 lb. ( 6.8 kg ) with battery installed
Keypad	4 fixed function keys and 4 menu keys
Display	128 x 64 element graphical LCD with backlighting
Battery Capacity	NiCd replaceable packs, extended life battery to power Voyager™ for up to 8 hours depending on ambient and column temperature
Serial Output	RS-232, 9600 baud for connection to Windows™ based PC and communication to Voyager SiteChart software
Detectors	Photoionization detector with quick-change electrodeless discharge UV lamp, 10.6 eV (standard) Electron Capture Detector (optional)
Concentration Range Monitored.	Typical low detection limits are 5 ppb to 50 ppb.
Power	10-18 VDC, 115 or 240 VAC, adapter provided
Applicable Chemicals	VOCs and SVOCs
Participant Burden	
Field Burden	gas cylinders last only 8 hours
Analytical Costs	?
Comments	This instrument uses photoionization detector (PID) or electron capture detector (ECD), making it much more sensitive (and more suitable for environmental use) than instruments using TCD or SAW.
Other References	None

Authors	<a href="http://www.monitorinstruments.com/products1.htm">http://www.monitorinstruments.com/products1.htm</a>
Title	MG2100 Portable Mass Spectrometer
Citation	<a href="http://www.monitorinstruments.com/products1.htm">http://www.monitorinstruments.com/products1.htm</a>
Matrix	Air
Method Type	Portable mass spectrometer
Manufacturer's Specifications:	
Mass Analyzer:	Cycloidal Mass Range: 2-100 amu standard;2-200 amu expandable
Ion Source:	Electron impact (EI); Adjustable eV
Vacuum System:	Ion getter pump (triode); turbomolecular pump,optional
Gas Inlets:	Flow-By system, capillary, batch inlet, optional temperature & pressure control, corrosive gas flow-by
Stream Selection:	Optional discrete solenoid type; dead end or continuous flow, added in blocks of 8 streams, rotary multiposition
Gas Inlet Flow Rates:	0.125 atm cc/s (flow-by), 0.08 µLs (capillary)
Sensitivity:	5 x 10 <sup>-4</sup> A/mbar (faraday cup)
Min det partial pressure:	1 x 10 <sup>-12</sup> mbar (faraday cup)
Min det partial pressure ratio:	100 ppb (faraday cup) = 3 cts.
Signal to Noise Ratio:	150 db
Communications:	RS-232. RS-485, Modem, Fiber Optics
Response Time:	>=20 msec, depending upon application
Power Input:	80-250 VAC;12/24 VDC
Dimensions:	9" x 13" x 23" (230 mm x 330 mm x 585 mm)
Weight:	40 lbs. (20 Kg.)
Enclosure:	Portable enclosure and airship container standard
Applicable Chemicals	VOCs/SVOCs (m/z of fragment ions < 200)
Participant Burden	This is a small instrument (see specs) and probably makes little noise
Field Burden	can probably be operated remotely
Analytical Costs	capital cost – unknown
Comments	portable MS !
Other References	None

Authors	Moorfield Associates Tel: +44 (0) 1565 722609 ... Fax: +44 (0) 1565 722758
Title	Quadrupole Mass spectrometer Products
Citation	<a href="http://www.moorfield.co.uk/newprodqms2.htm">http://www.moorfield.co.uk/newprodqms2.htm</a>
Matrix	air
Method Type	portable mass spectrometer with thermal desorber (TDS)
Monitoring Time Frame	continuous, long term (?)
Dimensions:	530(w) X 450 (h) X 230(d)mm
	Weight 26 KG
Power Sources:	240V AC or 110V AC at 170W
	12VDC Via Vehicle Adaptor Kit
	12VDC Via Battery Pack
Standard I/O:	4 analogue Outputs
	2 analogue Inputs
	2 digital outputs
	2 digital inputs
Detection Limits:	VOC's: <2 ppb (std) or < 2 ppt ( with TDS)
	Halogens: <1ppm
	General Gases: < 10ppm
Response Time:	<100 ms (capillary)
	<1s (membrane)
	< 90s (TDS)
Operating Modes:	Analogue (raw data)
	Histogram (Survey)
	MID( Ion v Time)
	MCD (Concentrations v Time)
	Task Automation.
PC Requirements:	PC is normally supplied, if a user PC is provided minimum required is Pentium 200 with 1 free com port.
Applicable Chemicals	VOCs/SVOCs
Participant Burden	low (?) Instrument can run unattended
Field Burden	low (?)
Analytical Costs	(capital cost: \$42,000)
Comments	Has been evaluated by EPA ( <a href="http://fate.clu-in.org/gc.asp?tectypeid=44">http://fate.clu-in.org/gc.asp?tectypeid=44</a> )
Other References	None

SECTION 4.0  
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