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Chapter 25

Measurement of Atmospheric Dispersion Using Gaseous Tracers

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Abstract: The use of tracer studies can be a very valuable tool when establishing a model for atmospheric dispersion assessment. Tracer studies are the best and most accurate way to validate and/or verify existing models as well as support the design of a new model. Therefore, the basic components of a tracer study are presented. They touch on equipment as well as certain techniques for performing tracer studies. Then, the dissemination methods of various tracers are addressed along with the collection and analysis for the various tracers. Finally, issues regarding quality control and quality assurance, such as random sampling, are investigated.

Key Words: atmospheric tracers, electron capture detector (ECD), sulfur hexafluoride (SF_6), Perflourocarbon (PFC), dissemination, Fickian diffusion, quality assurance, quality control, model validation, dispersion modeling, calibration, surrogate, chromatograph.

1 Introduction to Atmospheric Tracer Studies

In the modern industrialized world, thorough study of the transport and fate of airborne chemical vapors has become necessary to fully understand the effects of these chemicals on human health and the environment, both acutely and with prolonged exposure. In circumstances where chemical species of interest cannot

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[3] SCS Tracer Environmental is a separate operating group within Sterns, Conrad, and Schmidt Consulting Engineers, Inc. (SCS Engineers, Inc.) as a result of a merger between Tracer Environmental Sciences and Technologies, Inc. (Tracer ES&T) and SCS Engineers on 9/30/2009.

be directly measured (such as when the source no longer exists or has been substantially modified) or must be simulated (prior to constructing an industrial facility, for example) chemical surrogates known as tracers are employed to simulate emissions. Tracers are also utilized to determine the impacts of a single existing emission source where multiple sources may exist. Sample gathering at various receptors in the area of interest followed by quantitative analysis of samples for the selected tracer provides direct measurement of dispersive dilution of emissions from a subject source. Additionally, quantitative tracer dispersion data provides a valuable tool with which to validate and “fine tune” both diagnostic and prognostic atmospheric dispersion models. The scope of application for tracers ranges from microscale, such as characterizing building ventilation systems, to documenting atmospheric transport of pollutants across continents.

Ideally, a suitable tracer would be a chemical species that does not normally occur or is minimally present in the environment to be characterized. It should exhibit physical characteristics similar enough to the chemical(s) of interest to behave as a faithful transport surrogate. Further, an ideal tracer would possess no negative health or environmental characteristics. In addition to its uniqueness in the environment, it should be amenable to unequivocal identification and quantification by accepted analytical practice.

2 Historical Perspective and Application of Atmospheric Tracers[4]

As a result of early above-ground nuclear weapons testing, the long-range effects of atmospheric transport and diffusion of airborne particles became of interest to the federal government as early as the 1940’s. In the 1950’s it was realized that radioactive fallout was an exceedingly complex issue, involving extremely long range transport through the atmosphere and affecting all aspects of the environment (NOAA, 2004). Investigations into the physics of atmospheric transport began to appear in the literature in the late 1950s (Cramer, et al., 1958; Haugen, 1959).

The invention of the electron capture detector (ECD) (Lovelock and Lipsky, 1960) arguably helped usher in the age of environmentalism with its selective sensitivity to pesticides and CFCs (Simmonds et al., 1973). This invention also opened the door to the use of sulfur hexafluoride as a conservative gaseous tracer with limits of detectability in the previously unattainable parts-per-trillion by volume (pptv) range (Turk et al., 1968; Dietz and Cote, 1973). Increasing background levels of SF_6 (Maiss and Levin, 1994) and its identification as a greenhouse gas have prompted the development of methods to utilize fully

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[4] Additional data and information on past tracer studies can be found at http://www.jsirwin.com/Tracer_Data.html

perfluorinated alkyl-substituted cycloalkanes (perfluorocarbons or PFCs) as atmospheric tracers (Lovelock and Ferber, 1982; Dietz, 1987; D'Ottavio et al., 1986; Lagomarsino, 1996). It is likely that the use of SF_6 as an atmospheric tracer will be phased out in the near future due to environmental concerns arising from its high global warming potential (GWP). PFCs exhibit extremely low global background and are detectable at concentrations of parts per quadrillion (ppqv) by volume. Additionally they are chemically inert, thermally stable and non-toxic to the extent that they have been investigated as blood plasma substitutes. (Dagani, 1982).

Perfluorocarbons are the tracer of choice for most atmospheric dispersion studies where a combination of sensitivity and/or the need to simultaneously tag multiple sources is required. Sulfur hexafluoride is still employed for studies over short distances or inside buildings where multiple sources are not required. Short-range tracer experiments (such as for nuisance odor complaint resolution) are frequently performed to define local source-receptor relationships as well as to characterize building ventilation systems. Additionally, PFC tracers have been used to locate leaks in underground storage tanks and underground cabling (Dietz, 1992; Ghafurian et al., 1999). Longer-range transport studies have been carried out in urban areas (Draxler, 1989; Britter et al., 2000; Cooke et al., 2001), within geographical regions (Ferber et al., 1986; Green, 1999; Kim et al., 2002) and across continents (Draxler et al., 1991; Nodop et al., 1998). While the global background of PFCs is extremely low, their global warming potential is extremely high (10^3 to 10^4 times that of CO_2). Their long estimated atmospheric lifetimes of 3,000 to 50,000 years (WMO, 1999) have led to their being called the "immortal molecules." Thus, the future may see the imposition of limitations on their use.

3 Typical Components of a Tracer Study

As with any field project, attention to details, adequate planning, and competent personnel provide for successful execution. To best plan, manage and execute an atmospheric tracer study, it is advantageous to divide the effort into logical technical components. These technical components include:

- Dissemination Methods
- Sampling Systems
- Analytical Laboratory Equipment and Procedures
- Data Processing
- Quality Assurance
- Support Meteorological Measurements

Integrated into these basic technical components are the management steps necessary to properly implement a study. The underlining aspects contributing to the management of tracer studies include:

- Technical Study Design
- Logistical Considerations

- Preparation Phases
- Field Operations
- Quality Control and Quality Assurance
- Budget Control and Project Timeline

Tracer studies require a somewhat different approach than most ambient air monitoring exercises. The challenge begins with the design, such that one properly estimates the correct mass of tracer to be released. This determination may need the assistance of a model, but if the environment in which the test is to be conduct is not easily represented by a model, then other intuitive methods must be used to properly specify the tracer release. Hence, experience plays a substantial role in the proper planning of a tracer experiment. A second challenge arises in designing a receptor network that adequately intercepts the tracer plume to provide appropriate data density within the targeted concentration range. Frequently, scientists with good instrumentation and monitoring skills fail at executing tracer studies because they are inexperienced in mentally visualizing the simulated plume and do not fully understand the limits of their analytical capability. In such instances, the downwind receptor network of samplers is inadequate to capture the plume structure with sufficient data density to provide meaningful and useful results. Additionally, the same inexperience can result in over estimating the tracer release rate, which frequently proves to be a very costly mistake both in terms of tracer released, and difficulty analyzing field samples.

It cannot be over-emphasized that exceptional attention is required to the subject of maintaining separation between dissemination equipment and/or personnel and sampling equipment and/or personnel. When dealing with picoliter and femptoliter range analytical sensitivity it takes little contamination to render samples useless. Contamination of samples is the most common mistake made by those who are inexperienced in conducting tracer studies.

3.1 Tracer Dissemination

Dissemination of tracers consists of two aspects. First, a dissemination rate must be estimated that will provide a concentration at the center of the sampling grid that will be within the sensitivity range of the analytical method used to quantify field samples. This aspect of program design also has economic implications as the release of excessive amounts of tracer equates to higher than necessary program cost.

Second, a means must be provided to ensure that the dissemination rate is accurately controlled and constant throughout the dissemination period. The measurement and recording of actual dissemination rate of tracer chemicals is vital to a successful tracer study and adequate attention needs to be given to these aspects.

Third, it is highly recommend that any equipment, tools, personnel and other test related items that are involved with the dissemination of the tracer chemicals must not come near the sampling and analytical systems of the same experiment.

3.1.1 Dissemination Rate Estimation

Determining the rate at which gaseous tracers will be released in a specific test, generally requires the application of a dispersion model. Using a model to estimate results that will be used to validate that model may seem contradictory. However, model results allow determination of an approximate release rate of the tracer gas such that the expected downwind impacts (from the closest receptor to the most distant) will lie within a targeted concentration range appropriate for the analytical method used. For example, if the analytical detection range is 1 part per trillion to 10 parts per billion, a tracer release rate that provides an approximate 100 pptv concentration at the center of the receptor grid is recommended. This level provides 2 decades of latitude (higher or lower) in the actual concentration measurement, which is generally ample to capture any variability in model prediction.

It is also helpful to work in X/Q space since it is well known that most ambient dispersion situations resides between 1×10^{-4} to 1×10^{-8} sec/m^2. In very near-field dispersion experiments, X/Q values greater than 1×10^{-4} sec/m^2 will need to be considered and very long range studies likely involve X/Q values less than 1×10^{-8} sec/m^2. The ability to successfully quantify this entire spectrum of dispersion ranges depends upon the ability to expand the active range of detection in the tracer analytical capability. Additionally, the ability to reach very low detection levels, enables one to release less tracer chemicals, which provides not only a cost benefit to the study budget, it limits any seen and unforeseen environmental impact.

3.1.2 Dissemination Methods

It is important that tracer vapor be thoroughly mixed either into the ambient air or into an air stream for delivery to a point source such as a vent or a stack. The methods employed for SF_6 differ from those used for the PFCs due to their physical characteristics.

Sulfur hexafluoride is a liquid under pressure as it is normally encountered in steel cylinders. The pressure of gaseous SF_6 above the liquid varies with ambient temperature but is generally between 100 psig and 180 psig. The typical method for dissemination of SF_6 is to control the release of the pressurized vapor by means of a suitably calibrated mass flow controller. This works well with a single cylinder for release rates up to about 5 kg/hour in ambient temperatures warmer than approximately 5-10 degrees Celsius. At higher flows or lower temperatures, the cooling of the cylinder caused by the rapid vaporization of the liquid reduces cylinder pressure, often to a point below that at which the mass flow controller will operate properly. For release rates greater than 5 kg/hour, multiple cylinders are frequently connected to a manifold to reduce cooling in individual cylinders. In extreme cases, electric heating jackets may be required to warm the cylinder contents and maintain cylinder pressure.

The PFCs are generally high vapor pressure liquids. As such, different dissemination techniques are required than are used for SF_6. Dissemination of PFCs requires that the liquid material be vaporized either through direct heating of the liquid or mechanically by the creation of rapidly evaporating micro-droplets. A peristaltic pump is typically used in both approaches to deliver a constant volumetric flow of PFC.

The liquid flow can be thermally vaporized by introducing it to a heated plenum where the vapor is entrained in an air stream that is piped to the desired release location. Alternately, if an ambient release is required, simply dripping the liquid on a heated surface is generally sufficient.

Mechanical means may also be utilized, in ambient releases, to create micro-droplets of the liquid that rapidly evaporate. This can be accomplished by several methods including sonic nebulization or by dripping the liquid PF onto a rapidly rotating serrated disk.

A mechanical balance or strain gauge device is frequently paired with data recording equipment to provide a backup record of dissemination rate and flow history.

3.2 Sampling Techniques

Analyzers that provide realtime concentration data for SF_6 have appeared over the years based on a design by Simmonds and Lovelock (Simmonds 1976). At least one commercial version (Scientech TGA-4000) was available. In their various incarnations these analyzers were expensive and had a reputation for being somewhat temperamental in operation. Since they relied on a stoichiometric reduction of atmospheric oxygen, variations in ambient O_2 concentration with altitude or within confined spaces, for example, resulted in considerable signal drift. Careful attention to flow control and electronic signal processing yielded individual instruments that performed nearer expectations but still possessed unique operating characteristics and performance.

Most atmospheric dispersion studies utilize a fixed network of sampling equipment to acquire time-averaged samples over averaging periods ranging from minutes to several hours. Selection of the averaging period is generally based on the downwind distance at which samples are to be obtained with longer averaging times being employed at greater distances. Shorter averaging times may be advantageous with shorter plume fetches or where it is desirable to characterize plume characteristics such as meander.

For field sampling of SF_6 or PFC, sufficient testing should be conducted to ensure that the sampling systems do not retain a history of past contact of tracer laden air and/or are unable to retain a valid sample over the storage time between sampling and analysis. It is extremely important that the components (tubing, valves, pumps, etc.) of the sampling system not have the inherent capability of adsorbing the tracer chemicals. It is equally important that the materials selected for sample containers not allow permeation of the tracer molecules, thus affecting the tracer concentration over time. Prior to deployment in to the field, all sample containers should be flushed with ultra-zero air to ensure that no contamination is present in any sample containers. Ideally, the final flush of each sample container would be analyzed for contamination but, practically, random analysis is generally sufficient.

3.2.1 Sulfur Hexafluoride Sampling

SF_6 samples are generally collected in inert bags made of Tedlar®. While available in capacities ranging from less than one liter to more than 10 liters, sample analysis requires less than 1 ml of sample (Section 3.3). Thus, the capacity used will be dictated by the characteristics of the sample acquisition apparatus.

The most common portable sampler for SF_6 contains an air pump, valves, and control electronics to obtain multiple samples in a single container. These samplers are generally battery-operated portable devices capable of being programmed for start time, sample duration and sample volume. Samples represent time-averaged concentration over the selected sample duration. Managing the duty cycle of a fixed flow rate pump generally controls sample volume.

A second type of sampler (commonly called a “lung” sampler) consists of a single sample bag mounted in a sealed enclosure whose inlet is connected to ambient air. A pump draws a vacuum on the sealed chamber expanding the sample bag and drawing sample in. The evacuation flow rate can be quite rapid making this method most useful when obtaining nearly instantaneous samples such as those required in nuisance odor studies.

Variations on these methods have appeared over the years and, for example, have utilized disposable hypodermic syringes instead of Tedlar® bags.

3.2.2 Perfluorocarbon Sampling

The extreme sensitivity that PFCs offer is due to their ability to be adsorbed onto suitable sorbent material such as carbonaceous molecular sieve. Thus, several liters of sample can be captured either as a field sample directly on sorbent tubes or in Tedlar® bags whose contents are concentrated onto a specially designed enrichment “trap” connected to the inlet of the laboratory gas chromatograph. The large volume of sample provides an effective increase in sensitivity of a thousand fold or more.

Bag sampling utilizes the same equipment and procedures as for SF_6 described above. Sorbent tube samplers can be either active where a pump draws air through the tube or passive where Fickian diffusion provides the “pumping.” In either approach, the amount of air sampled must be known in order to calculate the concentration of PFC. This can be done in the mechanically pumped version by controlling the flow rate. In the passive sampling approach, a naturally occurring universally distributed chemical species may be used as a marker to calculate sample volume.

3.3 Analytical Methods

Analysis of samples returned from the field is performed by gas chromatography using an electron capture detector (ECD). The ECD exhibits extreme sensitivity and selectivity to halogenated and perfluorinated compounds. Two different sample introduction methods and gas chromatographic configurations are used for analysis of SF_6 and perfluorocarbon tracers. Both methods employ digital data systems to both record and quantify the chromatographic peaks. There are many such systems available commercially both as integral parts of a chromatography system or as after-market devices able to be used with many different gas chromatographs.

3.3.1 Sulfur Hexafluoride Analysis

Analysis of samples containing SF_6 is performed using a fixed-volume sample valve to introduce the sample to the chromatographic column where the SF_6 is separated from oxygen and (depending on the carrier gas used) nitrogen. As the separated components emerge from the column, they enter the ECD where they cause a change in its operating current. This change is amplified and conditioned and the resulting electronic signal processed by a chromatographic data system. A typical chromatogram for SF_6 is presented in Figure 1.

3.3.2 Perfluorocarbon Analysis

The successful use of PFCs as atmospheric tracers is due to both their low atmospheric background concentrations and their amenability to detection at low concentrations by electron capture gas chromatography (Simmonds et al., 1976; DeBortoli and Pecchio, 1985; Lagomarsino, 1996). Direct injection of a sample, as previously described for SF_6, would realize detectability in the low pptv range. Detection limits may be significantly enhanced by utilizing sample enrichment (D’Ottavio et al., 1986; Lagomarsino, 1996).

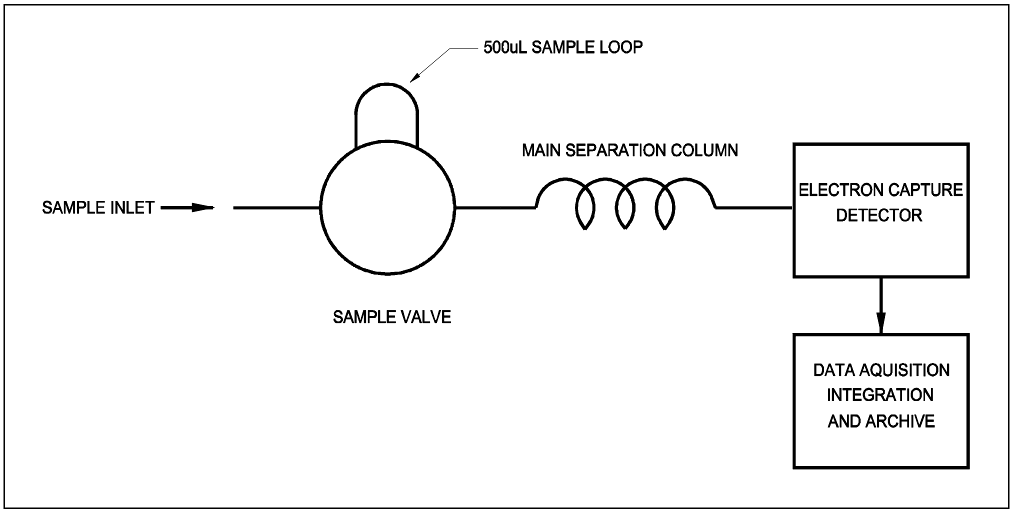
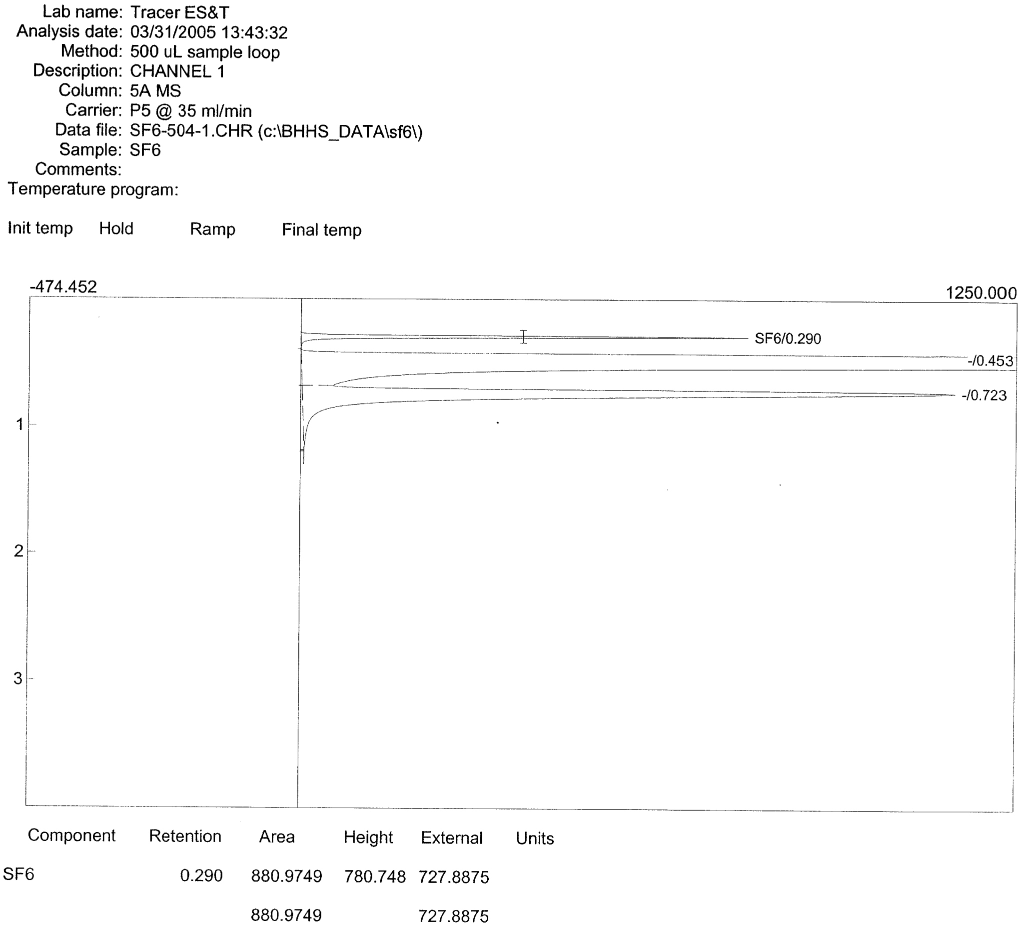


Figure 1. SF_6 Gas Chromatograph Configuration.



Lab name: Tracer ES&T
Analysis date: 03/31/2005 13:43:32
Method: 500 uL sample loop
Description: CHANNEL 1
Column: 5A MS
Carrier: P5 @ 35 ml/min
Data file: SF6-504-1.CHR (c:\BHHS_DATA\sf6\)
Sample: SF6
Comments:
Temperature program:

Init temp Hold Ramp Final temp

Component	Retention	Area	Height	External	Units
SF6	0.290	880.9749	780.748	727.8875	
		880.9749		727.8875	

Figure 2. SF_6 Chromatogram.

A recently developed technique allows detection at the sub-ppqv level (Simmonds et al., 2002). Most perfluorocarbon based tracer studies employ sample enrichment techniques in order to optimize the amount of tracer materials needed to perform the study. This enhancement technique can result in substantial savings in project costs. Figure 3 presents a block diagram of a basic perfluorocarbon gas chromatograph. For analysis of samples taken in, for instance, Tedlar® bags, a controlled volume of sampled air is drawn through an adsorbent trap by a vacuum pump. The total volume sampled is determined by the setpoint of a mass flow controller and a fixed time interval. Perfluorocarbons (as well as other compounds) are adsorbed onto the trap. Several liters of sample may be concentrated in this manner. Returning air to the laboratory for concentration has the advantage of allowing replicate analysis of a sample either for quality assurance purposes or if the need to re-analyze a sample occurs for any reason.

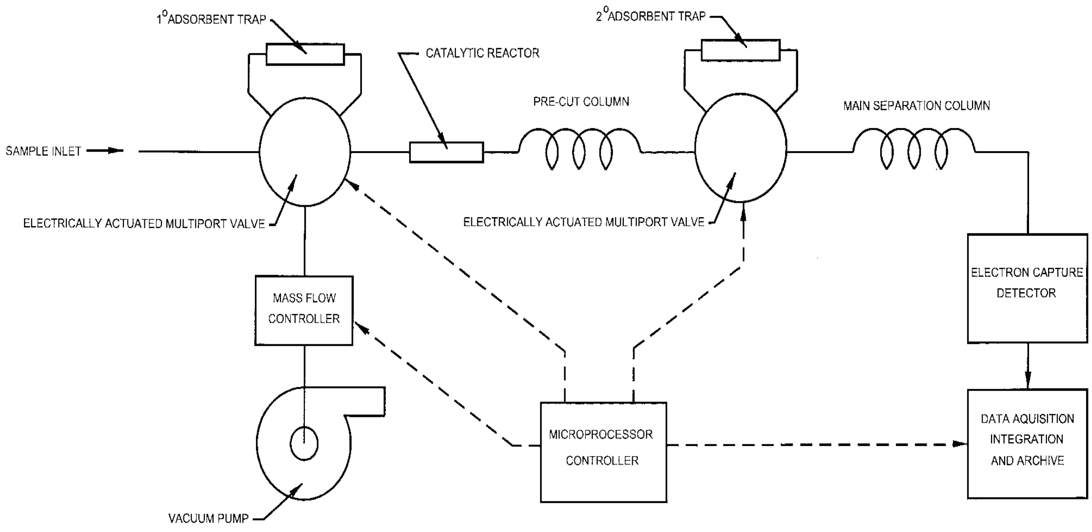
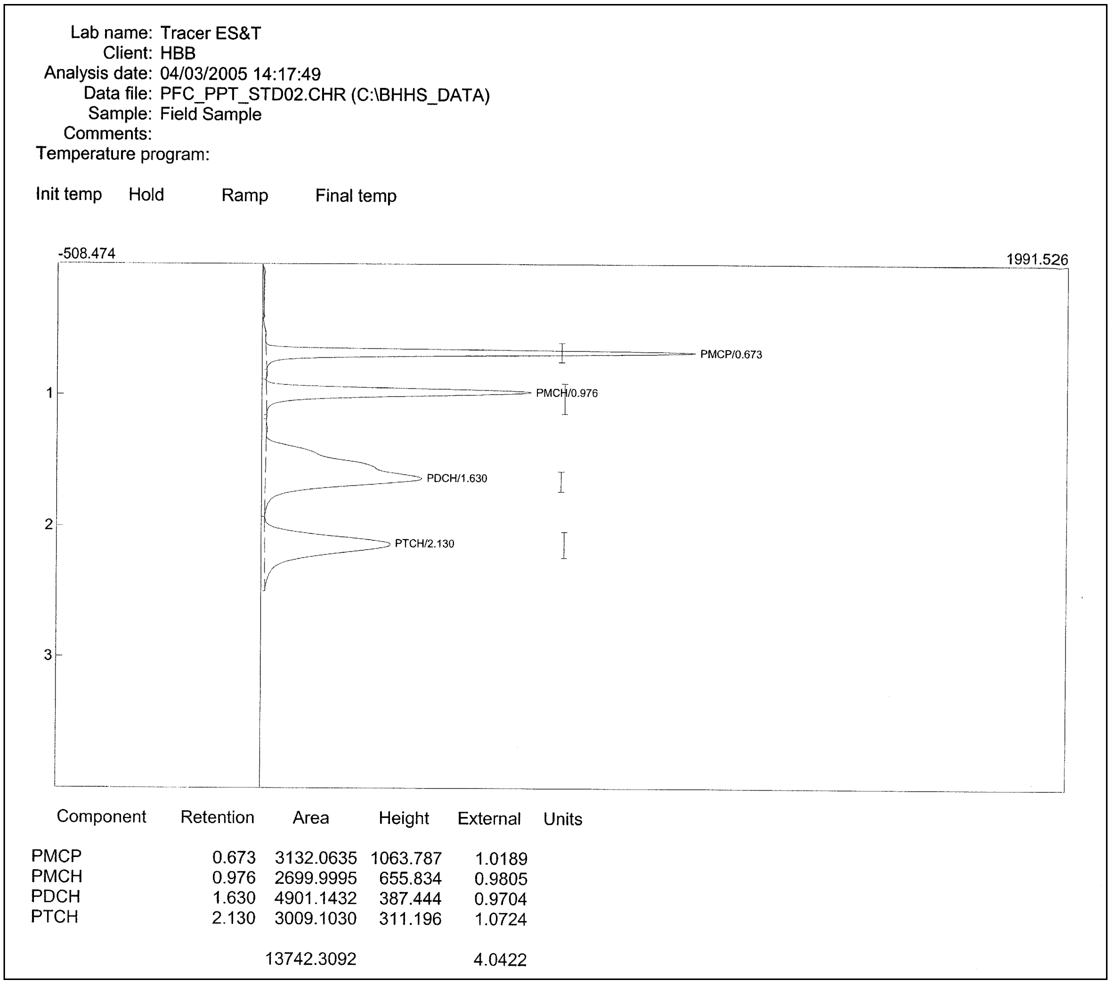


Figure 3. Basic Perfluorocarbon Gas Chromatograph Block Diagram

In the case of samples that have been obtained on sorbent tubes, the chromatograph is configured to allow the sorbent tubes to be connected in the primary trap loop. Sampling devices are available for the inlet of the gas chromatograph that allows several sorbent tubes to be loaded and analyzed under automatic control.

In either method, the primary trap now contains both the desired PFCs and other potentially interfering compounds such as chlorofluorocarbons (CFCs). The trap is rapidly heated to desorb the adsorbed material and the resultant mixture of chemical species is swept by carrier gas through a catalytic reactor where all compounds other than the stable PFCs are destroyed. To provide further isolation of the desired components, the sample passes through a short chromatographic column to a secondary adsorbent trap. The timing of valve switching is such that the flow to the secondary trap ceases after the last tracer of interest emerges from the pre-column. Since all interfering species have been destroyed the secondary trap now contains only the PFCs of interest. This trap is then thermally desorbed onto the analytical column and finally to the ECD.

Figure 4 provides an example of a chromatogram for selected PFCs. It should be noted that this chromatogram was generated using a packed column and provides incomplete resolution of the isomers of perfluorodimethylcyclohexane (PDCH) and perfluorotrimethylcyclohexane (PTCH). This was acceptable for this study and provided high sample throughput. Separation of the individual isomers of PDCH requires an appropriate capillary column.



Lab name: Tracer ES&T
Client: HBB
Analysis date: 04/03/2005 14:17:49
Data file: PFC_PPT_STD02.CHR (C:\BHHS_DATA)
Sample: Field Sample
Comments:
Temperature program:

Init temp Hold Ramp Final temp

Component	Retention	Area	Height	External	Units
PMCP	0.673	3132.0635	1063.787	1.0189	
PMCH	0.976	2699.9995	655.834	0.9805	
PDCH	1.630	4901.1432	387.444	0.9704	
PTCH	2.130	3009.1030	311.196	1.0724	
		13742.3092		4.0422	

Figure 4. PFC Chromatogram

3.4 Meteorological Measurements

Most tracer dissemination studies, especially those in support of numerical modeling, can require a large base of field meteorological data for interpretation of results. Depending upon the specific model being validated and/or confirmed by way of a tracer study, several meteorological parameters must be measured and recorded. The underlying requirement is to obtain enough meteorological data to reasonably enable the reconstruction of wind field conditions coincident with each test trial on a time scale that is at least equivalent to the time averaging used to define the tracer concentration measurements. For example, if the tracer measurements are reported on a 1-hour averaging period, then valid meteorological measurements should have similar 1-hour averages or less. Meteorological sensors should meet EPA-PSD monitoring guidelines. This generally requires that all support wind and temperature sensors must be operated at a minimum of 1 Hz sampling frequency to obtain valid and comparable time averages. Depending upon the complexity of the environment in which testing is conducted, multiple wind and stability sensors may be required to better define test condition micro-meteorology. At minimum, one system at the point of dissemination (if at a fixed position) and one or more systems situated at downwind tracer sampling locations are recommended. In highly complex terrain situations, vertical profiling of wind and temperature is desirable to gain a better understanding of the complex physical parameters affecting the transport mechanisms that drive the tracer plume.

4 Quality Assurance

As with any field measurement program, stringent quality assurance and quality control is required to ensure that the data collected is valid, defensible and accurate. All measurement methods should follow protocols that will ensure traceability to National Institute of Standards and Technology (NIST) standards and/or good engineering practices as called for by ASTM (D-4844, D-3614-07, E-741-00, E-2029-99, D-6196-03, for example). Additional standards and protocols would include Class 4 Protocol for weights and measures. Quality Control procedures should be applied to every aspect of field operations and laboratory analysis. This effort should include the obvious components such as tracer purity and calibration of release and sampling systems. Special attention is not lost on assuring that analytical results meet the highest degree of accuracy and precision attainable. Ample documentation must be collected to ensure the traceability of every data point collected. All samples must have complete chain of custody records and be analyzed in observance of regulatory accepted protocols to ensure precision and accuracy as well as reproducibility.

In addition to chain of custody, quality control efforts for sampling operations should include a sufficient number of duplicate field samples to ensure that the samples collected are accurate and reflective of local conditions. Additional blanks and spiked samples should be introduced into the sample queue as defined in the program QA plan. Replicate analysis of calibration standards during periodic performance checks will provide a measure of system variability. However, random replicate analysis of samples should be performed as a check on the entire analytical process for field samples.

Bulk calibration standards in pressurized cylinders should be produced to NIST traceable standards by a third party. The equipment and techniques required for production of precise dilutions of gases and liquid vapor to the low concentrations used in tracer studies are best left to specialty gas vendors. Certified mixtures obtained from these sources are used in-house to generate a response curve for the laboratory gas chromatograph. The frequency of calibration curve generation and periodic response checks will depend on the analytical backlog. For instance, a continual flow or samples from the field may require the laboratory to operate around the clock for extended periods. In this case, initial calibration curve generation with response check samples every 4 hours will indicate when calibration curve regeneration is required as set forth in the program plan. If samples are returned infrequently, once a week for example, it is advisable to develop a new calibration curve even if the GC had been operational but idle in the intervening period.

The organization that conducts the tracer field study should employ its own QA/QC Program for air measurement systems in general and for tracer projects specifically. Such a program must be designed to maintaining adequate Quality Control (QC) (routine internal checks) and Quality Assurance (QA) (external QC) to assure the provisions of data, which adheres to predefined requirements for completeness, precision, accuracy, representativeness, reproducibility, and comparability. Generally such a QA/QC program, whether it is authored specifically for tracer studies or generally for an ambient air monitoring program, must be tailored from principals found the US EPA's Quality Assurance Handbook for Air Pollution Measurements and define minimum criteria upon which acceptable data will be generated. Program components that are addressed by a QA/QC program include:

- Document Control
- Organization and Personnel Qualifications
- Quality Planning
- Personnel Training
- Pre-Test Preparations
- Material and Supplies Procurement
- Equipment Performance
- Preventative Maintenance
- Calibrations
- Configuration and Inventory Control
- Corrective Action
- Sample Collections and Chain of Custody
- Data Handling and Analysis
- Data Validation
- Audit Procedures (in field and in lab)
- Quality Reporting

5 Data Management Techniques for Tracer Studies

Accurate and accountable data management is essential to the success of any tracer study. Typically, a tracer study will generate thousands of data records that require verification and validation. Therefore a system of keeping track of every data point regarding a field sample is very important. When conducting a tracer study the flowing parameters are important relative to each air sample collected:

- Date and time
- Exact location
- Type of Tracer
- Tracer Concentration value
- Analytical and sampling support data (calibrations, etc.)
- Confirmed units of measure

Generally, there are also several accompanying data sets that merge with tracer data. These include tracer release rates (confirmed measured values) and coincident meteorological data. The common aspect of all these data sets is the time/date when the data was generated.

Spreadsheets are very useful in organizing data sets as we have found that database programs are somewhat overkill. Spreadsheets are highly transportable, flexible and allow for a variety of presentations and applications.

6 Applying Tracer Data to Validation of Model Performance

One of the primary purposes in conducting tracer field studies is to generate a unique database of field measurement data that can be applied to gauge the performance of candidate atmospheric dispersion models. It is well known that models, both proprietary and public domain, may not be capable of addressing all dispersion scenarios with similar accuracy and precision metrics. Often times, models are applied to situations and settings for which they were not designed and under such circumstances performance is unknown. Under such circumstances, scenario specific tracer data can be used to evaluate the performance of candidate models to enable the selection or validation of the appropriate model. When such evaluation is necessary, it is recommended that the analyst follow ASTM D6589-05 (Standard Guide for Statistical Evaluation of Atmospheric Dispersion Model Performance) (ASTM, 2005). Additional validation and calibration techniques are discussed by Canepa and Irwin (Canepa and Irwin 2005).

While there are many components to a model evaluation effort (ASTM, 2005), an important step is statistical evaluation with field data (usually defined to be tracer data). The basic approach is to compare field observations or measured data of selected chemicals (tracers) with modeled values of the same parameters under an identical scenario. The model that depicts the smallest bias and deviation with regard to field data is usually the best candidate. But other issues come into play, such as comparisons with other models, particularly those models that are more widely accepted in the peer review process, scientific peer reviews, software reviews and sensitivity analysis. Information for all these evaluations provides for a good understanding on the limitations and applicability of the model of choice.

Conducting field studies in support of meaningful model evaluations, much uncertainty exists in defining how much data should be generated. Sampling or Estimation Theory (Walpole, 1972) is a useful tool in determining a valid sample size with which to represent a situation or scenario within a predefined confidence interval. We have found that to achieve the equivalent of a measured annual average within a 90% confidence interval for a selected meteorological scenario (wind-speed, stability, etc.) nearly 800 to 1,000 parameter-hours of tracer data may be required. Hence, with 30 samplers, this would mean approximately 25 to 30 hours of data (hourly averages) would be required. With lower confidence level requirements, such as 80% or less, substantially less data is needed (Larsen, 1971).

Sampling array design is another critical aspect of a tracer study design. Generally, a test is conducted with downwind arrays comprised of fixed arcs at select radial distances. In such test designs, there is uncertainty in defining how densely to place the samplers on each arc. We have found success in using a simple Gaussian model to determine the expected width of an instantaneous plume at each arc position under neutral to slightly stable conditions. It is then recommended to design the sampler spacing density such that at least 3 samplers will always be in the modeled plume, simultaneously. Furthermore, the angular range of the array on each arc should match the expected angular range of wind direction anticipated during the field-testing plus the angular width of the previously modeled plume. This will ensure that all samplers will probably be able to sample the tracer plume within the design sampling time interval.

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