

SECTION 1.0

INTRODUCTION

The Clean Air Act Amendments of 1990 renew and intensify national efforts to reduce air pollution at a level that surpasses all previous efforts in environmental regulation. The Amendments, as set forth, list 189 hazardous air pollutants, also called air toxics, and require the Environmental Protection Agency to promulgate new control standards for the principal sources of such emissions. These 189 hazardous air pollutants are chemicals that were not previously regulated under the National Ambient Air Quality Standards, that applied to a small number of the most common pollutants. The requirements of the Clean Air Act dictate immediate sampling and analysis to obtain data for the determination of emission factors. These emission factors will be used to determine control measures. However, since many of the analytes listed in the Clean Air Act Amendments of 1990 have not previously been regulated, the fundamental questions of how to sample and analyze to produce data of a quality sufficient to achieve the objective of emission factor determination must be addressed.

Before any testing of stationary sources is conducted, it is desirable that a written sampling and analytical protocol be available to ensure that data acquired during source testing are accurate and of known quality. Alternatively, validation of a proposed sampling and analytical methodology can be performed according to EPA Method 301.¹ Because of the concern over the presence of low concentrations of these 189 hazardous air pollutants in air, existing sampling and analytical methods were reviewed in order to determine the applicability of these methods to the 189 hazardous air pollutants. For some of these hazardous air pollutants, the existing sampling and analytical methodologies are directly pertinent to the analyte of interest in emissions from stationary sources, and the performance parameters for the compounds have been completely defined. For some portion of the 189 hazardous air pollutants, data were available to substantiate, at least in part, performance of an analytical methodology, but no information was

available in the literature to establish whether the compound could be sampled quantitatively. For a significant percentage of the list of 189 hazardous air pollutants, assignment to a sampling and analytical methodology could be made tentatively only on the basis of chemical or physical correspondence to other compounds which have been sampled and analyzed with the methodology. For most of the 189 hazardous air pollutants, sampling and analytical methodology available at the present time can serve only as screening methods to establish presence or absence under a given set of conditions.

There is a great deal of concern in assigning analytes to any given sampling and/or analytical methodology, since definitive information that the specified methodology is actually effective for the analyte in question does not exist. The following concerns must be satisfied when a methodology is applied:

- Does the sampling methodology sample the analyte effectively and quantitatively?

Some of the areas which cause concern are: If temperatures in a sampling train are not high enough, some analytes may not reach the sampling medium. A given analyte may not be retained quantitatively by the sampling medium of the train. An aqueous impinger as a component of a sampling train may cause decomposition of some analytes. There are many other problems which can occur in conjunction with sampling which may render a sampling methodology incapable of quantitative sampling for a given analyte.

- Does the laboratory sample preparation methodology transfer the analyte quantitatively from the sampling train to the analytical instrument?

Some of the areas which cause concern are: Analytes may not be extracted quantitatively from the sampling media under the standard analytical conditions of a given method, analytes may decompose in the handling of the samples, analytes may react with other analytes or with reagents used in the sample preparation

process, or analytes may be lost in a concentration step. There are many other problems which can occur in the process of sample preparation which can result in the inability to generate quantitative and reproducible data.

- Can the analytical method produce precise, accurate, and quantitative results for all of the analytes in question?

Some of the areas which cause concern are: Analytes may decompose in the analytical process or may react in the course of analysis, analytes may not be amenable to a given method of analysis because of polarity, volatility, or other properties, analytes may require modification such as derivatization for optimum analysis, or other chemical or physical properties of the analytes may cause poor or unsuccessful performance of the analytical methodology.

To sample and analyze constituents of emissions from stationary sources adequately, it is necessary to define the quality objectives which are required for the measurement. If the data quality objectives require the use of a validated methodology, the proposed method must be qualified. The only way to be assured of successful data from a given sampling and analytical methodology is to have a method which is validated for the analyte of interest. The sampling and analytical parameters which require definition in order to have a validated methodology are the bias (systematic error) and precision (random error). When these parameters have been defined for a given hazardous air pollutant in a particular sampling and analytical methodology, the methodology is validated: that is, the performance of the entire sampling and analytical methodology under field conditions has been evaluated. To validate a method for a given analyte, the following procedures must be performed:¹

- A known concentration of an analyte must be introduced in the sampling procedure and carried through the entire sampling and analytical procedure to assess the bias of the proposed method;
- Alternatively, the proposed test method may be compared against a previously validated test method in order to assess bias; and

- Multiple or collocated simultaneous samples must be collected to determine the precision of the test method.

Sampling procedures have been established which will allow the determination of the bias and precision of data from field testing. These approaches include:¹

- Isotopic spiking, for analytical methods that require gas chromatography/mass spectrometry (GC/MS) for analysis;
- Comparison against a validated test method; and
- Spiking of the analyte.

In these approaches, procedures have been specified to perform the spiking and obtain a sufficient number of spiked samples to allow statistical determination of the validity of the proposed test method.¹ When these precision and bias parameters have been established, a methodology is considered validated for a particular compound and a particular type of source.

The ultimate goal of both the regulatory and the regulated communities is to have validated test methods available for any analyte which may require testing. However, the need for information is immediate since the Clean Air Act Amendments have been passed, and completely validated test methodologies are presently available for only a small number of analytes. The regulatory requirements will not allow the gathering of information to be deferred until validated test methodologies are available for each of the 189 hazardous air pollutants, nor are resources available for the Environmental Protection Agency to provide validated methodology for every possible analyte. It will therefore be necessary to use methodology which presently exists to gather screening information for the broadest possible number of analytes, until broad-based methods are validated for large numbers of analytes. The purpose of the catalog of methods

presented here is to identify methods with the broadest possible applicability to the 189 hazardous air pollutants listed in the Clean Air Act Amendments of 1990. Many single-analyte methods are already validated for specific source categories, but the focus of this document is screening methods with broad coverage.

Under this program, the literature has been surveyed to determine the applicability of existing methodology. The primary goal was to use methodology applicable to the largest number of analytes listed in the Clean Air Act Amendments, with the full realization that a broad coverage by a methodology may require some sacrifice of sensitivity and accuracy. Specialized sampling and analytical methodologies may be available to apply to a single analyte, for example, or to one particular family of analytes. If a survey method is used instead of a specialized methodology, detection limits will be higher and there is a risk that trace quantities of the analyte in question will not be observed. On the other hand, if the survey methodology indicates the presence of significant quantities of an analyte for which a specialized methodology is available, an informed decision can be made on whether to use the specialized methodology in subsequent testing. The need for validation of proposed methodologies has been recognized. Assignments of analytes to a specific methodology have been made on the basis of previous validation studies and/or physical properties (available physical properties for the chemicals of the Clean Air Act list are supplied in Appendix A). The range of applicability of a given sampling or analytical method, when available, is included as a part of the method description in Section 3.0. Section 2.0 includes several tables which summarize the potentially applicable sampling and analytical methods for chemicals listed in the Clean Air Act Amendments. Section 4.0 provides some general information on cost for the sampling and analysis procedures. The appendices provide a listing of available physical properties (Appendix A), a summary of NIOSH and OSHA methods and applicable analytes (Appendix B), and a listing for the Clean Air Act list analytes from the Problem POHC Directory, prepared by Southern Research Institute² (Appendix C).

When a sampling/analytical methodology is selected for a given analyte or group of analytes, the first priority should be given to the use of existing Federal Register methods (40 CFR Parts 60 and 61) which have been validated specifically for the analytes of interest in stationary sources. A secondary priority in selection of methods should be given to existing Federal Register methods for other programs such as OSW RCRA trial burns. A tertiary priority is assigned to methods from state agencies or other Federal agencies such as NIOSH or OSHA. The lowest level of priority in selection of sampling/analytical methods should be given to methods which are research candidates, draft methods, or test methods, which have possible applicability to the analytes and matrix but have no validation data available.

Many of the sampling and analytical procedures need additional development and validation efforts to improve accuracy and precision. It should be stressed that a method which requires validation is not an inferior method; the method simply requires additional experimentation to define precision and bias. The performance of the method for a given analyte and source may be entirely acceptable, but until validation data are available, the user cannot know that the performance of the method will be acceptable prior to use.

Methods cited in this document are presently in use, regardless of validation status. Remote sensing techniques, such as Fourier Transform Infra-Red and Fourier Transform Ultra-Violet, have potential as emission inventory and air toxics factor measurement methods. Air toxics emission rate analysis using remote sensing measurement methods has not been validated at this time, and extensive field testing is required to establish accuracy and precision for these methodologies. Newer surface analytical techniques to measure semivolatile and condensable toxic air pollutants that may be associated with particulate materials (especially PM-10) are also being investigated. Present techniques for sampling and analysis require laborious, time-consuming, and costly extraction procedures to concentrate and analyze toxic organics on

particles. Some of the newer instrumental techniques such as laser-induced mass analysis or time-of-flight techniques may prove feasible for future air toxic analysis.

1.1 References

1. Method 301, Protocol for the Field Validation of Emission Concentrations from Stationary Sources, EPA 450/4-90-015. Effective February 1991.
2. Problem POHC Reference Directory, EPA 600/3-90/094, Effective January 1991. Prepared by Southern Research Institute.