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Program Objectives and Status For the U.S.EPA Program on FTIR-Based Open-Path Monitoring

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ABSTRACT

The Office of Research and Development of the U.S. EPA supports a methods development program for FTIR-based, open path monitoring of trace gases in the air. This type of system provides an estimate of the average concentration of individual trace gases over distances up to approximately one kilometer by interpreting changes in the infrared absorption spectrum. The EPA program has four objectives. The first is to develop a guidance document to explain the nature of these systems, their uses, and their performance-limiting features. The second is to provide a method describing recommended procedures for operating the systems to take data; the third is to support an international effort by L'Organisation Internationale de Metrologie Legale (OIML) to specify acceptable performance levels for commercial FTIR-based systems, and the last is to support the development of a library of reference spectra in the infrared at the National Institute of Standards and Technology (NIST). These objectives are completed or in progress. Current year emphasis is on the review and release of the TO-16 methods document that is intended for publication as part of the EPA's Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.

INTRODUCTION

The use of open path optical techniques for monitoring of trace species has some unique and compelling advantages. One of the most important is that no sampling is required, and questions of sample integrity that almost always plague point monitors are avoided. Another is that multiple trace species can usually be analyzed concurrently by interpretation of the spectral measurement data. The National Exposure Research Laboratory, U.S.EPA has the objectives, among others, of characterizing exposure to trace species and of developing databases to support modeling of atmospheric processes. Because of its potential advantages, open path monitoring is being evaluated, and cooperative arrangements with industry have been established to encourage commercial developments and interest in this area. One of the areas of interest is the use of Fourier Transform Infrared (FTIR)-based open path monitoring. This technique is of particular interest because of the occurrence of the spectra of many trace gases in the middle infrared. However, water vapor and carbon dioxide absorption in this spectral region interfere with straightforward quantitation. The process leading to a determination of

trace gas concentration therefore represents a challenge in detecting compounds at trace levels as they disperse from sources or are formed in the environment. At the current stage of development, the main application for these systems is fence line monitoring around industrial emission sources or near other concentrated sources of pollutants. The EPA is supporting the development of commercial systems through evaluation studies and the interpretation of data taken with these systems. These efforts have resulted in the publication of information products and in the support of complementary efforts in the international area by the L'Organisation Internationale de Metrologie Legale (OIML) and by the National Institute of Standards and Technology (NIST).

The current year interest is on the completion of the initial version of TO-16, which will be published as a methods guidance document in an updated version of the EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. During the last year, the initial draft of this document has been reviewed by the AO1 committee of the Air & Waste Management Association (A&WMA) and a revised draft has been prepared for EPA clearance.

COMPONENTS OF THE U.S.EPA's PROGRAM

FT-IR Open Path Monitoring Guidance Document

This document was first printed by ManTech Environmental Technology Inc. as a report submitted to the EPA sponsor in March, 1993 and then in a revised form in February, 1995. A further revised form was published in April, 1996 as an EPA/Office of Research and Development document with the document number EPA/600/R-96/040 (1). Pending the availability of funding, this document will be further revised by ManTech and will include guidance on the use of gas cells to establish system response to known trace gas concentrations. Other topics to be covered include a more detailed treatment of water vapor interference in FTIR-based measurements. New insights with respect to existing topics will also form the basis for revisions.

TO-16 - Long-Path, Open-Path Fourier Transform Infrared Monitoring of Atmospheric Gases - Discussion of Comments on Draft TO-16

The Chairman of the AO1 Committee of the A&WMA, Dr. Bob Spellicy, agreed to coordinate the review of the draft TO-16 document and to provide Dr. George Russwurm of ManTech Environmental Technology (the EPA in-house contractor) with the results of the review. Dr. Russwurm provided the draft TO-16 document in September, 1995, and completed a revision in October, 1996. This draft revision is being distributed at this meeting and is being submitted for EPA clearance prior to official distribution. TO-16 will also be included for the first time in an updated version of the EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, due for publication in the first quarter of 1997. The revision includes reviewer comments and some additional information developed after the 1995 draft was completed. Some of the method guidelines that were considered during the revision are:

Performance-Based Guidance. The method must provide performance-based guidance which could be incorporated into standard operating procedures (SOPs) created by the user for specific applications. As a result, no specific software packages, instrumentation packages, or operating systems are mentioned in TO-16. The general analytical approach using classical least squares (CLS) fitting is retained, while other competitive techniques are discussed as potentially equivalent and possibly better. The CLS approach is explained in its most generic form, referring to any software package that incorporates the principles embodied in the mathematical formalism for CLS as presented

by Haaland (2). This approach is in keeping with EPA's general policy of documenting an approach that is known to work but allowing that equivalent methods can be used if they can meet performance objectives.

Automation of Systems. The method should explain the steps in obtaining quantitative data with the FTIR-based systems while leaving the automation of these steps to the operator/manufacturer. The commercial incentive to provide automation is definitely present in this case and will depend on the cooperation of operators and manufacturers. Automation of this type is already available for some systems and the offering companies enjoy a commercial advantage by virtue of it.

Adding a List of Examples to the Text. A listing of specific examples of applications for FTIR-based systems was considered to be beyond the scope of this document and, if attempted, might compromise the completion and eventual improvement of TO-16. Such a document has been discussed previously with members of the AO1 committee, but as a review appropriate for a journal article.

Sequence of Procedures. In some cases the order of performance of a procedure, e.g., generating a background spectrum, requires the results of another procedure which may not have been explained yet, e.g., accounting for spectral shifts. A subsection entitled "Additional Procedures Referenced" has been added to direct the reader to the information needed from another place in the document.

Revision of Section 8 - Specific Standard Procedures. The original Sections 8.2 and 8.3 have been revised. Section 8.2 of the revised draft is a statement of a general procedure for the generation of concentration data, and Section 8.3 combines the original sections 8.2 and 8.3 to give the recommended approach to developing both a means of identifying a spectral analysis region appropriate for a given target gas and a means for accounting for interferences.

Background Generation. Alternate means of background acquisition and use are now included as part of Section 8 since in some cases (such as isolation of a nearby emission source contribution from other sources) the synthetic background approach is not the method of choice. The generation procedure for synthetic backgrounds is however still considered challenging and ways to simplify the procedure are continuing.

Water Vapor Reference Spectra. Field-generated water vapor reference spectra are indispensable for attempting quantitation so their generation has been emphasized in TO-16. Although the possibility of providing some minimum number of clean water vapor reference spectra with TO-16 has been considered, at this point TO-16 is envisioned as part of a large volume containing the seventeen TO documents and no supplemental materials.

Dealing with Spectral Shifts. Depending on the width of spectral absorption features of the target gas, correction of spectral shifts may not be necessary. A discussion of the importance of spectral shifts is provided, showing that the wavenumber shift of the target gas absorbance spectra must be considered relative to the full width half height (FWHH) of the absorbance feature used for analysis and to the error in measurement acceptable under the data quality objectives (DQOs) for the specific project. Deutrated water vapor (HDO) lines have been suggested as a reference point for determining spectral shifts in one spectral region with the possibility of shifting field spectra as they are acquired. However, no general consensus has been achieved in the user community as to the actual reference lines to be used.

Dealing with Stray Light and Background Radiation. Stray light is not a problem when its contribution is low, which is the most frequent situation. The analyst has to determine if stray light is a problem in a particular system; coadding spectra over a half hour period to define the stray light (in the

absence of variations other than random fluctuations) is recommended.

Production of a Recommendation on FTIR Spectrometer Systems by the Working Group for the OIML Technical Committee 16 on "Instruments for Measurement of Pollutants"

EPA has supported the effort by the OIML Technical Committee 16, under the leadership of Sam Chappell of the NIST, to complete the first committee draft OIML recommendation "FTIR Spectrometer Systems for Measurement of Air". This document has been formulated and has been distributed to the OIML member nations.

Support of the NIST Spectral Reference Standards Program Directly and Through the A&WMA Spectral Reference Standards Subcommittee

EPA has encouraged the NIST to generate a set of reference spectra for general use, much the same as NIST Standard Reference Materials are used. Interest in this project was formalized at the 1994 Optical Sensing Symposium with the formation of the A&WMA Spectral Reference Standards Subcommittee. Based on initial discussions with Walt Lafferty and his co-workers at NIST and their successful efforts at finding internal NIST support, Pamela Chu of the NIST is now leading a program to develop this data base. She has recently provided an update of progress at the 1996 Annual Meeting of A&WMA in Nashville, TN (3). Table I shows a list of the first twenty target compounds chosen for analysis by NIST and is current as of this date. As originally projected, the spectra for ten of these compounds were completed in the FY96. The availability of these spectra, their format, and who the distributer will be are topics being decided at the NIST. The initial indications are that the spectra will be provided in an ASCII format suitable for all users along with a software package to degrade the spectra to match spectra at different resolutions.

CONCLUSIONS

The EPA-sponsored program on the use of open-path FTIR-based systems for monitoring of trace species is in place, with the distribution of the draft version of the methods guidance document TO-16 as of November, 1996. The guidance deals with most aspects of field monitoring, leaving however, some few issues such as the use of short in-line cells (for checking performance) to the discretion of the system operator as an open issue. The development of additional guidance information is planned in the near future. A strong emphasis is placed on quality assurance, with many individual checks on system performance as specified in Section 9 of the document.

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Dr. George Russwurm and Dr. Hunter Daughtrey, Jr. of ManTech Environmental Technology, Inc., Dr. Pamela Chu of NIST, Dr. Sam Chappell of the NIST, Dr. Bob Spellicy of Radian International, and Dr. Bill Herget are acknowledged as having provided the major part of the information making this presentation possible.

DISCLAIMER

This article has been subjected to review by the U.S. Environmental Protection Agency and cleared for publication. Mention of trade names of commercial products does not constitute endorsement or recommendation for use.

REFERENCES

1. G.M. Russwurm and J.W. Childers; *FT-IR Open-Path Monitoring Guidance Document*, EPA/600/R-96/040, U.S. Environmental Protection Agency, Research Triangle Park, NC 1996.

2. Haaland, D.M., and Easterling, R.G. *Appl. Spectrosc.* 1982 36, 665-673.

3. Chu, P., Rhoderick, G.,Wetzel, S., Lafferty, W. and Fuenther, F., "A Quantitative Infrared Database of the Hazardous Air Pollutants," 1996 Annual Meeting of the Air & Waste Management Association, Paper 96-TA26A.05, Nashville, TN.

TABLE I. NIST INITIAL TARGET COMPOUND LIST*

This column completed FY96	This column under study
Methanol	trans 1,3-Butadiene
Ethanol	Ethylene oxide
Acetonitrile	2-Propanol
Acetone	Acrylonitrile
Propylene oxide	Methyl t-butyl ether
Methyl ethyl ketone	Vinyl acetate
Benzene	Ethyl acetate
Toluene	Ethyl t-butyl ether
Ethylene	N-Butanol
Sulfur dioxide	Ethyl acrylate

*Provided by Dr. Pamela Chu of the National Institute of Standards and Technology.

Key Words: FOURIER TRANSFORM, INFRARED, OPEN-PATH, ABSORPTION

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