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Project Summary

Evaluation of a FTIR Mobile Source Measurement System

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An initial evaluation was made of a prototype Fourier transform infrared spectrometer on its ability to measure mobile source emissions. This prototype represents the commercialization of Research Technology developed by the Ford Motor Co. The system utilizes a Mattson Instruments Co. interferometer coupled to a Masscomp computer. The required software is still incomplete. This has resulted in the inability to correct errors or optimize results. Unreliability of both hardware and software has been a major shortcoming of this system. When operating properly, the system measures carbon dioxide, nitric oxide, and formaldehyde accurately, both when compared to bag analysis and on direct point-by-point comparisons with real-time data. Carbon monoxide is measured low, whereas methanol is about 35 % high. Real-time analysis appears to be available for a variety of other compounds such as ammonia, hydrogen cyanide, nitrous acid, nitrous oxide, formic acid, a number of individual hydrocarbons, etc. Completion of the evaluation awaits the final software translations and improvements in reliability.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

There is a need for improved analysis of organic species that may be emitted from mobile sources. Ideally such measurements would include analysis already made and be flexible enough to add additional measurements in the future. Fourier transform infrared spectroscopy (FTIR) has shown the potential for providing such analysis.

Two groups have demonstrated the direct application of this technique to the problem, (l) Nicolet *in conjunction* with Volkswagen and (2) Ford Motor Co. Ford has licensed their technology to Mattson Instruments for use on their brand of FTIR instruments. The Ford system was better developed and had superior characteristics in selectivity and limits of detection. The Nicolet system uses a more classical approach. The Ford system uses multiple wavelengths, and matrix deconvolution by subtractive procedures. Because this approach uses multiple wavelengths, it should be more specific. This approach has the limitation in that the multiple wavelengths used may overlap those used by other compounds. The choice of an absorption band within its linear range of response is important. The combination of wavelengths chosen are called masks. A compound that has a wide range of concentrations in various situations will have multiple masks, each with a different set of wavelengths and their corresponding absorption coefficients.

The Office of Mobile Sources, Office of Air and Radiation of the US EPA has become very interested in this technology to solve or reduce several analytical problems associated with the use of alternate fuels. Of particular interest is the analysis of formaldehyde and methanol. Ford Motor Co. has also sought to have the technique recognized as an approved alternative to the classical analytical procedures.

In addition, the FTIR technique has potential in the research and characterization of mobile source emissions. It can quantitate components not normally sought and, if the spectra is known, identify new components not previously identified. This can be accomplished in real time, as the emissions are occurring. This allows the evaluation of emission control systems and their temporal effects, (when do they start/stop working, etc.), as has been demonstrated by Ford Motor Co.

To perform this evaluation, NSI was authorized to procure an appropriate system.

This system as received in April 1988 was very incomplete. Ford had initially developed the system on a spectrometer that it had built which utilized a DEC PDP 11/40 computer to process the data. They subsequently purchased a regular Mattson Instruments spectrometer and adapted some of the software to it. They have since received a unit identical to ours but generally use the older systems.

When Mattson Instruments began to use the Ford software on their equipment they found that their normal computer was too small. A Masscomp Computer was used that had far superior speed and central processing unit capabilities. The memory and bulk storage capacity of the unit we received has been shown to be still too small. A software problem occurred when Masscomp updated its operating system, which is a version of UNIX. Such updates occur fairly frequently and the new versions are often not upwardly compatible. Such updates must be installed because Masscomp can not guarantee to deliver another unit capable of operating on the old operating system. This problem will continue until Mattson Instruments can supply further orders for the specific computer. This has necessitated two rewrites of the software.

The FTIR was expected to analyze the regulated mobile source emissions as well as a wide variety of other emissions. These measurements were expected to be made in real-time and in the batch mode on bags. Initially the unit we received could not perform real-time analysis or even continuous analysis for a short period of time. During this period we were only able to exercise the instrument on calibration and similar tests. Unfortunately continual problems with the spectrometer have resulted in a very poor service record. These problems appear to be related to the basic spectrometer.

After the updated software was received at the end of September we were able to start a reasonable evaluation program. This program has been inhibited by software limitations, largely because software has not yet been translated. This problem is addressed in the full report.

Initial evaluation of the FTIR system in relation to analytical results from simultaneously collected bag samples showed that the system, as configured, correctly analyzed carbon dioxide, nitric oxide, and formaldehyde. Carbon monoxide appeared to be about 10 % low. This discrepancy probably occurred because the best mask range could not be used. This mask contained an error in its construction and the software that allows creation and editing of masks has not yet been translated. Methanol results were 35 % high. The analytical signal was noisy. These problems may also be mask related.

The FTIR system was compared with our other analytical techniques on a real-time basis. The results were fully compatible with those described above. With this technique, comparison can be made of the emission rates of individual compounds and concurrent measurements such as catalyst temperature. Many emissions such as formaldehyde have a reasonable noise level between 0.1 and 0.2 PPM. It was possible the follow the emissions of nitrous oxide, ammonia, methane, ethylene and propylene. The hydrocarbons agreed well with concurrent gas chromatographic analysis of bags. Acetylene was measured at about half the level measured by the GC, whereas consistently high values for ethane and 1,3-butadiene were reported by the FTIR.

Other compounds sought but not seen in significant concentrations included nitrogen dioxide, nitrous acid, hydrogen cyanide and formic acid. Most of these compounds had acceptable noise levels in the very low PPM range.

Conclusions

The system appears to have a large potential for utilization in both routine emissions measurements, where it could replace several instruments currently used, and in research evaluations of fuels and vehicle emissions. The ability to adapt the basic routine instrument to analyze additional compounds that mig be required due to changes in technolo is very attractive. This would require or a change in the mask set utilized. N change or addition of instrumentati would be required. This potential must l further explored.

The research potential of the system large. The emission rate of individu components may be followed ar evaluated. This capability requires on that they have a reasonably intense ar specific infrared spectra.

The system evaluated is a prototyp system that is still incomplete. It is nc apparent that a larger hard drive and larger mass storage system are nece sary for the archival storage of th spectra for future evaluation.

Hardware reliability is a major issu The system rarely operates for more th a few weeks at a time without th necessity of service. The problems whic appear to be in the spectrometer a inexplicable because the basic hardwa is the same as that in the top of lir version of the Mattson Instruments con mercial system. According to Mattson di ferences between our system and th commercial system are in the comput and its peripherals.

Software deficiencies fall into sever categories and each have their ow priority.

Software reliability must be improve to a point where the system will operat properly when started.

The software is not currently use friendly, which would be required f routine application by non-spectrosco ists.

It is highly desirable that the system b operable in the multi-user mode.

It is also desirable that data display an processing be allowed during dat acquisition.

The ability to create, edit, and modi masks is a requirement for a workin system. This ability is currently availab only through the Ford Motor Co. and th use of their initial system.

The system has no graphics capabilit It would be desirable to be able to pl spectra on the screen and to manipulat these spectra. Currently, spectra ar created, stored, translated and can the be transmitted for external hardcop plotting. Spectral subtraction is the onl function available for spectral manipu lation. This function is extremely awkwar and time-consuming to use because the external plotting requirement, whic requires that, for each subtractive itera tion, the resultant spectra be create translated, transferred and a hard cop plot created. Baseline correction and smoothing are examples of common spectral tasks that can not be performed. Such functions are highly desirable if optimal utilization is to be made of the unit.

The default mask set should be changeable. With its current default mask set, the system comes up ready to test cars operating on ethanol. This mask set must be changed each time the system is started.

Multiple masks are required for compounds which are present over a wide range of concentrations. The system can now use only one mask per run. If the concentration of an individual component varies over a wide range, reprocessing the data with multiple masks and selecting the "appropriate" data from each data set are required. An "automatic span" selection of the appropriate mask is highly desirable.

The system does not reprocess data automatically. If an FTP is to be reprocessed with a separate mask set, each scan must be recalled individually, more than 600 scans for the three bags of the Federal Test Procedure. This is not practical and should be changed before the system is finalized.

The restrictions to 512 scans and the 3 s per scan are inhibiting.

The current system is restricted to real-time analysis by the software available. This is very limiting.

Recommendations for Future Work

These recommendations assume that the appropriate software and hardware modifications to make this a practical working system will be made within a reasonable period of time. Because the effort is considerably larger than apparently had been envisioned by Mattson Instruments and Ford, a maximum effort to cooperate and encourage completion of this work should be continued.

The current evaluation is incomplete. As the software/hardware is updated each change must be evaluated for efficacy and reliability.

The currently available masks, that have not yet been evaluated, should be tested for specificity, noise level, limits of detection, and linear range.

The analog inputs recently incorporated into software must be checked and evaluated.

A "Mini-dilution System" is part of the total FTIR System. This Mini-dilution tunnel allows a more concentrated signal to be seen by the FTIR with a concurrent lowering of the limits of detection. This addition should be evaluated.

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The complete report, entitled "Evaluation of a FTIR Mobile Source Measurement System," (Order No. PB 89-180 822/AS; Cost: $13.95, subject to change) will be available only from:

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