

Conf-9206184--1

CONTINUOUS EMISSION MONITOR FOR INCINERATORS*

ANL/CP--76118

Jack Demirgian

DE92 015261

Analytical Chemistry Laboratory
Chemical Technology Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
(708) 252-6807

To be presented at

U.S. Department of Energy
Information Exchange Meeting
on Characterization, Monitoring, and Sensor Technologies
June 3-4, 1992
Dallas, TX

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

CONFIDENTIAL
JUN 14 1992

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

*Work supported by the U.S. Department of Energy under Contract W-31-109-Eng-38.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CONTINUOUS EMISSION MONITOR FOR INCINERATORS*

Jack Demirgian

Analytical Chemistry Laboratory
Chemical Technology Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
(708) 252-6807

CONTINUOUS EMISSION MONITOR FOR INCINERATORS

SUMMARY OF TECHNOLOGY

This paper describes the development of Fourier transform infrared (FTIR) spectroscopy to continuous monitoring of incinerator emissions. Fourier transform infrared spectroscopy is well suited to this application because it can identify and quantify selected target analytes in a complex mixture without first separating the components in the mixture. Currently, there is no on-stream method to determine the destruction of hazardous substances, such as benzene, or to continuously monitor for hazardous products of incomplete combustion (PICs) in incinerator exhaust emissions. This capability is especially important because of Federal regulations in the Clean Air Act of 1990, which requires the monitoring of air toxics (Title III), the Resource Conservation and Recovery Act (RCRA), and the Toxic Substances Control Act (TSCA).

An on-stream continuous emission monitor (CEM) that can differentiate species in the ppm and ppb range and can calculate the destruction and removal efficiency (DRE) could be used to determine the safety and reliability of incinerators. This information can be used to address reasonable public concern about incinerator safety and aid in the permitting process.

TECHNOLOGY OBJECTIVE

The objective is to develop and field test an FTIR spectrometer as a continuous emission monitor for a hazardous waste incinerator. The prototype equipment will be laboratory tested at Argonne National Laboratory (ANL). The equipment will then be transported to a U.S. Department of Energy (DOE) incinerator or an incinerator representative of a DOE incinerator for field testing. Initial work at ANL consists of assembling and testing an FTIR system that will be used as a CEM. Testing will be done with exhaust gases produced by a laboratory incinerator at ANL. The FTIR library of chemicals will be expanded to include additional important species. After laboratory testing, the equipment will be field tested. A complete report will be prepared to document the equipment, methodology, and analytical results.

To achieve these goals, advances must be made in hardware design and engineering and software analysis in both the time and spectral domain.

TECHNOLOGY NEED

This technology is needed to monitor organic products of incomplete combustion as mandated by the Clean Air Act of 1990. Currently, there is no acceptable method to continuously monitor these organic chemicals.

SIGNIFICANCE OF THE TECHNOLOGY BEING DEVELOPED

The method currently in use for incinerator monitoring is analysis by gas chromatography/mass spectrometry (GC/MS). This method can only analyze a single sample under specific conditions during a trial burn. The gas chromatography (GC) run takes at least 30 min, and data analysis can take days, if all detected components must be identified. There are no alternatives for a continuous emission monitor other than FTIR.

POTENTIAL APPLICATIONS

The technology developed in this project can be used to monitor any exhaust stack for selected organics. Some examples include painting facilities and oil refineries. In most cases, the only modifications required are an expansion of the spectral library.

The analysis for selected components in a mixture has broad applications for measuring ambient air emissions and determining air quality. An example of a successful application of FTIR spectroscopy is monitoring automobile emissions.

The development of time-domain data analysis and the advancement of classical least squares (CLS) and partial least squares (PLS) data analysis will facilitate the adaption of this technology to optical remote detection of plumes using either active or passive systems.

STATUS

A. Work Completed

A laboratory incinerator was constructed and used to burn liquid feeds such as toluene and chlorobenzene. An FTIR spectrometer equipped with a heated long-path length cell was interfaced to the incinerator gas stream through a glass transfer line. With this experimental setup, it is possible to evaluate FTIR spectroscopy as a CEM under different incinerator operating conditions. Figure 1 shows the spectroscopic difference when the incinerator is operated at 1100°C and 920°C. When incompletely combusted, PICs such as benzene and methane are detected.

The incinerator-operating parameters given in Table 1 were varied while continuously monitoring for methane, toluene, benzene, and carbon monoxide emissions. The effects on emissions of the varying conditions for Cases I to IV were easily followed by the CEM. In each case, the FTIR worked perfectly as a CEM.

As reported in Table 1, the concentrations of analytes were below detection level when the incinerator was at ~1100°C (Cases I and IIIA). During cooling (Cases IIIB and IIIC), both methane and benzene were formed. As the incinerator continued to cool, toluene also appeared. The concentration of CO also correspondingly increased.

B. FY92 Tasks

The work for the first year of this project (FY92) consists of two subtasks. The first subtask is concerned with the laboratory development of the FTIR technology for continuously monitoring hazardous waste incinerators. The second subtask is concerned with engineering an FTIR system which can be transported to an incinerator for field testing.

Subtask 1 consists of developing the technology. An effort will be made to test cell and transfer line materials to determine their stability to the corrosive stack gas effluent. The most important consideration is the stability of the materials to the hydrogen chloride (HCl) that will be present. A special concern is that certain stable materials such as Teflon will

reversibly absorb HCl. This adsorption would result in slightly lower concentrations of HCl during the burning of highly chlorinated wastes and, due to degassing, a higher concentration of HCl when non-chlorinated wastes are burned.

Work has begun on characterizing laboratory flue gases that are similar to the flue gas of the hazardous waste incinerator to be monitored. In completing this subtask, the laboratory incinerator must be modified for the appropriate feed. Multiple burns will be conducted at temperatures, feed rates, and oxygen ratios that are within and beyond the trial burn conditions for the field incinerator. The components in the stack gas will be analyzed under all these conditions. When the PICs are identified, a spectral library for these PICs will be constructed. The spectra will include those for each of the PICs with and without other PICs. This analytical library will continue to be expanded as required.

The data will be analyzed to determine their qualitative and quantitative accuracy. Both CLS and PLS algorithms will be employed to determine the superior method. Quantitative accuracy will be verified by the "method of additions" in which the FTIR cell will be spiked with a concentration equal to that analyzed. Matrix blanks will also be analyzed to determine if there are false positives.

Automation software must be developed and tested. The software will transmit the raw data to storage; perform a time-domain analysis; Fourier process the interferogram; quantitatively analyze the data; and print, store, and transmit the data. The software will run in the Microsoft Windows environment. The data will be stored on a "write once read often" (WORM) drive for security reasons. A final report summarizing the technology development required to field an FTIR CEM will be written.

The second subtask involves designing the optics and building an FTIR system that will be transported and used at a hazardous waste incinerator. First, the system will be unique in two respects. The optical system will be designed to accommodate two long-path cells. If the primary cell requires cleaning or is no longer within QA/QC limits, the second cell can be activated to maintain continuous monitoring while the primary cell is cleaned or repaired. Second, the entire cell and transfer line will be heated to 150°C. Although it is more difficult to operate at elevated temperature, major condensation problems are eliminated. All components will be documented in an instrument manual.

FUTURE PLANS

Work in FY93 will be performed at the DOE incinerator to be monitored. The FTIR system will be field tested for the entire year. Data will be evaluated at the field site, and system enhancement will be an ongoing activity. Effort will be focused on improving the hardware and overall data quality to achieve EPA certification. The EPA will be involved in evaluating data quality throughout the procedure.

In FY94 work should be completed. Field tests will be continued during this period to satisfy EPA concerns about data quality. The result of the final year of this project should be EPA certification. The procedures will be issued as standard operating procedures, and the method, including forms, will be presented in a manual.

UNRESOLVED ASPECTS

Several technological advances must be completed before FTIR technology can be routinely used in the field. First, hardware must be ruggedized and a turnkey system developed. Second, because existing equipment requires operation by trained spectroscopists, the instrumentation and operating software must be completely automated with internal error checking. Third, software must be developed to enhance detection levels and optimized for accuracy and precision. Current work using digital filtering in the time domain has demonstrated the potential to improve detection levels by an order of magnitude. This work must be adapted to extractive FTIR systems. Finally, spectral domain analysis must also be improved. Currently, both CLS and PLS data analyses are being evaluated. Both algorithms must be tested and improved in conjunction with time domain processing.

POTENTIAL COOPERATIVE EFFORTS

A Cooperative Research and Development Agreement (CRADA) is currently under development with Clean Air Engineering (CAE) and Hughes to advance the commercialization of the system after EPA certification. In addition, CAE will assist in developing stack sampling technology.

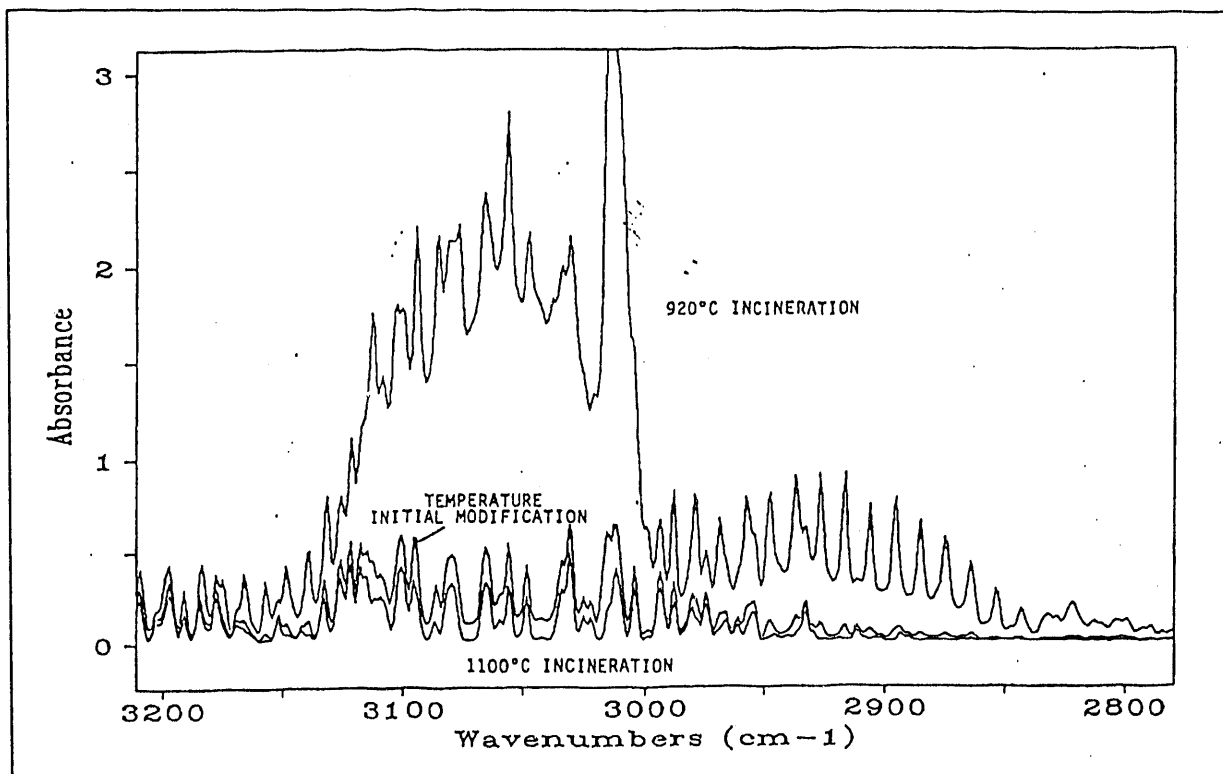


Figure 1. Spectral Comparison of Toluene Incineration During Temperature Modification.

Table 1. Data for Destruction of Toluene

	Case I	Case II	Case IIIA	Case IIIB	Case IIIC	Case IV
Incinerator Temperature (°C)	1005	900	1100	Decreasing from 1100	920	1100
Residence Time (sec)	1.17	1.27	1.06	1.22	1.22	0.63
Air Ratio	1.37	1.42	1.55	1.57	1.57	1.62
Toluene Feed Rate (g/min)	0.107	0.105	0.063	0.058	0.058	0.063
Air Rate (cm ³ /m)	7332	7332	7524	7524	7524	12631
Toluene Concentration in the Inlet (ppm × 10 ⁻³)	3.58	3.09	2.05	1.89	1.89	1.22
Methane Concentration in the Inlet (ppm × 10 ⁻⁴)	5.59	5.60	5.47	5.47	5.47	5.65
Concentration in the Exhaust (ppm × 10 ⁻¹)						
Methane	0	815 ± 303	0	351 ± 207	5580 ± 1200	ND
Toluene	0	18 ± 13	0	0	161 ± 27	0
Benzene	ND*	134 ± 23	ND	412 ± 9.8	379 ± 247	13 ± 9
Carbon Monoxide	0	454 ± 34	0	175 ± 18	1429 ± 129	158 ± 18
Chlorobenzene	ND	ND	ND	ND	ND	ND
Soot Observed	0	Excess	0	Excess	Excess	Some
Toluene DRE (%)	>99.94	99.4	>99.95	>99.9	91.5	>99.8

*Not Detected

**DATE
FILMED**

8/04/92

