

INCINERATION OF TOLUENE AND CHLOROBENZENE
IN A LABORATORY INCINERATOR¹

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by

Zhuoxiong Mao and Michael J. McIntosh
Energy Systems Division

Jack C. Demirgian
Analytical Chemistry Laboratory
Chemical Technology Division

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Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

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Zhuoxiong Mao and Michael J. McIntosh
Energy Systems Division

Jack C. Demirgian
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Argonne National Laboratory
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ABSTRACT

This paper reports experimental results on the incineration of toluene and chlorobenzene in a small laboratory incinerator. The temperature of the incinerator, the excess air ratio and the mean residence time were varied to simulate both complete and incomplete combustion conditions. The flue gas was monitored on line using Fourier transform infrared (FTIR) spectroscopy coupling with a heated long path cell (LPC). Methane, toluene, benzene, chlorobenzene, hydrogen chloride and carbon monoxide in the flue gas were simultaneously analyzed.

Experimental results indicate that benzene is a major product of incomplete combustion (PIC), besides carbon monoxide, in the incineration of toluene and chlorobenzene and is very sensitive to the combustion conditions. This suggests that benzene is a target analyte to be monitored in full-scale incinerators.

INTRODUCTION

Incineration has generally become recognized as a preferred treatment technology in the management of hazardous wastes. However, public concern related to incinerator stack emissions has greatly impeded the needed buildup of incinerator capacity in the U.S. Currently, the monitoring of incinerator emissions, if done at all, is done indirectly through the measurement of surrogates such as carbon monoxide and total hydrocarbons. There is no on-stream method which can detect specific hazardous components in the emissions. Therefore, development of an on-stream continuous emissions monitor (CEM) that can differentiate species in the ppm and ppb range would demonstrate the safety and reliability of incinerators.

Recent development of Fourier transform infrared (FTIR) spectroscopy, combined with extensive use of computers, has shown that FTIR is a promising method for continuous monitoring of stack emissions from incinerators [1-4]. However, prior to applying this technique, particular optimum target analytes to be monitored must be determined. This requirement is essential because not only the principal organic hazardous constituents (POHCs) but also the incomplete combustion products (PICs) should be monitored.

In this study, toluene and chlorobenzene were incinerated in a laboratory incinerator both in complete and in incomplete combustion conditions. The purpose of the work was to determine what incomplete combustion products in the toluene and chlorobenzene incineration should be included as target analytes in the emission monitoring.

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DESCRIPTION OF EXPERIMENT

1. Lab Incinerator

Figure 1 shows the experimental equipment setup for the laboratory incinerator and the FTIR/LPC emissions monitor. The alumina-walled incinerator was 3.81 cm in diameter and 64 cm in height. Fuel (usually CH₄) and primary air were premixed and injected through 8 holes (0.12 cm in diameter) in the base plate. Secondary air was supplied through a 0.2 cm circumferential slot, 2.5 cm above the premixed fuel inlet holes. Chlorobenzene was injected with a micrometering pump through an injection probe located 2.5 cm above the burner holes. A tube-evaporator heated to 250°C was used to evaporate chlorobenzene before it entered the probe. Electric heaters outside the incinerator were necessary to compensate for conduction heat loss. A thermocouple located at the secondary air inlet was used for monitoring flame temperature. Another thermocouple, 23 cm above the burner holes, was used to indicate the average incinerator temperature. The flue gas entered a quench section where it was quenched to 250°C by Hastalloy coils cooled to 160°C. The injection probe and the burner base plate were cooled with Dowtherm-A, a heat transfer fluid, which was circulated at 130°C. Flue gas filtered with glass wool passed through a length of glass tubing and entered the LPC. The filter, tubing and LPC were encased in metal sheathing (copper or aluminum), which was maintained at 150 to 180°C by electrical heating to prevent water from being condensed.

2. Analytical Measurement

A Nicolet 8220 FTIR spectrometer coupled with Nicolet DX software was used for all analytical measurements. An MCT-A detector cooled with liquid nitrogen was used, and the resolution of the FTIR was 2 cm⁻¹. The FTIR was linked to a personal computer (PC), which used Nicolet PCIR version 3.0 software to perform classical least-squares (CLS) analysis.

A custom-designed heated (150°C) Hanst 4-22 long-path cell (Infrared Analysis, Anaheim, Calif.) was set at pathlength 15.4 m. The sample compartment of the FTIR spectrometer was modified to accept the heated cell. The cell was connected to a vacuum pump so that it could be evacuated and subsequently filled with calibration gases when the system was off-line.

Calibration gases were purchased from Scott Specialty Gases and were certified to be within 2% of the reported concentration. Data precision was determined by duplicating runs for each standard. The percent deviation was less than 1%, as reported in a previous paper [3].

Hydrogen chloride concentration was obtained using a 75 ppm gas standard. However, a quantitatively accurate reference spectrum could not be obtained. The HCl gas was both reacted with and adsorbed onto the cell and the transfer line. This became evident when spectral data were collected at 2 to 3 min intervals after the cell was filled with an HCl standard gas and inlet and outlet stopcocks were closed. The spectral absorption of HCl continuously decreased after each data-collection interval, due to adsorption. Hence, the HCl concentrations presented in this paper, while internally consistent, cannot be considered quantitatively accurate.

Table 1 lists the detection limit for each target analyte in this study. The absorbance peak height for each compound with known concentration was determined from its standard, and the peak-to-peak noise in the corresponding wave number region was determined by expanding a blank spectrum in that region. The detection limit was then calculated by assuming an acceptable signal-to-noise ratio of 4:1. The detection level for a given analyte is a function of its molar absorptivity and is limited by the noise and the pathlength of the system. Methane is a strong infrared absorber and can be detected at concentrations as low as 70 ppb. Other compounds, which have lower absorptivity, are detected in the ppm range. The detection limit can be further improved by either increasing the pathlength or reducing the noise.

RESULTS AND DISCUSSION

1. Monitoring at Stable Incineration Temperatures

The FTIR/LPC system was used to continuously monitor emissions from the laboratory incinerator when toluene or chlorobenzene was incinerated at various stable incineration temperatures. Table 2 shows an example for the continuous monitoring at one set of conditions, in which chlorobenzene was completely destroyed.

Before the injection of chlorobenzene, the incinerator was brought to the desired stable condition and emissions from methane combustion were analyzed to ensure that the combustion was complete. Then, chlorobenzene was injected at a constant rate of 0.0708 g/min by a micrometering pump.

The first sample was taken 10 min after starting injection. Only benzene and hydrogen chloride were detected at concentrations of 7.78 ± 3.0 ppm and 646.8 ± 17.1 ppm, respectively. Other target analytes were not detected. The following samples were taken at 10 min intervals and gave similar results, indicating a stable and complete destruction of chlorobenzene. The FTIR/LPC system was able to detect the emissions concentration changes after the injection of chlorobenzene.

Although chlorobenzene was completely destroyed at the stated conditions, another toxic component, benzene, was emitted at a significant concentration, 7.5-8.5 ppm. Hydrogen chloride, as a combustion product of chlorobenzene, was detected at concentrations of 580 to 850 ppm in the emissions. These values were significantly lower than those calculated when chlorobenzene was assumed to be totally converted to water, CO₂ and HCl, as discussed earlier.

The monitoring was continued after the injection of chlorobenzene was stopped. Benzene and hydrogen chloride did not immediately disappear from the emissions, but their concentrations gradually decreased. This could not be explained as a slow response of the FTIR/LPC system, since the response was proven to be fast, as shown in the beginning of the injection of chlorobenzene. An explanation could be that benzene and HCl, especially HCl, were adsorbed on the wall of the system (including incinerator, filter, transfer lines and long path cell). The adsorption of HCl caused HCl emissions concentrations to be systematically low in the incineration of chlorobenzene, and the desorption of HCl was responsible for the continuous HCl emissions after the injection of chlorobenzene was discontinued.

A similar phenomenon was reported by Mason et al. [5] during a boiler trial burn, in which stack concentrations of waste species continued for several hours after waste firing was completed. The mechanism of hysteresis has not been fully understood, and the FTIR/LPC system provides a useful tool to look into this problem.

2. Effect of Operating Conditions on Toluene and Chlorobenzene Incineration

Table 3 shows results on toluene incineration at temperatures from 900°C to 1100°C. It is noted that toluene can be completely destroyed at temperatures above 1000°C, if the air supply and the residence time are sufficient. At 900°C, toluene was detected in the effluent, along with methane, benzene and carbon monoxide, indicating its incomplete combustion. It is interesting to note that benzene was detected in the effluent at run 4 even though the temperature was 1100°C, and toluene was completely destroyed. This can be attributed to the insufficient residence time of combustion mixture in the incinerator.

Table 4 summarizes results of the incineration of chlorobenzene in the lab incinerator at temperatures of 800-1100°C. As shown in Table 4, when the excess oxygen ratio was 1.63, chlorobenzene was detected in the flue gas at all temperature levels except 1100°C, indicating the incomplete destruction of chlorobenzene under these conditions. Although chlorobenzene was not found at 1100°C, benzene and carbon monoxide were still detected in the flue gas. The benzene concentration reached a maximum at around 900°C. This could correlate with a mechanism change

in the destruction of chlorobenzene. As the temperature decreased the destruction and removal efficiency (DRE) of chlorobenzene decreased as well, resulting in more toxic emissions. Hydrogen chloride concentration was found in the range of 650-750 ppm for all temperatures, which was consistent with the fact that the chlorobenzene injection rate was similar in all runs. However, the measured value was significantly lower than expected, as discussed previously.

The mean residence time was kept unchanged when excess oxygen ratio was increased from 1.63 to 2.65. This was accomplished by adding auxiliary pure oxygen into the secondary air stream while the total secondary air flow rate was maintained constant. The oxygen concentration in the inlet was increased from 19.8% to 32.1%. The increase of the excess oxygen ratio greatly improved the DRE of chlorobenzene. Even at temperatures as low as 900°C, chlorobenzene was still completely destroyed. Benzene was detected at all temperature levels, but at concentrations much lower than that in the previous set. The increase of excess oxygen ratio also greatly reduced the CO emissions.

Another experiment at 1100°C was conducted with an excess oxygen ratio of 1.54 and an inlet oxygen concentration of 30.5%. This condition was obtained by introducing pure oxygen into the secondary air stream while reducing the flow rate of secondary air by 60% to keep the excess oxygen ratio close to 1.63. The mean residence time was then increased from 1.06 s to 1.70 s. No significant change of emission concentrations was found except for CO and HCl. It was found, by comparing run 11-2 and run 11-3, that a decrease of excess air ratio caused a slight increase of CO emission. Oxygen concentration in the inlet was found to have more impact on the CO emission, comparing run 11-1 with run 11-3. The high concentration of HCl in run 11-3 was believed to be caused by the decrease in total volumetric flow rate and the constant chlorobenzene injection rate.

Toluene concentration was reported as zero in all runs of chlorobenzene incineration. Since the spectral absorbance of toluene overlaps that of benzene and chlorobenzene, toluene provided a test to see if the method would report false positive results. Relative to toluene the method appears, in this sense, to be accurate.

Soot was found in the glass wool filter for all cases except in run 11-2 in the chlorobenzene incineration. Soot accumulated in the filter gradually increases the pressure drop and affects the pressure and the flow rate of the system. Therefore, continuous monitoring was limited to 1-2 hours to avoid this problem. After each run, the filter was cleaned and the glass wool was replaced.

3. Monitoring under Decreasing Temperature Conditions

Table 5 shows the results of data collected every 10 min in a continuous run; the incinerator was first brought to its stable condition at 1100°C, and then the temperature was continuously decreased to 830°C over a period of 80 min while feed rates of air, methane and chlorobenzene were maintained at constant values.

At temperatures above 1000°C, chlorobenzene was not detected in the emissions, but benzene and carbon monoxide were found at significant concentration levels. When the temperature decreased to below 1000°C, incomplete destruction of chlorobenzene was observed. A maximum of benzene concentration in the flue gas occurred around 950°C, showing that benzene is a very stable combustion by-product. Hydrogen chloride concentration in the emissions was found to be in the same range as that in the stable temperature case.

Figure 2 shows actual infrared spectra taken at different temperatures, along with the reference standards for methane, benzene, chlorobenzene, and hydrogen chloride in the wave-number regions 3200-2600 and 1220-840 cm^{-1} . By visual comparison of the sample spectra with

the reference standards, hydrogen chloride bands can be seen in all cases. Also seen are chlorobenzene bands in the wave-number region $1140\text{-}1000\text{ cm}^{-1}$ at temperatures of 913 and 833°C , respectively. Methane bands overlap with bands of hydrogen chloride, benzene and chlorobenzene, but the major peak of methane can be found at 833°C . Benzene and chlorobenzene bands are highly overlapped with each other in the region of $3140\text{-}3000\text{ cm}^{-1}$ and cannot be visually distinguished. Besides these bands, there are many other peaks, which are believed to be water bands. Nicolet software, which performs a least-squares fit of the sample spectrum to the reference spectra, provides quantitative analysis results, as shown in Table 5.

The data obtained under decreasing temperatures were qualitatively consistent with the data at the corresponding stable temperatures. If the hysteresis of the system and uncontrolled factors in the incineration were considered, the consistency of the data was quite satisfactory. This demonstrates that the FTIR/LPC as a continuous emissions monitor can effectively detect dynamic changes in the incinerator emissions.

4. Benzene: An Important Target Analyte

Benzene was not present in the feedstock, but it was detected in most runs. Even when chlorobenzene was completely destroyed, benzene concentration in the flue gas was found to be as high as 10 ppm.

As a product of incomplete combustion (PIC), benzene could be formed from chlorobenzene under local oxygen-starved conditions through C-Cl bond rupture or displacement of a chlorine atom by a hydrogen atom. Once benzene is formed, it is more difficult to destroy than chlorobenzene, according to a study on thermal stability ranking of hazardous organic compounds [6]. Therefore, the condition for complete destruction of chlorobenzene is not expected to completely destroy benzene.

Similar results were found in toluene incineration and in other studies. For example, Trenholm and Lee [7] listed benzene as one of the most frequently identified PICs in air emissions of hazardous waste incinerators. Turey et al. [8] reported that benzene was identified as a good PIC surrogate when a mixture of six compounds, which were expected to be very difficult to destroy, was thermo-decomposed in the absence of oxygen.

Selection of target analytes for on-line emissions monitoring is an important but challenging task. The current work, along with other studies, suggests that benzene is an important analyte to be considered for continuous monitoring in full-scale incinerators.

CONCLUSIONS

The FTIR/LPC system has been successfully used to continuously monitor selected target analytes in emissions generated by the incineration of toluene and chlorobenzene. Benzene was found to be a major PIC and is suggested as a target analyte to be monitored in full-scale incinerators. Hysteresis of incineration was observed in this study. Increasing the oxygen concentration in the inlet was found to greatly reduce the temperature required for complete destruction of chlorobenzene.

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Table 1. Detection Limit for Target Compounds (Cell: 150°C, 1 atmosphere)

Compound	Concentration (ppm)	Absorbance (Unit of peak height)	Peak Position (cm ⁻¹)	Noise Level	Detection Limit (ppm)
CO	42.8	0.0524	2176	0.0007	2.4
CH ₄	0.907	0.0625	3017	0.0012	0.07
CH ₁	75	0.0769	2963	0.0012	4.7
Benzene	47.6	0.0914	3057	0.0012	2.5
Toluene	44.2	0.0906	3042	0.0012	2.3
Chlorobenzene	49.8	0.1212	1091	0.0005	0.8

Table 2. Continuous Monitoring Results in Steady-State Experiment (1000°C, chlorobenzene injection rate 0.0708 g/min, excess oxygen ratio 2.64, mean residence time 1.13 s)

Time (min)	Concentration (ppm)						
	CH ₄	Toluene	Benzene	Chlorobenzene	CO	HCl	
10	0	0	7.78±3.0	0	0	646.8±17	
20	0	0	8.25±3.3	0	0	862.9±23	
30	0	0	7.59±3.0	0	0	651.2±17	
40	0	0	8.38±3.0	0	21.7±6.9	585.6±16	
50	0	0	7.81±3.0	0	0	588.7±16	
60	0	0	7.78±3.1	0	0	648.0±17	
65		(Stop injection of chlorobenzene)					
75	0	0	4.20±2.7	0	0	132.2±8	
100	0	0	2.92±2.7	0	0	35.4±7	

Table 3. Data for Destruction of Toluene at Various Conditions

Run No.	1	2	3	4
T (°C)	900	1005	1100	1100
<u>Gaseous Feeds</u>				
(cm ³ /min)				
Primary Air	1200	1200	1200	1741
Secondary Air	6132	6132	6324	10890
Auxiliary Oxygen	0	0	0	0
Methane	436	436	436	758
<u>Liquid Feed</u>				
(g/min)				
Toluene	.105	.107	.063	.0625
Excess Oxygen Ratio	1.41	1.37	1.55	1.60
Residence Time (s)	1.27	1.17	1.06	0.63
<u>Inlet Concentration</u>				
Oxygen (%)	19.8	19.8	19.8	19.8
Methane (%)	5.60	5.59	5.47	5.65
Toluene (ppm)	3093	3579	2056	1216
<u>Outlet Concentration</u>				
(ppm)				
Methane	815±303	0	0	ND
Toluene	18±13	0	0	0
Benzene	134±23	ND	ND	13±9
Carbon Monoxide	454±34	0	0	159±18
Chlorobenzene	ND	ND	ND	ND
Soot Observed	Yes	No	No	Little
DRE of Toluene (%)	99.42	>99.94	>99.89	>99.81

Table 4. Data for Destruction of Chlorobenzene at Various Conditions

Run No.	11-1	11-2	11-3	10-1	10-2	9-1	9-2	8-1	8-2
T (°C)	1100	1100	1100	1000	1000	900	900	800	800
<u>Gaseous Feeds</u>									
(cm ³ /min)									
Primary Air	1200	1200	1200	1200	1200	1200	1200	1200	1200
Secondary Air	6324	5162	2600	6324	5162	6324	5162	6324	5162
Auxiliary Oxygen	0	1249	718	0	1249	0	1249	0	1249
Methane	436	436	436	436	436	436	436	436	436
<u>Liquid Feed</u>									
(g/min)									
Chlorobenzene	.0631	.0692	.0740	.0680	.0708	.0659	.0723	.0669	.0680
Excess Oxygen Ratio	1.64	2.65	1.54	1.62	2.64	1.63	2.64	1.63	2.66
Residence Time (s)	1.06	1.05	1.70	1.14	1.13	1.24	1.23	1.36	1.34
<u>Inlet Concentration</u>									
Oxygen (%)	19.8	32.1	30.5	19.8	32.1	19.8	32.1	19.8	32.1
Methane (%)	5.47	5.41	8.7	5.41	5.41	5.41	5.41	5.41	5.41
Chlorobenzene (ppm)	1689	1833	3180	1821	1875	1764	1915	1792	1801
<u>Outlet Concentration</u>									
(ppm)									
Methane	0	0	0	0	0	2.43±0.7	0	1.0±0.3	0
Toluene	0	0	0	0	0	0	0	0	0
Benzene	10.2±3.1	7.2±3.0	11.7±4.4	50.9±3.6	7.9±3.0	125.2±9.0	7.11±2.9	41.1±5.0	15.3±3.6
Chlorobenzene	0	0	0	2.5±1.0	0	194.6±9.	0	135.1±5.8	18.7±2.2
Carbon Monoxide	87.5±7.8	0	12.8±3.3	215±9.5	3.6±1.2	482.9±13	3.1±6.8	393.1±14	216.7±11
Hydrogen Chloride	674±18	695±8	988±33	691±18	664±18	765±25	658±17	665±2	755±21
Soot Observed	Yes	No	Little	Yes	Yes	Yes	Yes	Yes	Yes

DRE of Chlorobenzene

Table 5. Continuous Monitoring Results in Unsteady State Experiment (Excess Oxygen Ratio 1.62, chlorobenzene injection rate .0695 g/min.)

Time (min)	T (°C)	Outlet Concentration (ppm)					DRE of Chlorobenzene (%)	
		CH ₄	Benzene	Chlorobenzene	CO	HCl		
10	1101	0	9.08±2.8	0	46.4±6.6	573.2±15	>99.95	
20	1104	0	10.1±2.9	0	77.0±7.3	708.6±18	>99.95	
30	1069	0	10.0±2.9	0	15.0±6.5	623.0±16	>99.95	
40	1008	0	27.9±3.0	0	162.6±8	611.2±16	>99.95	
50	958	3.2±.7	196.3±8.2	63.5±5.2	438.2±17	774.6±25	96.6	
60	913	1.4±.5	101.7±5.8	93.0±5.3	372.9±14	641.0±20	95.0	
70	862	2.0±.6	71.5±5.6	111.5±6	400.1±15	614.4±19	94.0	
80	833	7.0±1.0	156.4±15	462.2±22	612.7±25	699.5±26	75.2	
82			(Stop injection of chlorobenzene)					
97	776	0	8.4±2.9	0	12.5±6.6	64.8±7.8		

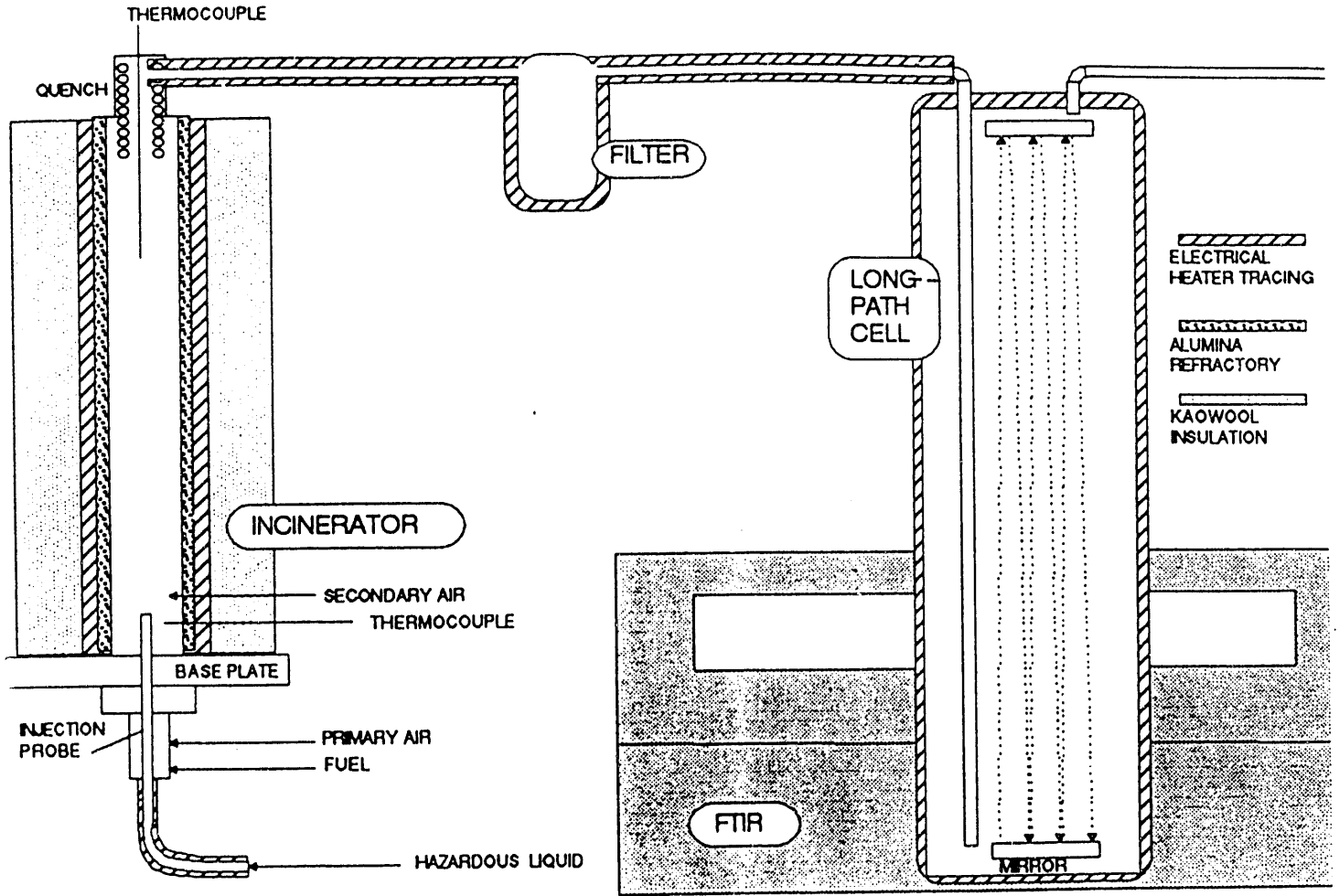


Figure 1. Laboratory incinerator with the FTIR/LPC emissions monitor

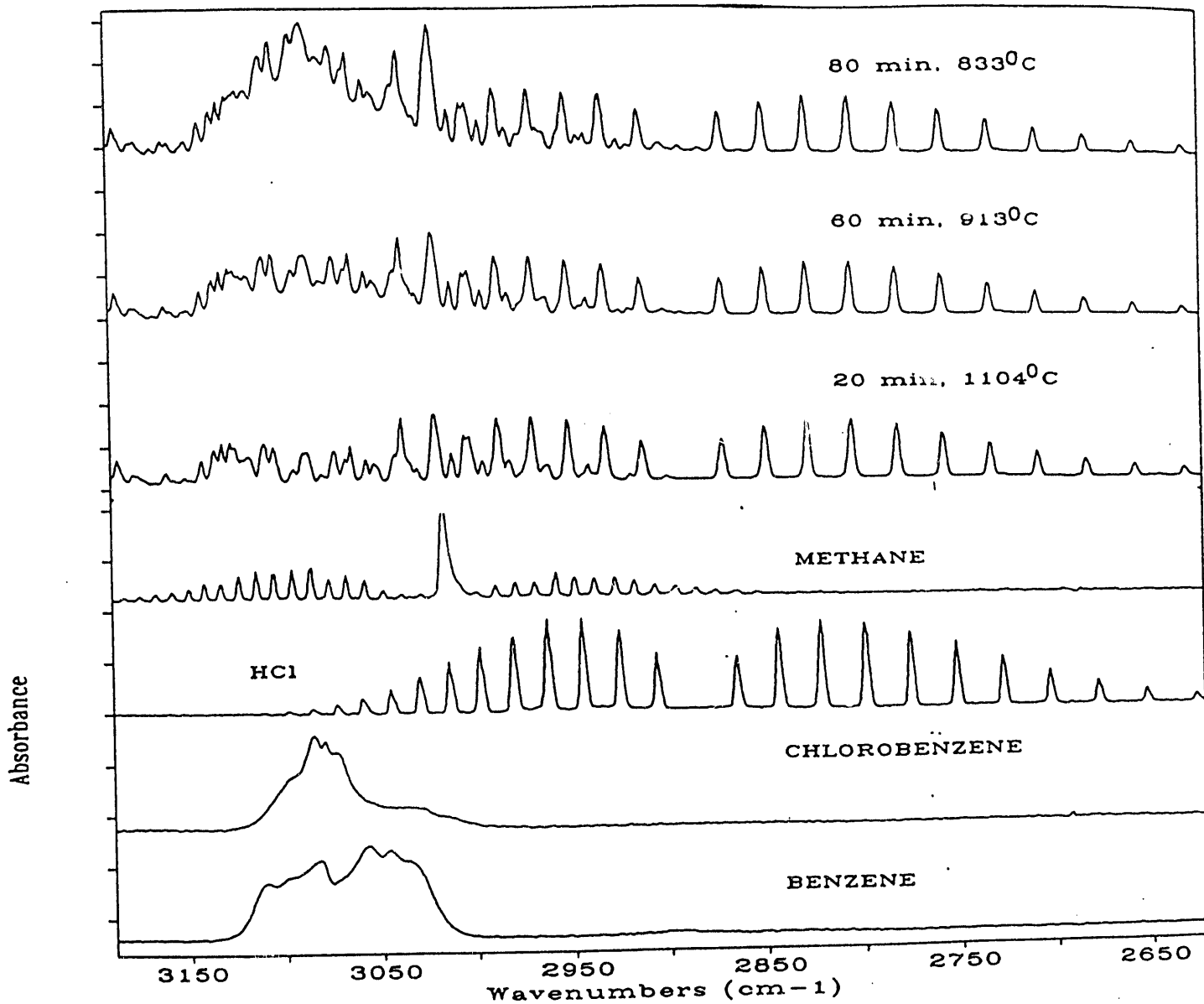


Figure 2a. Infrared Spectra Taken During a Period of Temperature Decrease

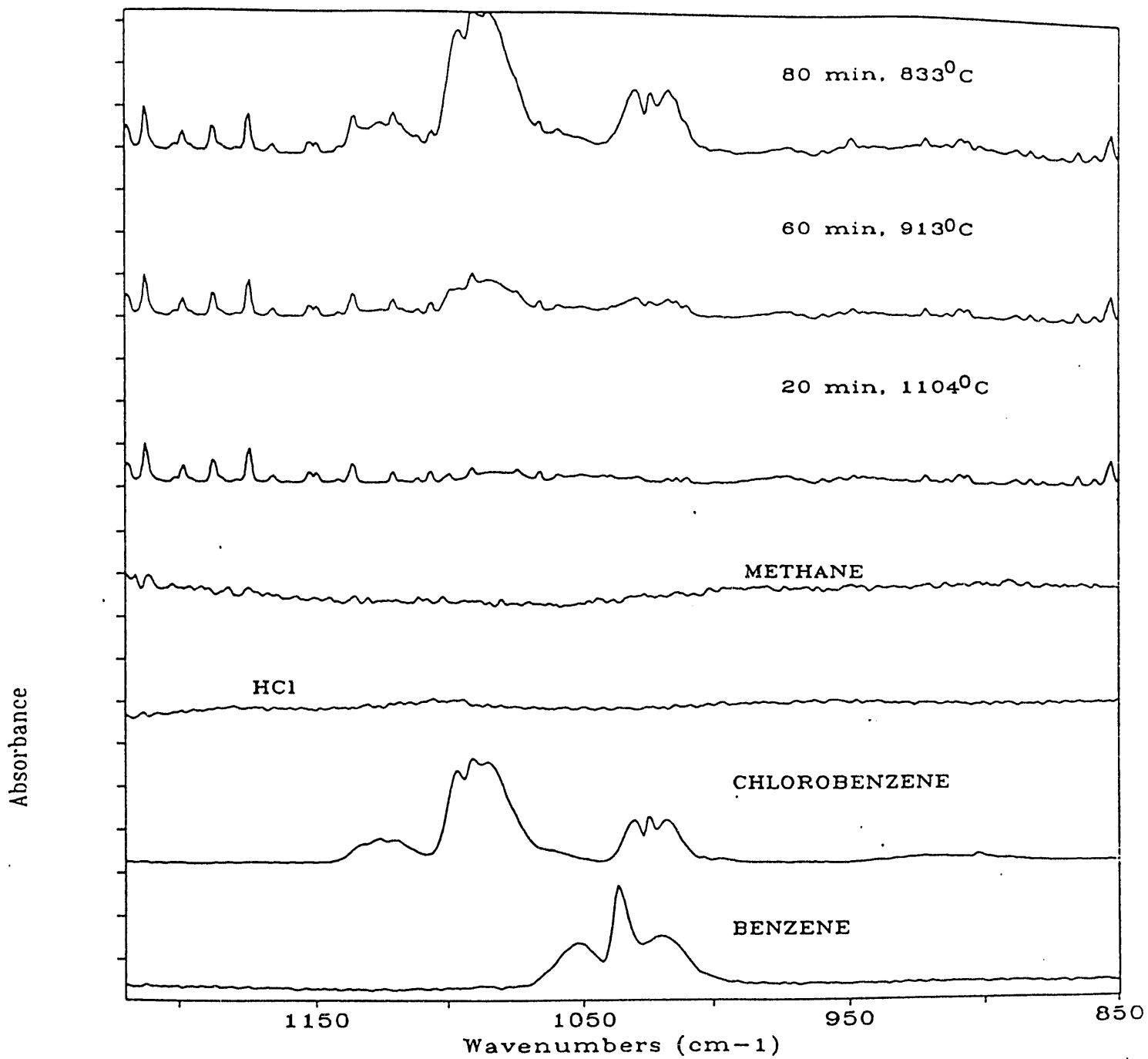


Figure 2b. Infrared Spectra Taken During a Period of Temperature Decrease

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