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THE POTENTIAL OF PASSIVE-REMOTE FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY TO DETECT ORGANIC EMISSIONS UNDER THE CLEAN AIR ACT\*

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THE POTENTIAL OF PASSIVE-REMOTE FOURIER TRANSFORM INFRARED (FTIR)  
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**ABSTRACT**

The Clean Air Act of 1990 regulates the emission of 189 air toxics. Currently, there is no existing technology by which a regulatory agency can independently determine if a facility is in compliance. We have successfully tested the ability of passive-remote Fourier transform infrared (FTIR) spectroscopy to detect chemical plumes released in the field. Additional laboratory releases demonstrated that FTIR spectroscopy can detect target analytes in mixtures containing components which have overlapping absorbances. The FTIR spectrometer was able to identify and quantify each component released with an average quantitative error of less than 20% using partial least squares (PLS) analysis and 40% using classical least squares analysis (CLS) when calibration files containing pure components and mixtures were used. Calibration files containing only pure analytes resulted in CLS outperforming PLS analyses.

**INTRODUCTION**

The Clean Air Act of 1990 regulates the emission of 189 air toxics. Sources of air toxics will be required to self-monitor their own facilities. At this time, the Environmental Protection Agency (EPA) has no independent means to determine if a facility is in compliance. The problem is especially acute if there is public concern about the emissions of a facility such as a pulp mill or an incinerator.

The potential of a passive-remote FTIR sensor to assure compliance of a facility with the Clean Air Act will be discussed. Passive-remote FTIR sensors would monitor natural emissions of organic molecules in the atmospheric bandwidth region of 8-12  $\mu\text{m}$ . This method has potential for monitoring a wide variety of toxic species because most organic molecules have a unique "fingerprint" in this spectral region.

A passive-remote FTIR sensor must be able to qualitatively identify an air toxic in the environment. The instrumentation must first detect the air toxic with a low probability of false positives or false negatives. Hence, it must be able to detect the air toxic in an environment that contains other components which have overlapping absorbances in IR spectra. It must also function in a continually changing background so that it can track a plume to its source.

A field test is required to assess the ability of an FTIR spectrometer to track a plume. The field test described in this paper was performed at a Drug Enforcement Administration site. Pure chemicals were released in the environment to simulate the concentrations found at illegal drug laboratories. A ground-based XM21 FTIR spectrometer was used to monitor the plumes.

The ability of this technology to identify a target analyte in a mixture containing components which have overlapping absorbances was tested in the laboratory. A remote-passive FTIR sensor was constructed from a conventional Nicolet 6000 FTIR spectrometer. Mixtures containing totally overlapping absorbances were quantitatively released in front of the instrument. The ability to detect single components in the presence of completely overlapping spectral bands was determined using PLS and CLS software.

## EXPERIMENTAL

### Field Releases

Releases simulating methamphetamine and cocaine laboratories were performed in an open area. The methamphetamine laboratory simulation consisted of a Freon-11 release. A mobile office trailer was used. The Freon-11 was poured into a cooking pot sitting on a hot plate. A window fan vented the evaporating liquid through an adjacent window. Sulfur hexafluoride ( $\text{SF}_6$ ) was released immediately before and after the Freon-11 release. Freon-11 was released for 21 min at an average rate of 3.7 g/s.

A cocaine laboratory simulation consisted of acetone and ethyl ether releases. An 8-ft by 2-ft (2.4-m by 0.6-m) metal tray was covered by plastic sheeting. Evaporation was achieved by use of 24-125 W infrared lights immediately above the liquid. A standard floor fan was used to blow the evaporating liquid down wind. Acetone was released for approximately 30 min at an average release rate of 2.8 g/s, and ether was released for approximately 30 min at an average release rate of 4.2 g/s.

### Field Instrumentation

The ground-based XM21 FTIR spectrometer was placed approximately 30-50 m from the release point. There was a 2 m/s crosswind. The XM21 spectrometer collected data at  $4 \text{ cm}^{-1}$  resolution, a data collection rate of 10 kHz, and a scan speed of approximately 4 scans per second.

### Laboratory Releases

It was necessary to convert the liquids studied to low concentration vapors. A vaporizer was constructed to convert an accurately measured liquid stream to a vapor phase release in the low ppm-m concentration level. This vaporizer has been described elsewhere.<sup>1</sup> The liquid flow, which is adjusted through the use of a syringe pump, determined the concentration of the release. When mixtures were released, the liquids were mixed together and then placed in the syringe.

All releases were performed in a hood with the FTIR instrument positioned 2 m from the release point. A blackbody (modified hot plate) was constructed as a reference source. The surface of the hot plate was ground down until it was flat, and a 1/2-in.-thick aluminum plate was screwed onto the surface to increase the thermal mass of the hot plate. The surface was blackened with candle soot. The temperature of the blackbody was monitored by drilling a hole in the aluminum plate to its approximate midpoint and inserting a thermocouple. The blackbody was plugged into a Variac, and the voltage was regulated so that the blackbody temperature remained within 50-52°C.

### Laboratory Instrumentation

A Nicolet 6000 FTIR spectrometer was modified for use in this project. The source, entry optics, and aperture were removed to make the FTIR a passive system. The inlet optics were replaced with a four-mirror design, which allowed focusing at a target 2 m from the interferometer. The beam width was 2.5 cm. A diagram of the apparatus is shown in Figure 1.

The vaporizer released precise amounts of each chemical at 37°C in front of the blackbody, which was kept at 50-52°C. The energy that was not absorbed traveled to two flat pick-off mirrors (A), which were used to aim on the target. The energy then traveled to a 60 degrees off-axis objective paraboloid mirror (B), which focused the energy on a magnifying collimating off-axis mirror (C). The energy then entered the interferometer and passed through the bench mirrors and empty sample chamber, terminating at an MCT-A detector.

A background interferogram was collected for each sequence of analyte released. Interferograms were also collected for releases of pure or mixed components of selected chemicals. The data were processed by the ratioing of sample to background spectra. All data were transferred to a personal computer (PC) using FILTRN software on the Nicolet 1180 computer and SECSTRN software (Galactic Industries, Inc.) on the PC.

## Quantitation Software

All identification and quantitation of chemical components were done using LabCalc software (Galactic Industries, Inc.). The data were analyzed using both CLS and PLS algorithms. Data were converted from the Nicolet format to the LabCalc format using the LabCalc Nicolet driver.

## Experimental Method

In a typical experiment, the initial background is determined with the vaporizer on and all zone temperatures stable. Next, a 20 mL syringe filled with pure analyte is placed in the syringe pump, and the syringe pump (calibrated for each fluid) is started at the lowest speed. After a 2-min equilibrium time, 128 scans are collected and coadded. Data collection time is approximately 2 min. The syringe pump is then turned to the next setting, and the process repeated with all the pure liquids and mixtures studied. A typical background spectrum is shown in Figure 2.

## FIELD TEST RESULTS

The passive-remote FTIR spectrometer consists of entry optics, an interferometer, and a detector. The entire system is contained in a small package, which can weigh as little as 16 lb (7.3 kg). The spectrometer uses ambient energy as its source. The sampling area can be anywhere within the field of view of the spectrometer. The spectrometer obtains emission spectra, the amplitude of which is a function of the analyte concentration and the temperature of the background and the plume.

Passive-remote systems are ideal for detecting a solvent plume and tracing the plume to its origin. The primary obstacle in developing a functioning field system is the constantly changing background. A moving spectrometer would encounter sky, grass, trees, asphalt, cement, roofing materials, and siding materials as backgrounds. Each background would be at its own temperature and would emit a different background infrared envelope. The infrared blackbody window even varies when a sky background is used due to the absorption of infrared energy by atmospheric water, which is emitted in pulses.

Most passive-remote instruments cope with the variable background by collecting a background spectrum with no analyte present and subtracting this background from the sample. Similar results can be obtained by the ratioing of the spectrum with analyte to the background spectrum. These methods are often unsatisfactory because it may not be possible to obtain a comparable background. Also, data analysis must immediately follow data collection so that appropriate background and sample spectra can be determined.

The U.S. Army, Chemical Research, Development, and Engineering Center (CRDEC) has advanced the technology of adapting to changing backgrounds in two ways. The XM21 FTIR spectrometer has a series of internal blackbodies, which it uses as a reference. The internal blackbodies provide a point of reference for all spectra. The spectrometer's internal computer also compares the change in each successive spectrum to determine if an analyte is present. The newest CRDEC unit, a modified Midac FTIR, uses a digital filtering algorithm to eliminate the background from the sample. This unit was developed by R. Kroutil and G. Small.<sup>2</sup>

The XM21 was designed to operate under battlefield conditions. Its internal blackbody helps to stabilize the response, and the MCT-A detector is optimized for the atmospheric bandwidth window of 1200-900  $\text{cm}^{-1}$ . The optical system makes it simple to eliminate alignment problems.

The XM21 detected the  $\text{SF}_6$  releases with a large signal-to-noise (S/N) ratio. Figure 3 shows a typical  $\text{SF}_6$  spectrum. At the simulated methamphetamine laboratory, Freon-11 was released from a window in a trailer. The Freon-11 was also detected with a large S/N ratio. The spectrum of a Freon-11 standard and the actual spectrum obtained during the release are shown in Figure 4.

The cocaine laboratory simulation consisted of acetone and ethyl ether releases. The acetone releases were more difficult to detect because the primary absorption band is 1220  $\text{cm}^{-1}$ , which is beyond the region for which the detector was

designed. The acetone and ethyl ether releases were performed by pouring each liquid into 8-ft (2.4-m) long trays in open sheds and evaporating the liquid with the use of heat lamps. The XM21 was able to detect both these solvents in the open area and in the 60-ft canopy. The reference and actual release spectra for acetone and ethyl ether are shown in Figures 5 and 6, respectively.

#### LABORATORY RESULTS

The ability of an FTIR spectrometer to discriminate between a target analyte and an environmental impurity which may have an overlapping spectral absorbance is critical if FTIR is to be used for compliance assurance. We will report quantitative results obtained in the laboratory for a two-component mixture consisting of isopropanol (IPROH) and dimethyl methyl phosphonate (DMMP) and a three-component mixture consisting of methanol (MEOH), DMMP, and IPROH. These components all have overlapping peak absorbances over the bandwidth for the atmospheric window.

#### Two-Component Mixture

Data were obtained for pure IPROH, pure DMMP, IPROH-DMMP (1:2 volume ratio), and IPROH-DMMP (2:1 volume ratio). The spectral data for each run are shown in Figure 7.

The PLS and CLS analysis results were compared using approximately half the releases as calibration standards. The data are presented in Table I. Both mixtures and pure components were in the calibration set. PLS slightly outperformed CLS for the quantitation of IPROH in the mixture, and CLS slightly outperformed PLS for the quantitation of DMMP in the mixture. One value for the PLS analysis had a high error. If this value is not considered, PLS and CLS are approximately equal for the quantitation of DMMP in the mixture. Diethyl malonate (DEM) was added to the spectral library of the two-component mixture to determine if either algorithm would show a false positive. The results are presented in Table II. In this case, there were no false positives. Both algorithms correctly identified only IPROH and DMMP as present. However, the quantitative results were changed. The average percent deviation for the quantitation of IPROH using PLS data analysis improved from 12.3% to 8.6% with DEM in the library. The percent error of DMMP also improved from 29.3 to 26.4% average error when DEM was added to the library. The results for CLS data analysis were just the opposite. The percent error of 21.1% for IPROH deteriorated to 31.5% when DEM was added to the library. The results were much more drastic for DMMP, where the percent error increased from an average of 19.9% to 46.3% when DEM was added to the library.

The reason for the improvement of data quality for PLS and the deterioration of data quality of CLS is not immediately clear. PLS always works better with a larger data set. However, little work has been done on the effect of using a large library where many components are not present. The deterioration of CLS data is also not understood.

#### Three-Component Mixture

Data were obtained for pure MEOH, pure DMMP, pure IPROH and mixtures of the three-components in the ratios 1:1:2, 1:2:4, 2:1:3, and 10:1:5. The spectral data for the pure components and their mixtures are given in Figures 8-14. Extensive data analysis was performed using both PLS and CLS algorithms. Two PLS data analysis runs were performed. Both PLS data sets and a CLS data set are shown in Table III. PLS1 had the same number of standards that were used for our other data analyses. Regression analysis showed that two standards deviated the most from the linear fit of the data but were not considered outliers. Another calibration set was run, PLS2, without these two standards. Elimination of these two standards improved the quantitative accuracy of IPROH on the two mixtures, but pure IPROH results deteriorated. It had minor effects in all other cases.

The accuracy of PLS was significantly better than that for CLS. The PLS algorithms were accurate within an average value of 20%. The CLS average was closer to 40%. CLS seemed to perform better with low concentrations of methanol. The most difficult detection was in the 10:1:5 mixture. The DMMP peak was visually not

Table I. Comparison of PLS and CLS data analyses for IPROH-DMMP mixtures.

SEQUENCE		ISOPROPANOL FLOW RATE						DMMP FLOW RATE					
FILE		PLS ANALYSIS			CLS ANALYSIS			PLS ANALYSIS			CLS ANALYSIS		
NAME	ACTUAL	CALC	% DEV	CALC	% DEV	ACTUAL	CALC	% DEV	CALC	% DEV	CALC	% DEV	
PURE IPROH	A5055	0.19	0.27	43.7	0.31	64.2	0	-0.01			-0.13		
	A5057 *	0.29	0.32	11.4	0.39	35.2	0	0.00			-0.15		
	A5059	0.38	0.38	-0.8	0.43	13.9	0	-0.01			-0.14		
	A2061 *	0.67	0.61	-9.6	0.66	-1.9	0	-0.02			-0.13		
	A5063	0.97	0.88	-9.3	0.92	-4.7	0	-0.03			-0.12		
	A5065	1.4	1.27	-9.6	1.30	-7.2	0	-0.04			-0.12		
	A5067 *	1.9	1.90	0.2	1.96	3.3	0	-0.06			-0.14		
PURE DMMP	A5070	0	-0.02		-0.02		0.19	0.06	-57.9	0.00	-100.0		
	A5072 *	0	-0.01		0.03		0.29	0.31	5.2	0.21	-26.9		
	A5074	0	-0.01		0.01		0.38	0.44	14.7	0.37	-1.6		
	A5076 *	0	-0.03		-0.01		0.67	0.86	28.2	0.82	21.6		
	A5078	0	-0.08		-0.06		0.97	1.18	21.1	1.18	19.4		
	A5080	0	-0.07		-0.04		1.4	1.50	7.4	1.51	7.8		
	A5082 *	0	-0.03		0.00		1.9	1.67	-12.2	1.87	-11.9		
IPROH:1 DMMP:2	A5085	0.097	0.13	29.9	0.09	-9.3	0.19	-0.09	-147.4	-0.11	-155.3		
	A5087 *	0.13	0.17	32.3	0.15	14.6	0.25	0.17	-32.8	0.17	-32.4		
	A5089	0.22	0.25	13.6	0.23	5.0	0.45	0.42	-7.6	0.44	-2.4		
	A5091 *	0.32	0.37	14.1	0.35	10.0	0.65	0.75	14.6	0.78	20.0		
	A5093 *	0.47	0.52	10.9	0.53	13.0	0.83	1.05	13.3	1.08	16.1		
IPROH:2 DMMP:1	A5095	0.63	0.83	0.3	0.70	10.3	1.3	0.99	-24.0	0.95	-27.1		
	A5098	0.19	0.18	-6.8	0.10	-47.9	0.097	0.01	-87.6	0.08	-14.4		
	A8011 *	0.25	0.26	3.2	0.18	-28.0	0.13	0.04	-73.1	0.15	11.5		
	A8013	0.45	0.40	-10.7	0.30	-33.1	0.22	0.16	-27.3	0.30	35.5		
	A8015 *	0.65	0.61	-6.6	0.51	-22.0	0.32	0.31	-3.1	0.47	45.6		
A8017 *	0.93	0.92	-0.6	0.85	-8.3	0.47	0.54	14.0	0.69	46.2			

\* USED IN CALIBRATION STANDARD

Table II. Comparison of PLS and CLS data analyses for IPROH-DMMP mixtures containing DEM added to the spectral library.

SEQUENCE		ISOPROPANOL FLOW RATE						DMMP FLOW RATE						DEM FLOW RATE			
FILE		PLS ANALYSIS			CLS ANALYSIS			PLS ANALYSIS			CLS ANALYSIS			PLS ANALYSIS		CLS ANALYSIS	
NAME	ACTUAL	CALC	% DEV	CALC	% DEV	ACTUAL	CALC	% DEV	CALC	% DEV	ACTUAL	CALC	% DEV	CALC	% DEV	CALC	% DEV
PURE IPROH	A5055	0.19	0.27	41.1	0.32	66.9	0	0.02	0.05	0	-0.00			-0.06			
	A5057 *	0.29	0.30	2.1	0.40	36.6	0	0.00	0.08	0	-0.01			-0.05			
	A5059	0.38	0.39	1.1	0.45	17.1	0	0.02	0.05	0	0.01			-0.05			
	A5061 *	0.67	0.66	-1.3	0.66	1.0	0	-0.00	0.04	0	0.02			-0.05			
	A5063	0.97	0.89	-8.1	0.94	-3.1	0	0.01	0.03	0	-0.01			-0.04			
	A5065	1.4	1.26	-10.5	1.31	-6.6	0	0.01	0.02	0	0.00			-0.03			
	A5067 *	1.9	1.90	0.1	1.98	4.4	0	-0.00	0.00	0	-0.00			-0.03			
PURE DMMP	A5070	0	0.01		-0.01		0.19	0.13	-33.7	0.12	-37.9	0	-0.00			-0.04	
	A5072 *	0	0.00		0.01		0.29	0.29	-0.3	0.30	3.8	0	-0.00			-0.03	
	A5074 *	0	-0.01		-0.00		0.38	0.39	3.2	0.41	6.8	0	0.00			-0.02	
	A5076	0	0.02		0.03		0.67	0.72	7.2	0.75	12.2	0	-0.01			-0.03	
	A5078 *	0	0.00		-0.01		0.97	0.96	-0.8	1.01	4.1	0	0.00			-0.03	
	A5080	0	-0.00		0.02		1.4	1.22	-12.9	1.28	-8.9	0	0.01			-0.01	
	A5082	0	0.01		0.06		1.9	1.34	-29.3	1.41	-25.8	0	0.01			-0.01	
PURE DEM	A3023 *	0	0.01		0.06		0	0.01	-0.01	0.29	0.28	-4.1	0.34	17.2			
	A3025 *	0	-0.01		0.05		0	-0.01	-0.00	0.36	0.40	6.0	0.46	22.1			
	A3027 *	0	0.00		-0.05		0	0.00	0.01	0.67	0.66	-1.0	0.60	-10.4			
IPROH:1 DMMP:2	A5086	0.097	0.07	-27.8	0.06	-38.1	0.19	0.09	-66.8	-0.03	-113.7	0	-0.01			-0.01	
	A5087 *	0.13	0.12	-7.7	0.14	7.7	0.25	0.25	0.0	0.19	-26.0	0	0.01			-0.01	
	A5089	0.22	0.21	-6.4	0.23	5.0	0.45	0.42	-6.8	0.39	-14.2	0	-0.00			-0.00	
	A5091 *	0.32	0.33	3.1	0.37	16.2	0.65	0.66	1.2	0.66	0.6	0	-0.00			-0.00	
	A5093 *	0.47	0.47	-0.4	0.56	22.6	0.93	0.93	-0.6	0.91	-2.5	0	-0.01			-0.01	
	A5095	0.63	0.60	-4.3	0.73	16.0	1.3	0.83	-36.2	0.86	-34.1	0	0.01			-0.02	
IPROH:2 DMMP:1	A5098	0.19	0.19	0.0	0.08	-59.6	0.097	0.10	-2.1	0.05	-45.4	0	-0.01			0.01	
	A8011 *	0.25	0.27	6.8	0.13	-48.9	0.13	0.12	-8.9	0.07	-47.7	0	-0.07			0.04	
	A8013	0.45	0.43	-4.4	0.28	-38.9	0.22	0.22	-0.9	0.17	-23.2	0	-0.01			0.04	
	A8015 *	0.65	0.63	-3.1	0.47	-28.2	0.32	0.32	-1.3	0.29	-10.0	0	-0.00			0.06	
	A8017 *	0.93	0.94	0.6	0.81	-13.0	0.47	0.48	2.1	0.47	0.4	0	0.01			0.06	

\* USED IN CALIBRATION STANDARD

Table III. Comparison of PLS and CLS data analyses for MEQH-DMMP-IPROH mixtures.

SEQUENCE	FILE NAME	METHANOL FLOW RATE		DMMP FLOW RATE		CL8 ANALYSIS		ISOPROPANOL FLOW RATE		CLS ANALYSIS					
		PLS ANALYSIS 1		PLS ANALYSIS 2		PLS ANALYSIS 1		PLS ANALYSIS 2		CALC % DEV					
		ACTUAL	CALC % DEV	ACTUAL	CALC % DEV	ACTUAL	CALC % DEV	ACTUAL	CALC % DEV	ACTUAL	CALC % DEV				
PURE MEQH	A3080	0.19	0.20	4.2	0.20	7.9	0.11	-41.1	0	-0.07	-0.05	0	-0.10	-0.01	-0.07
	A3082	0.29	0.30	4.5	0.30	2.4	0.16	-43.8	0	-0.06	0.05	0	-0.05	0.01	-0.00
	A3084	0.38	0.43	13.9	0.45	17.4	0.12	-68.7	0	0.00	0.25	0	0.08	0.09	0.09
	A3086	0.67	0.67	0.3	0.67	0.6	0.35	-47.8	0	0.03	0.27	0	0.00	0.11	0.12
	A3088	0.97	0.91	-6.0	0.92	-5.6	0.06	-93.4	0	0.02	0.25	0	-0.03	-0.03	0.06
	A3090	1.4	1.36	-2.9	1.37	-2.4	1.19	-16.0	0	0.04	0.13	0	-0.03	-0.06	-0.01
	A3092	1.9	1.79	-6.7	1.81	-4.9	1.80	-5.3	0	0.04	0.02	0	-0.09	-0.06	0.07
	A3095	0	0.11	6.36	0.11	6.88	44.99	0.08	44.99	0.19	0.20	0.41	0.13	0.11	0.03
	A3097	0	0.07	0	0.11	0	-0.13	0.08	0.19	0.20	0.47	0.05	0.03	0.03	0.05
	A4010	0	0.06	0	0.05	0	-0.11	0.08	0.29	0.31	0.20	0.62	0.05	0.09	0.01
PURE DMMP	A4012	0	0.00	0	-0.02	0	-0.02	0	0.67	0.76	0.77	0	-0.01	-0.01	0.01
	A4014	0	0.02	0	-0.09	0	0.04	0	0.97	1.10	0.99	0	-0.04	-0.02	-0.04
	A4016	0	-0.01	0	-0.17	0	0.08	0	0.97	1.10	1.15	0	0.00	-0.00	-0.03
	A4018	0	-0.05	0	-0.20	0	0.08	0	1.4	1.33	1.28	0	-0.01	-0.02	-0.06
	A4021	0	0.06	0.07	0.07	0.07	0	0.01	0	1.9	1.44	1.28	0	-0.01	0.14
	A4023	0	0.03	0.03	0.03	0.03	0	0.02	0	11.12	10.89	40.42	0.19	0.17	-0.28
	A4025	0	-0.02	0	-0.01	0	0.05	0	0	-0.07	-0.11	0.29	0.25	0.26	-0.90
	A4027	0	0.00	0	0.00	0	0.04	0	0	-0.08	-0.17	0.38	0.36	0.34	-11.8
	A4029	0	-0.02	0	-0.02	0	0.02	0	0	0.02	-0.02	0.67	0.64	0.61	-9.3
	A4031	0	-0.03	0	-0.02	0	-0.01	0	0	0.08	-0.13	0.97	0.86	0.89	-8.0
PURE IPROH	A4033	0	-0.06	0	-0.06	0	-0.07	0	1.9	1.44	1.28	0	-0.01	-0.02	-0.06
	A4036	0.095	0.07	-31.6	0.08	-29.4	20.94	0.08	24.68	0.08	-0.06	0.19	0.17	0.14	-28.4
	A4038	0.17	0.13	-24.7	0.12	-27.6	13.60	0.14	44.2	0.08	-0.06	0.29	0.25	0.26	-9.0
	A4040	0.24	0.22	-7.1	0.21	-13.8	0	0.05	0	0.20	0.32	0.28	0.28	0.34	-11.8
	A4042	0.35	0.39	12.3	0.38	7.7	0	0.04	0	0.27	0.32	0.37	0.36	0.34	-4.5
	A4044	0.48	0.56	16.6	0.55	14.8	0	0.02	0	0.47	0.47	0.63	0.64	0.61	-9.3
	A4046	0.72	0.71	-1.6	0.70	-2.4	0	0.02	0	0.63	0.63	0.81	0.86	0.89	-8.0
	A4049	0.054	0.24	337.0	0.26	305.2	0	0.09	0	0.67	0.67	0.69	1.4	1.41	0.9
	A4051	0.096	0.12	19.0	0.14	40.6	0	0.04	0	0.67	0.67	0.69	1.9	1.86	2.6
	A4053	0.14	0.16	-14.3	0.13	-4.3	0	0.02	0	0.67	0.67	0.69	1.9	1.86	2.6
MEOH:1	A4055	0.2	0.27	-1.9	0.28	3.3	0.15	-44.1	0.64	0.62	0.74	0.95	1.39	1.36	1.48
	A4057	0.27	0.27	-1.9	0.28	3.3	0.15	-44.1	0.64	0.62	0.74	0.95	1.39	1.36	1.48
	A4059	0.41	0.41	-0.2	0.41	-0.5	0.25	-40.2	0.83	0.52	0.65	1.4	1.48	1.44	2.6
	A4062	0.13	0.02	-85.4	0.05	-62.3	11.75	-0.03	-125.4	0.06	-0.03	0.08	0.04	0.20	-9.6
	A4064	0.22	0.19	-12.7	0.20	-7.7	0	0.16	-30.0	0.11	0.10	0.26	0.26	0.26	162.9
	A4066	0.32	0.31	-4.1	0.31	-1.9	0	0.17	-46.9	0.23	0.26	0.32	0.35	0.35	14.7
	A4068	0.46	0.42	-7.8	0.42	-7.8	0	0.18	-10.0	0.4	0.44	0.46	0.46	0.46	6.5
	A4070	0.63	0.66	4.1	0.65	3.6	0	0.19	-5.6	0.4	0.44	0.46	0.46	0.46	0.4
	A4072	0.97	1.02	5.1	1.01	4.4	0	0.09	-7.8	0.48	0.51	0.55	0.55	0.55	0.4
	A4075	0.24	0.24	0.8	0.25	5.8	0	0.28	17.9	0.024	-0.04	-0.06	0.12	0.19	0.18
MEOH:2	A4077	0.42	0.44	3.8	0.46	0.3	0.69	41.4	0.042	-0.01	-0.11	0.21	0.23	0.26	22.9
	A4079	0.61	0.62	1.0	0.61	-0.5	1.05	72.6	0.061	0.05	-16.4	0.3	0.30	0.30	-1.0
	A4081	0.88	0.89	1.0	0.90	2.3	1.42	61.4	0.081	0.10	0.0	0.44	0.41	0.41	-0.7
	A4083	1.2	1.75	46.0	1.76	46.7	2.20	91.1	0.12	0.24	95.0	0.69	0.71	0.75	27.5
	A4085	1.8	1.75	-2.7	1.76	-2.2	2.29	27.4	0.16	0.24	30.0	0.91	0.71	0.75	-17.4
	A4087	2.4	2.4	0.0	2.4	0.0	2.29	27.4	0.16	0.24	30.0	0.91	0.71	0.75	-17.4
	A4089	3.0	3.0	0.0	3.0	0.0	2.29	27.4	0.16	0.24	30.0	0.91	0.71	0.75	-17.4
	A4091	3.6	3.6	0.0	3.6	0.0	2.29	27.4	0.16	0.24	30.0	0.91	0.71	0.75	-17.4
	A4093	4.2	4.2	0.0	4.2	0.0	2.29	27.4	0.16	0.24	30.0	0.91	0.71	0.75	-17.4
	A4095	4.8	4.8	0.0	4.8	0.0	2.29	27.4	0.16	0.24	30.0	0.91	0.71	0.75	-17.4

\*USED IN CALIBRATION STANDARD

Table IV. Comparison of PLS and CLS data analyses for MEOH-DMMP-IPROH mixtures using only pure components in the calibration standard.

SEQUENCE MEOH-DMMP-IPROH

	FILE NAME	METHANOL FLOW RATE				DMMP FLOW RATE				ISOPROPANOL FLOW RATE							
		ACTUAL	PLS ANALYSIS		CLS ANALYSIS		ACTUAL	PLS ANALYSIS		CLS ANALYSIS		ACTUAL	PLS ANALYSIS		CLS ANALYSIS		
			CALC	% DEV	CALC	% DEV		CALC	% DEV	CALC	% DEV		CALC	% DEV	CALC	% DEV	
PURE MEOH	A3080	0.19	-0.18	-196.8	0.05	-73.7	0	0.01	0.01	0	-0.45	-0.06	0	-1.11	-0.27		
	A3082	0.29	0.29	-1.0	0.24	-16.6	0	0.04	0.03	0	-2.22	-0.56	0	-2.54	-0.78		
	A3084	0.38	1.07	182.1	0.47	22.9	0	0.04	0.04	0	-2.65	-0.97	0	-2.52	-1.26		
	A3086	0.67	1.31	95.7	0.73	8.8	0	0.10	0.09	0	-2.42	-1.61	0				
	A3088	0.97	1.41	44.8	0.99	1.6	0	0.16	0.14	0			0				
	A3090	1.4	1.35	-3.6	1.41	0.6	0	0.25	0.23	0			0				
	A3092	1.9	1.31	-30.9	1.88	-1.1	0	0.37	0.34	0			0				
				79.3		17.9											
PURE DMMP	A3095	0	0.76		0.27		0.19	0.18	-4.2	0.18	-5.3	0	-1.80	0.00			
	A3097	0	0.60		0.30		0.29	0.29	1.4	0.29	0.3	0	-1.55	0.19			
	A4010	0	0.49		0.33		0.28	0.37	-3.2	0.37	-2.6	0	-1.39	0.33			
	A4012	0	0.25		0.53		0.67	0.68	2.1	0.69	2.5	0	-1.17	0.75			
	A4014	0	0.28		0.71		0.97	0.96	-0.7	0.96	-0.8	0	-1.04	1.10			
	A4016	0	0.20		0.64		1.4	1.16	-17.2	1.16	-17.2	0	-0.91	1.38			
	A4018	0	0.32		0.53		1.9	1.27	-33.4	1.27	-33.3	0	-1.07	1.45			
									8.9		8.9						
PURE IPROH	A4021	0	-0.33		-0.08		0	-0.01	-0.01		0.19	-0.26	-236.3	0.10	-49.5		
	A4023	0	-0.62		-0.17		0	-0.01	-0.01		0.29	0.15	-46.9	0.25	-9.7		
	A4025	0	-0.92		-0.24		0	-0.01	-0.01		0.38	0.5	53.9	0.44	14.7		
	A4027	0	-1.16		-0.36		0	-0.01	-0.01		0.67	0.91	26.1	0.70	3.7		
	A4029	0	-1.36		-0.41		0	0.00	0.00		0.97	1.20	24.1	0.99	2.2		
	A4031	0	-1.55		-0.50		0	0.01	0.02		1.4	1.46	4.6	1.43	1.9		
	A4033	0	-1.74		-0.62		0	0.02	0.03		1.9	1.73	-8.9	1.88	-1.3		
													58.7		11.9		
MEOH:1	A4036	0.095	-0.24	-251.6	0.14	42.1	0.095	0.16	68.4	0.15	58.9	0.19	-0.36	-290.0	0.23	22.2	
	DMMP:1	A4038	0.17	-0.28	-263.5	0.28	62.9	0.17	0.29	71.2	0.29	68.2	0.34	-0.29	-184.4	0.29	15.9
	IPROH:2	A4040	0.24	0.12	-50.4	0.50	107.9	0.24	0.40	68.3	0.40	66.3	0.48	-0.84	-274.0	0.41	-15.0
		A4042	0.35	0.74	111.7	0.88	152.3	0.35	0.56	59.4	0.55	57.4	0.7	-1.69	-341.4	0.23	-52.5
		A4044	0.48	0.97	102.9	1.03	115.2	0.48	0.64	33.8	0.64	22.3	0.95	-2.01	-311.1	0.62	-34.9
		A4046	0.72	0.80	10.8	1.05	46.9	0.72	0.60	-16.7	0.59	-18.1	1.4	-1.75	-224.9	0.59	-58.1
					148.5		87.9			53.0		50.2			271.0		22.5
MEOH:1	A4049	0.054	-0.10	-288.9	0.28	422.2	0.11	0.17	57.3	0.17	50.9	0.22	-0.54	-347.3	0.07	-58.6	
	DMMP:2	A4051	0.096	-0.29	-399.0	0.15	56.2	0.19	0.26	34.2	0.26	34.2	0.28	-0.29	-175.0	0.76	100.8
	IPROH:4	A4053	0.14	-0.12	-187.9	0.29	107.9	0.28	0.34	21.4	0.34	21.4	0.55	-0.51	-192.2	0.50	9.3
		A4055	0.2	0.35	72.5	0.53	164.5	0.4	0.48	19.2	0.48	19.0	0.8	-1.16	-244.4	0.65	-19.0
		A4057	0.27	1.00	268.9	0.71	164.4	0.54	0.49	-9.1	0.49	-9.6	1.1	-2.08	-288.6	0.45	-58.8
		A4059	0.41	0.58	138.5	0.77	86.8	0.83	0.50	-39.3	0.50	-39.8	1.6	-2.04	-227.6	0.56	-65.0
			225.9		167.0			30.1		29.2			245.8		52.6		
MEOH:2	A4062	0.13	-0.28	-311.5	-0.08	-160.0	0.063	0.00	-96.8	0.00	-98.4	0.19	-0.34	-276.3	0.08	-60.0	
	DMMP:1	A4064	0.22	-0.22	-197.7	0.14	-38.2	0.11	0.13	18.2	0.13	15.5	0.34	-0.40	-216.5	0.18	-48.2
	IPROH:3	A4066	0.32	0.37	16.9	0.37	15.0	0.16	0.20	21.9	0.19	18.8	0.48	-1.22	-354.2	0.04	-90.8
		A4068	0.46	0.91	98.5	0.57	24.8	0.23	0.24	6.1	0.24	3.5	0.7	-1.98	-282.1	-0.11	-115.6
		A4070	0.63	1.06	67.8	0.88	39.4	0.32	0.41	26.6	0.40	23.8	0.95	-2.15	-326.1	-0.00	-100.4
		A4072	0.97	0.70	-27.8	1.12	15.5	0.48	0.51	6.0	0.49	2.9	1.4	-1.60	-214.6	0.19	-86.2
			120.0		48.8			29.3		27.1			295.0		83.5		
MEOH:10	A4075	0.24	-0.30	-223.3	0.17	-30.0	0.024	0.08	233.3	0.07	200.0	0.12	-0.28	-331.7	0.03	-75.0	
	DMMP:1	A4077	0.42	-0.47	-211.2	0.27	-11.7	0.042	0.16	290.5	0.15	256.7	0.21	-0.01	-103.3	0.05	-75.7
	IPROH:5	A4079	0.61	-1.38	-326.1	0.46	-25.1	0.061	0.28	2.0	0.26	332.8	0.3	1.32	340.0	0.34	13.7
		A4081	0.88	-1.27	-244.7	0.80	-9.5	0.088	0.39	337.5	0.36	313.6	0.44	1.21	173.9	0.21	-52.3
		A4083	1.2	-0.53	-143.9	1.75	46.1	0.12	0.62	414.2	0.58	384.2	0.59	0.23	-60.7	-0.37	-162.5
		A4085	1.8	-0.53	-129.3	1.75	-2.6	0.18	0.62	242.8	0.58	222.8	0.91	0.23	-74.5	-0.37	-140.5
			213.1		20.8			253.4		286.7			180.7		86.6		



observable for this mixture, as can be seen in Figure 14. CLS reported the DMMP as not detected (false negative). PLS did detect the DMMP, but with a 40% quantitation error.

The data were also analyzed with only pure components in the search library. The calibration standards used are noted by an asterisk in Table IV. The accuracy of the PLS algorithms deteriorated significantly, with quantitative accuracy greater than 100%. There were false negatives for low-concentration analytes. With high-concentration analytes, the CLS algorithm actually improved in accuracy for the pure analytes and for mixtures. With low-concentration analytes, accuracy deteriorated; however, CLS still outperformed PLS in these instances.

The addition of DEM to the data set did not improve PLS data accuracy, as it did in the two-component mixture. There were no false positives in the PLS data, as can be seen in Table V.

Table V. Comparison of PLS and CLS data analyses for MEOH-DMMP-IPROH mixtures containing DEM added to the spectral library.

SEQUENCE: MEOH-DMMP-IPROH (DEM IN CALIBRATION FILE)

	FILE NAME	METHANOL FLOW RATE			DMMP FLOW RATE			ISOPROPANOL FLOW RATE			DEM FLOW RATE		
		PLS ANALYSIS	CALC	% DEV	PLS ANALYSIS	CALC	% DEV	PLS ANALYSIS	CALC	% DEV	ACTUAL	PLS ANALYSIS	% DEV
PURE MEOH	A3080	0.19	0.21	8.9	0	-0.05		0	-0.01		0	-0.01	
	A3082 *	0.29	0.30	4.1	0	-0.04		0	0.01		0	-0.01	
	A3084	0.38	0.45	17.8	0	0.01		0	0.08		0	-0.00	
	A3086 *	0.67	0.67	0.0	0	0.02		0	0.00		0	-0.01	
	A3088	0.97	0.91	-6.1	0	0.04		0	0.10		0	-0.02	
	A3090 *	1.4	1.37	-2.2	0	0.06		0	-0.02		0	0.01	
	A3092	1.9	1.81	-4.6	0	0.05		0	-0.05		0	0.00	
				6.24									
PURE DMMP	A3095	0	0.11		0.19	0.19	-1.1	0	0.10		0	-0.00	
	A3097 *	0	0.06		0.29	0.28	-3.1	0	0.09		0	0.00	
	A4010	0	0.05		0.38	0.36	-4.7	0	0.09		0	0.01	
	A4012 *	0	-0.02		0.67	0.65	-3.4	0	-0.00		0	0.01	
	A4014	0	-0.09		0.97	0.90	-7.0	0	0.00		0	0.01	
	A4016	0	-0.17		1.4	1.08	-22.8	0	0.02		0	0.02	
	A4018	0	-0.19		1.2	1.19	-37.4	0	0.01		0	0.01	
PURE IPROH	A4021	0	0.06		0	-0.06		0.19	0.14	-27.4	0	0.02	
	A4023 *	0	0.03		0	-0.06		0.29	0.26	-9.3	0	-0.00	
	A4025	0	0.00		0	-0.06		0.38	0.33	-12.6	0	0.01	
	A4027 *	0	0.00		0	-0.02		0.67	0.61	-9.4	0	-0.01	
	A4029	0	-0.01		0	0.02		0.97	0.90	-7.5	0	0.01	
	A4031 *	0	-0.02		0	0.09		1.4	1.41	0.9	0	0.00	
	A4033	0	-0.07		0	0.16		1.9	2.00	5.1	0	-0.02	
PURE DEM	A3023 *	0	-0.02		0	-0.02		0	0.04		0.29	0.33	12.1
	A3025 *	0	-0.02		0	-0.00		0	0.03		0.38	0.42	10.3
	A3027 B	0	0.02		0	0.01		0	-0.04		0.67	0.62	-7.0
MEOH:1 DMMP:1 IPROH:2	A4036	0.095	0.09	-8.3	0.095	0.09	-8.4	0.19	0.22	13.2	0	0.00	
	A4038 *	0.17	0.13	-25.9	0.17	0.20	18.8	0.34	0.29	-13.8	0	-0.02	
	A4041 *	0.24	0.21	-11.7	0.24	0.33	35.4	0.48	0.46	-3.3	0	-0.00	
	A4042 *	0.35	0.39	9.4	0.35	0.48	36.3	0.7	0.71	1.0	0	0.00	
	A4044 *	0.48	0.55	14.4	0.48	0.63	30.8	0.95	1.35	42.3	0	0.00	
A4046 *	0.72	0.70	-3.3	0.72	0.67	-21.1	1.4	1.44	2.5	0	-0.00		
				11.83									
MEOH:1 DMMP:2 IPROH:4	A4049	0.054	0.27	396.3	0.11	0.09	-21.8	0.22	0.20	-10.9	0	0.00	
	A4051	0.096	0.14	42.7	0.19	0.27	41.1	0.38	0.96	152.6	0	-0.01	
	A4053	0.14	0.14	-0.7	0.28	0.31	11.8	0.55	0.63	14.7	0	-0.01	
	A4055 *	0.2	0.18	-9.0	0.4	0.46	16.0	0.8	0.82	2.2	0	-0.01	
	A4057 *	0.27	0.28	6.2	0.54	0.52	-4.3	1.1	1.04	-5.5	0	0.00	
A4059	0.41	0.40	-2.0	0.83	0.65	-33.7	1.6	1.30	-18.6	0	-0.03		
				11.91									
MEOH:2 DMMP:1 IPROH:3	A4062	0.13	0.05	-61.5	0.063	-0.03	-141.3	0.19	0.17	-11.6	0	-0.01	
	A4064 *	0.22	0.41	85.9	0.11	0.10	-12.7	0.34	0.20	-40.9	0	-0.01	
	A4066	0.32	0.46	42.2	0.16	0.17	8.1	0.48	0.30	-37.1	0	-0.02	
	A4068 *	0.46	0.42	-8.7	0.23	0.25	7.4	0.7	0.65	-7.9	0	-0.01	
	A4070	0.63	0.65	3.3	0.32	0.39	23.1	0.95	0.90	-5.7	0	0.00	
A4072 *	0.97	1.01	4.4	0.48	0.48	-0.4	1.4	1.42	1.5	0	0.01		
				34.36									
MEOH:10 DMMP:1 IPROH:5	A4075 *	0.24	0.26	7.1	0.024	-0.02	-170.8	0.12	0.18	46.7	0	0.01	
	A4077	0.42	0.46	10.2	0.042	0.02	-57.1	0.21	0.26	23.3	0	0.02	
	A4079 *	0.61	0.61	-0.8	0.061	0.04	-35.3	0.3	0.29	-2.7	0	0.01	
	A4081 *	0.88	0.90	2.2	0.088	0.10	9.1	0.44	0.44	-0.7	0	-0.01	
	A4083	1.2	1.76	46.8	0.12	0.23	95.0	0.59	0.76	28.6	0	-0.00	
A4085	1.6	1.76	-2.2	0.18	0.23	30.0	0.81	0.76	-16.6	0	-0.00		
				11.64									

\* USED IN CALIBRATION STANDARD

#### SUMMARY

Passive-remote FTIR spectrometers have been successfully field tested, and this demonstrated its capability for identifying a chemical plume. In addition, laboratory tests showed that this instrumentation can identify a single component in a mixture containing completely overlapping IR spectra absorbances. Therefore, FTIR technology has the potential for use as an independent method for compliance assurance under Title III, Air Toxics of the Clean Air Act of 1990. Moreover, the light weight and portability of the instrumentation are significant advantages.

Work must continue in developing a large spectral library data base consisting of analytes and backgrounds. Appropriate QA/QC procedures must also be developed to obtain EPA certification.

#### REFERENCES

1. J. Demirgian and S. Spurgash, "Remote Detection of Chemical Agents by Infrared Spectroscopy, Progress Report FY 1989," ANL/ACL-90/1, 1990.
2. G. Small, R. Kroutil, J. Ditillo, and W. Løerop, Anal. Chem. (1988) 60, pg. 264.

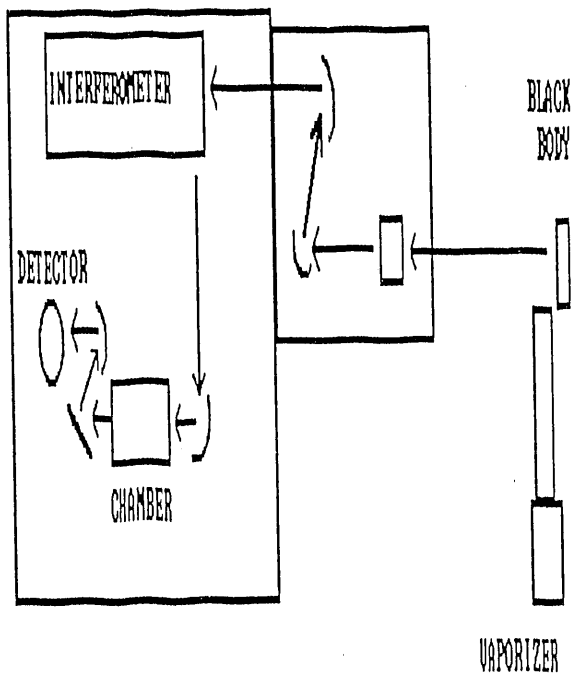


Figure 1. Schematic of the experimental apparatus.

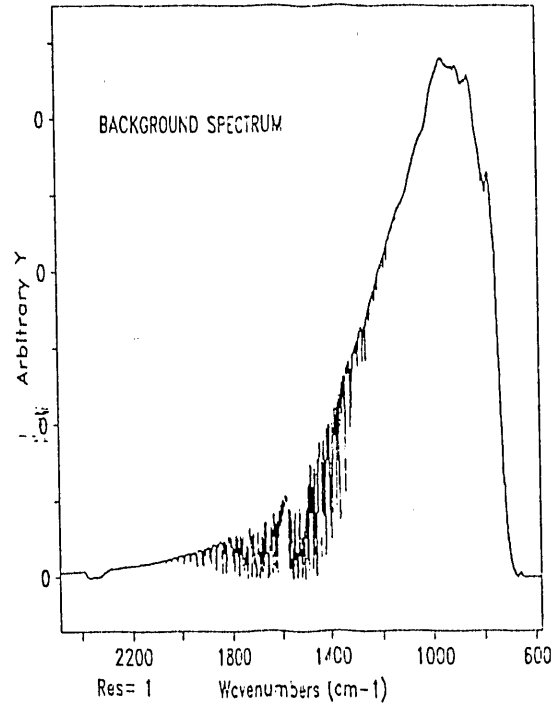


Figure 2. Background spectrum obtained using the Nic6000 and an MCT-A detector.

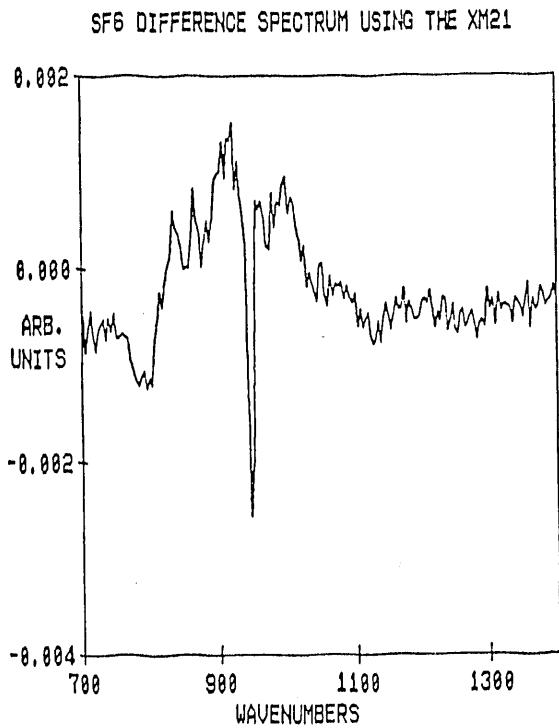


Figure 3. Passive-remote IR spectrum of SF<sub>6</sub> obtained during a field release.

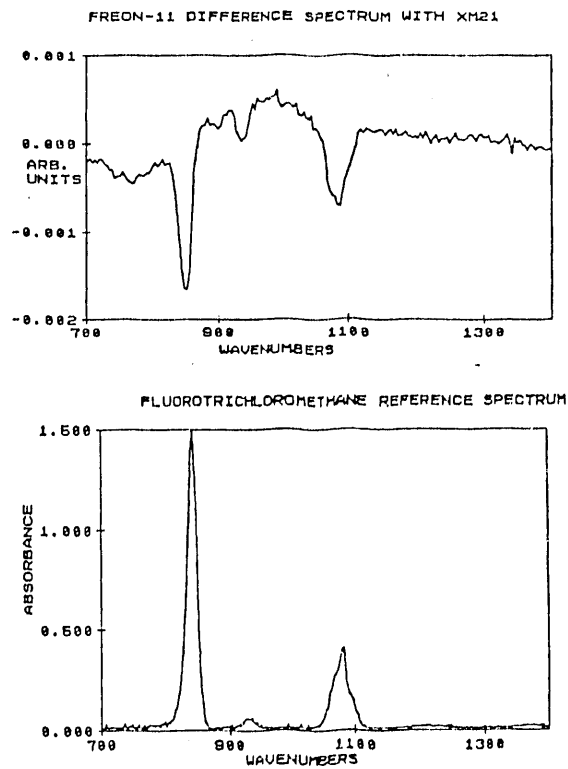


Figure 4. Passive-remote IR spectrum of Freon-11 obtained during a field release.

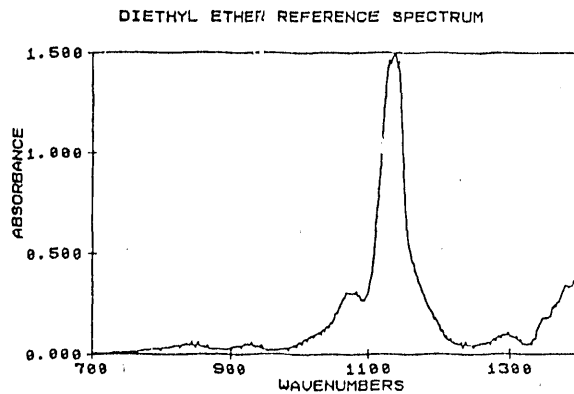
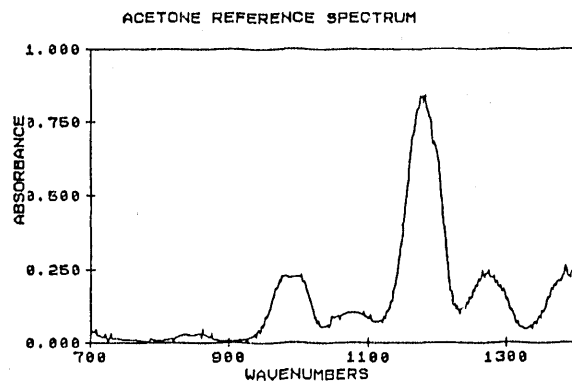
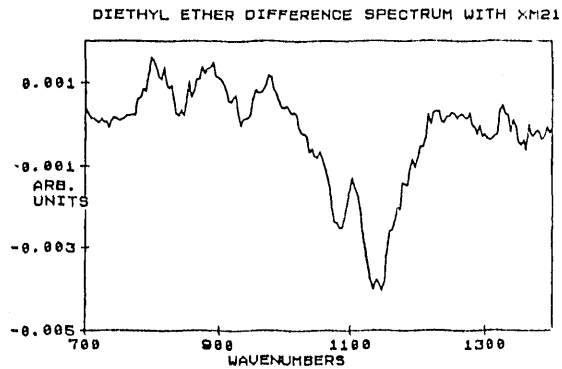
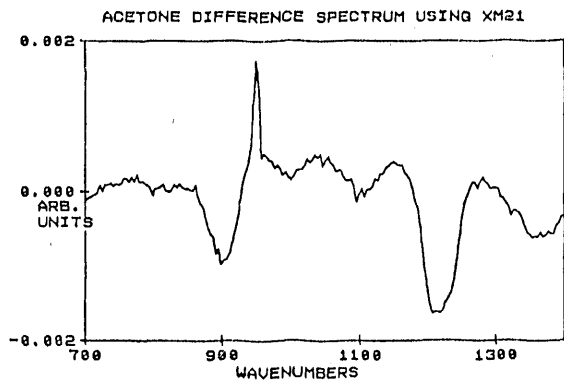


Figure 5. Passive-remote IR spectrum of acetone obtained during a field release.

Figure 6. Passive-remote IR spectrum of ethyl ether obtained during a field release.

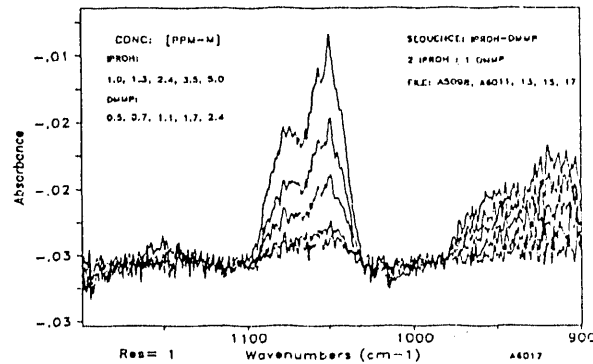
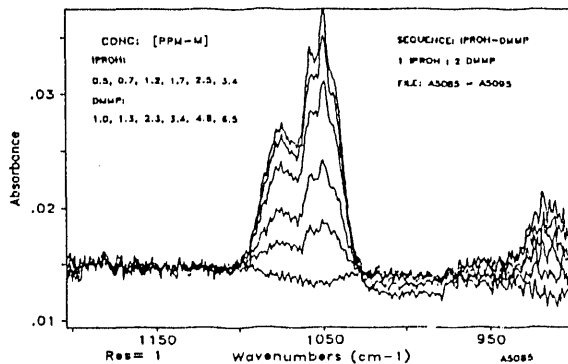
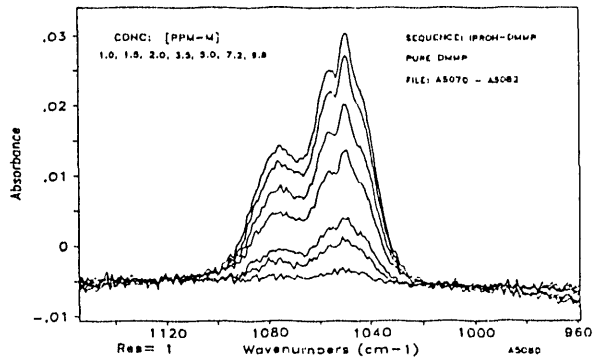
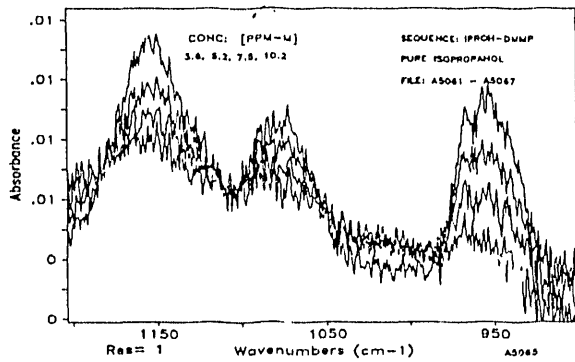


Figure 7. Passive-remote IR spectra of pure isopropanol, pure DMMP, and two isopropanol-DMMP mixtures.

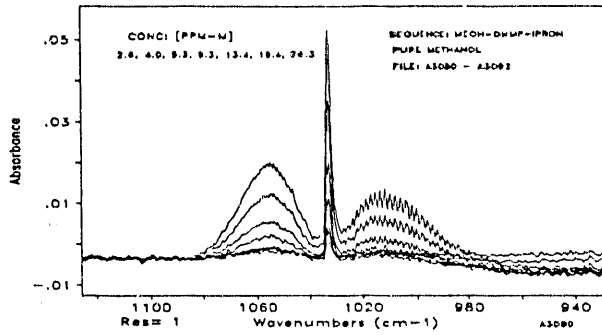


Figure 8. Passive-remote IR spectra of pure MEOH used for the analysis of a mixture of MEOH-DMMP-IPROH in the spectral region 1200-940  $\text{cm}^{-1}$ .

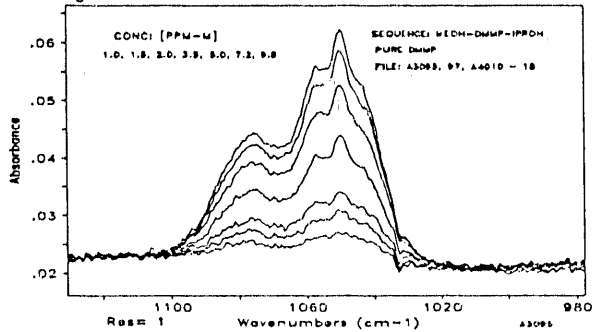


Figure 9. Passive-remote IR spectra of pure DMMP used for the analysis of a mixture of MEOH-DMMP-IPROH in the spectral region 1200-940  $\text{cm}^{-1}$ .

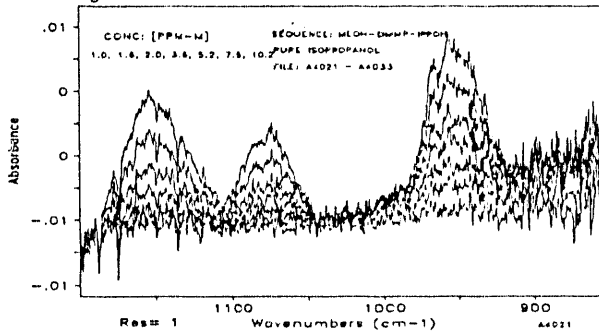


Figure 10. Passive-remote IR spectra of pure IPROH used for the analysis of a mixture of MEOH-DMMP-IPROH in the spectral region 1200-940  $\text{cm}^{-1}$ .

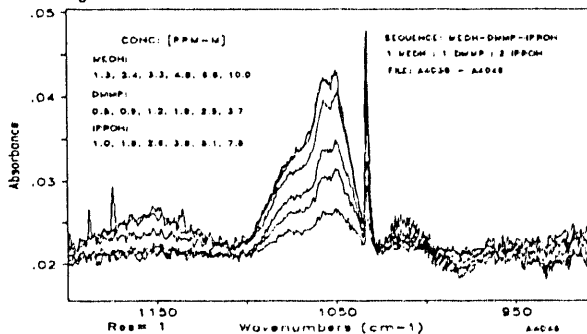


Figure 11. Passive-remote IR spectra of a mixture of MEOH-DMMP-IPROH with a volume ratio of 1:1:2 in the spectral region of 1200-940  $\text{cm}^{-1}$ .

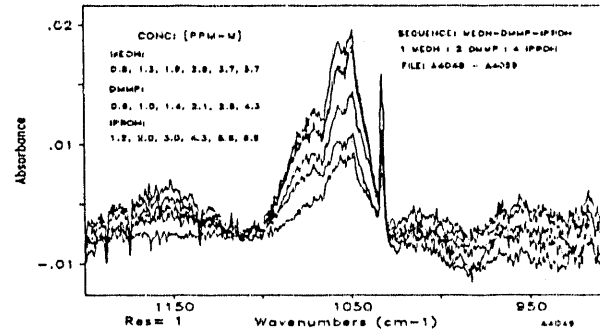


Figure 12. Passive-remote IR spectra of a mixture of MEOH-DMMP-IPROH with a volume ratio of 1:2:4 in the spectral region 1200-940  $\text{cm}^{-1}$ .

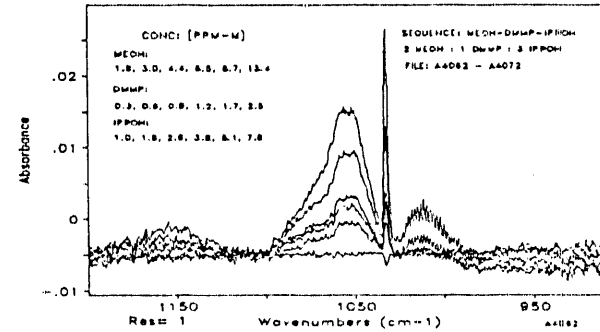


Figure 13. Passive-remote IR spectra of a mixture of MEOH-DMMP-IPROH with a volume ratio of 2:1:3 in the spectral region 1200-940  $\text{cm}^{-1}$ .

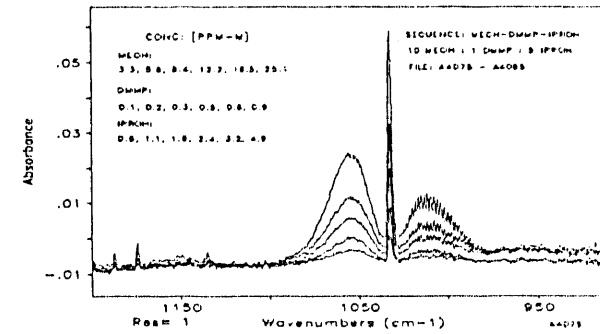


Figure 14. Passive-remote IR spectra of a mixture of MEOH-DMMP-IPROH with a volume ratio of 10:1:5 in the spectral region 1200-940  $\text{cm}^{-1}$ .

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