

Use of a portable infra-red analyzer for low-level hydrocarbon emissions

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Abstract

During some on-site tests, a portable infra-red (IR) analyzer was used successfully to monitor for hydrocarbon vapors. The detection limit of the IR analyzer is much lower than that of most other hydrocarbon vapor monitors and can be used in situations where, as in most ambient air monitoring situations, the levels are often less than a milligram per cubic metre (mg/m^3). Traditional procedures used to measure hydrocarbon concentrations at lower levels involves the collection of samples on-site, which are then transported to a laboratory for analysis. The advantage of providing continuous sampling data is that it may indicate trends in the hydrocarbon vapor emissions that may not be apparent using a grab-type sample. The initial tests were designed to determine if the IR analyzer was capable of monitoring the low-level hydrocarbons in a field situation. The findings from that initial work was followed by modification of the test procedure to include an upwind IR analyzer, shortened sampling cycles to produce more data, and additional canister samples collected outside the burn period. The metered grab samples, using Summa canisters, were collected over a 1 h period and any results would therefore, reflect an average value over the hour. The IR analyzer, with a sampling cycle of approximately 1 min, was able to produce a near real-time distribution of the hydrocarbon vapors in the test site emissions. Because the testing parameters and methods are quite different, it is difficult to compare these two methods, but indications suggest strongly that the use of this portable IR instrument could help to describe the hydrocarbon emissions downwind from a source, as well as to monitor for these hydrocarbons continuously, including situations where the levels are below detection limits of most portable detectors. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Infra-red detector; Portable instruments; Air monitoring; VOC; Burn emissions

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1. Introduction

1.1. *The test site*

The location for the test was the United States Coast Guard (USCG) Fire and Safety Test Detachment test facility on Little Sand Island in Mobile Bay, Mobile, AL. This test site has been used in the past for similar test procedures [1,2]. The source of the hydrocarbon vapor emissions was a test tank which contained brine onto which was pumped fresh diesel fuel which was ignited and allowed to burn in a controlled fashion for 1 h. The quantity of fuel was replenished over the duration of the test to sustain the burning for the full hour. When possible, as many as three burns, each of 1 h duration, were performed in a day. When multiple burns were performed, a minimum of 1 h between each burn was observed. The first set of burn events for this study took place on 26 September 1997 and 1 October, 1997 [3]. The second and most recent set took place between 25 August and 9 September, 1998 [4]. Both the Summa canisters and the infra-red detectors were among several instruments used to monitor the burn emissions. During the first sample set, the IR analyzer was located at a downwind position, approximately 60 m from the source. The nearest constant location of a Summa canister was 15 m nearer the burn in the same vector from the burn pan. There was some sample collection done using Summa canisters at the same location as the IR analyzer, but not for all six burns in the set. For the second set of data, the Summa canisters were placed side-by-side with the IR detector. As a background, for each Summa and IR sample collected, there was an ambient sample collected at an upwind location. Power was supplied to all instruments in the first sample set and, in the second set, the upwind sampling instruments by a large on-site diesel-powered generators that operated continuously throughout the day. The generators were situated away from the sample stream. Downwind instruments had shore power provided in the second set only.

At the beginning of each day, test instruments were turned on and allowed to warm up for the maximum allowable time. The Summa canisters that were used during the burns were opened and closed manually in coordination with the burn event. Thus, those canisters were used to collect sample solely while the burn was taking place. Also, during the burns associated with boom 4 in Mobile 1998, a second pair of canisters were used to collect air samples between the burn events, thus, they were turned on when a burn was complete and turned off again when the next burn began. The IR analyzer monitored continuously throughout the day, collecting samples both during and between burns.

1.2. *Summa canister sampling and analysis*

The canisters used for collecting the air samples were 6 l stainless steel pre-cleaned and evacuated Summa canisters. The canisters are widely used for ambient air sampling. An adjustable restrictor orifice was used at the inlet of the canister to meter the flow to approximately 25 ml/min. For a series of three 1 h tests, this would yield a sample volume of approximately 4.5 l. This sample volume was deemed to be the maximum while maintaining

a constant flow through the valve since, as the canister fills up, it becomes impossible for the weaker vacuum to keep the same flow rate through the orifice. The canister valve was operated manually. Each restricter orifice was purged thoroughly before the field tests and baked out overnight between uses.

The analysis was performed by the analysis and air quality division (AAQD) of environment Canada using a cryogenic pre-concentration technique with a high resolution gas chromatograph and quadrupole mass-selective detector (GC-MSD) as described in EPA methods TO-14 [5] and TO-15 [6]. An Entech Model 7000 pre-concentrator with auto-sampler (Entech Instruments, Inc., Simi Valley, CA) was used for sample pre-concentration. The instruments used for species identification and quantification were a Hewlett-Packard 5890 series II chromatograph with a Hewlett-Packard 5970 MSD. Volatile organic compounds (VOC) were separated on a 60 m, 0.32 mm i.d. fused silica capillary column with a 1.0 mm film thickness of J&W (J&W Scientific Inc., Folsom, CA) DB-1 bonded liquid phase.

All samples were diluted with clean, humidified air in order to provide sufficient positive canister pressure for proper operation of AAQD analytical systems. Air from each canister was drawn through the pre-concentrator's multi-stage trapping system and sample volumes were measured with a mass flow controller. A gaseous mixture of internal standard was added in combination with 500 ml of the sample into a glass bead trap maintained at -170°C . A three-stage concentration technique called Microscale Purge and Trap was used to separate water from the organic sample components. The sample with the internal standard was concentrated to approximately 0.5 ml in the cryogenic glass bead trap. The trap was then heated to 25°C while slowly flushing with 50 ml of helium to transfer the organics to a secondary Tenax trap maintained at -50°C . This process results in the transfer all of the VOCs with less than 1 ml of water. Then, while heating to 180°C , the VOCs were back-flushed to be further focused on an open-tubular focusing trap at -160°C . This cryofocusing trap was then ballistically heated to 100°C , resulting in rapid injection of VOCs onto the analytical column.

Temperature programming of the GC column was used to obtain optimum results. Column temperature was held initially at -60°C for 3 min, then raised to 250°C at a rate of $8^{\circ}/\text{min}$. The GC-MSD was operated in the selected ion monitoring mode (SIM). Identification of target analytes by SIM analysis is based on a combination of chromatographic retention time and relative abundance of selected monitored ions.

An instrument calibration standard was prepared using stock gas standards prepared in the laboratory of the AAQD from three multi-component liquid mixtures and Scott certified gas mixture cylinders (Scott Environmental Technology Inc., Plumsteadville, PA). Quantification was based on daily three point linear regression calibration curves obtained from analysis of this external standard mixture.

1.3. Portable infra-red analyzer

The two infra-red analyzers used in the field tests were both Brüel & Kjaer (B&K) Multi-gas Monitor Type 1302 (Brüel & Kjaer, Naerum, Denmark). The B&K 1302 has an optical filter carousel which holds six discreet wavelength filters. The gas selectivity is dependant on the optical filters installed in the unit. The detection is performed on a

closed cell using a paired photo-acoustic detector system. This method can be used in a field situation effectively, due to the ability to measure the differential values of the two detectors and eliminating effects of external vibration. Although portable, the instrument was connected to an AC source while in use.

The 1302 instruments were set up to monitor continuously throughout the sampling period. As soon as a sample had been analyzed, the cell was flushed and a new sample was drawn into the detection cell to begin the next analysis. Each cycle took approximately 2 min. For each sample cycle, data was generated for each of the wavelength filters. Data was stored internally by each 1302 instrument. One of the filters in each instrument is used to measure water vapor concentration. The results from this one filter were used to compensate for water vapor interference of the other filters. Results were calculated in mg/m^3 . The data is stored with three significant figures. The resolution for this instrument is dependant on the calibration factor used and the range of the values during the test period. For this field test, the resolution was $0.01 \text{ mg}/\text{m}^3$, unless the value exceeded $10 \text{ mg}/\text{m}^3$, in which case the resolution was $0.1 \text{ mg}/\text{m}^3$.

Of the optical filters installed in the 1302 instruments, the filter that was used as a means to detect total hydrocarbons for this study allows light with wavelength between $3.3\text{--}3.5 \mu\text{m}$ to enter the detection cell. This waveband is known to be in the range of IR energy absorbed by a typical carbon-hydrogen (C–H) bond, such as in a $-\text{CH}_3$ or $-\text{CH}_2$ group. This is a common organic molecular bond found on all aliphatic hydrocarbon vapors, as well as aromatic and other functional group compounds with an aliphatic portion or ligand. For example, benzene does not show an IR peak in this range, but ethylbenzene, toluene, and xylenes do, due to their aliphatic portions. The detection limit and the response factor varies depending on the compound. Because of the varied response to a wide range of compounds and a bias towards more responsive compounds, this is a general screening method and the value generated may not reflect the true balanced VOC concentration when the composition of the sample is unknown. The calibrant for this test was a certified Scott gas mixture of propane in air. Results will be presented in propane equivalents.

2. Results

2.1. Summa canister samples

Full laboratory analysis of the Summa canister samples includes speciated concentrations of 143 VOC/air toxic compounds (listed in Appendix A). Not all of the compounds are visible in the selected IR waveband. In order to present a comparison to results found with the IR instrument, a number of the compounds not visible with the selected IR filter were removed from the list. A total was then found for the remaining compounds. This total was used as an approximation of the VOCs in the sample which could be compared with the IR results. For each sample, there was a matching upwind sample collected. The values for each downwind sample was adjusted (reduced) by the total found at the upwind sample location (full results presented in Table 1). A summary of the results is shown in Table 2.

Table 1
Selected speciated components and VOC totals for all samples^a

Sample date	25 August 1998	25 August 1998	27 August 1998	27 August 1998	3 September 1998	3 September 1998	9 September 1998	9 September 1998	9 September 1998	9 September 1998
Sample location	DW2B	UW1B	DW2B	UW1B	DW2B	UW1B	DW2B	UW1B	DW2B	UW1B
Miscellaneous information	Boom 1, 1A	Boom 1, 1A	Boom 2	Boom 2	Boom 3	Boom 3	Boom 4	Boom 4	Post-burn	Post-burn
Initial volume (ml)	2755	4356	1013	1296	3964	4314	3680	4547	5815	4272
Dilution factor	3	2	8	7	2	2	2	2	2	2
Results in $\mu\text{g}/\text{m}^3$ compound name										
1-Propene	1.19	1.74	1.83	0.80	1.28	1.88	0.59	0.92	0.29	0.53
1-Propene	11.13	8.72	4.71	4.48	5.21	4.73	2.98	2.80	3.50	3.26
Isobutane (2-methylpropane)	2.30	1.88	0.75	0.70	2.23	2.25	1.34	1.20	1.56	1.36
1-Butene/2-methylpropene	2.01	1.79	3.66	1.10	1.05	1.63	0.38	0.64	0.52	0.44
1,3-Butadiene	ND	ND	ND	ND	0.11	0.32	ND	ND	ND	ND
Butane	5.15	4.36	1.45	1.45	5.08	4.50	2.63	2.06	2.79	2.60
<i>t</i> -2-Butene	0.13	0.23	ND	ND	0.14	0.18	0.06	0.17	0.10	0.10
2,2-Dimethylpropane	0.07	0.06	ND	ND	0.07	0.07	0.05	0.04	0.05	0.03
<i>c</i> -2-Butene	0.14	0.27	ND	ND	0.15	0.16	ND	0.12	0.07	0.08
Chloroethane	0.80	0.17	ND	ND	0.11	0.12	0.06	0.09	0.09	0.10
2-Methylbutane	6.18	5.24	1.74	1.87	7.12	6.67	2.33	1.84	2.42	2.26
1-Pentene	0.28	0.44	0.87	ND	0.32	0.53	ND	0.13	0.10	0.09
2-Methyl-1-butene	ND	ND	ND	ND	0.22	0.23	ND	ND	ND	ND
Pentane	4.16	3.70	1.20	1.20	4.03	3.74	1.63	1.31	1.91	1.78
Isoprene (2-methyl-1,3-butadiene)	1.87	2.86	0.98	1.62	0.47	0.60	0.39	0.69	0.88	0.77
Ethylbromide	0.09	0.26	ND	ND	ND	ND	ND	ND	ND	ND
<i>t</i> -2-Pentene	0.10	0.10	ND	ND	0.18	0.18	ND	0.03	ND	0.02
<i>c</i> -2-Pentene	0.09	0.15	ND	ND	0.19	0.19	ND	ND	ND	0.06
2-Methyl-2-butene	0.32	0.39	ND	ND	0.48	0.46	0.08	0.10	0.11	0.11
2,2-Dimethylbutane	0.26	0.21	ND	0.16	0.40	0.37	0.14	0.12	0.18	0.13
Cyclopentene	0.05	0.05	0.11	ND	0.11	0.07	ND	0.02	0.03	0.03
4-Methyl-1-pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-Methyl-1-pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cyclopentane	0.27	0.24	ND	ND	0.33	0.28	0.13	0.08	0.11	0.11
2,3-Dimethylbutane	0.36	0.30	ND	ND	0.45	0.42	0.14	0.09	0.13	0.10
<i>t</i> -4-Methyl-2-pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Methylpentane	NDR	NDR	NDR	NDR	NDR	NDR	NDR	NDR	NDR	NDR
<i>c</i> -4-Methyl-2-pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-Methylpentane	0.83	0.96	ND	0.38	0.97	1.02	0.35	0.33	0.49	0.41
1-Hexene/2-methyl-1-pentene	ND	0.44	1.14	ND	0.30	0.64	ND	0.25	ND	ND
<i>n</i> -Hexane	1.88	2.09	0.53	0.61	2.10	1.99	0.70	0.56	0.89	0.79
<i>t</i> -2-Hexene	ND	ND	ND	ND	ND	0.05	ND	ND	ND	ND

Table 1 (Continued)

Sample date	25 August 1998	25 August 1998	27 August 1998	27 August 1998	3 September 1998	3 September 1998	9 September 1998	9 September 1998	9 September 1998	9 September 1998
Sample location	DW2B	UW1B	DW2B	UW1B	DW2B	UW1B	DW2B	UW1B	DW2B	UW1B
Miscellaneous information	Boom 1, 1A	Boom 1, 1A	Boom 2	Boom 2	Boom 3	Boom 3	Boom 4	Boom 4	Post-burn	Post-burn
Initial volume (ml)	2755	4356	1013	1296	3964	4314	3680	4547	5815	4272
Dilution factor	3	2	8	7	2	2	2	2	2	2
Results in $\mu\text{g}/\text{m}^3$ compound name										
<i>t</i> -3-Methyl-2-pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>c</i> -2-Hexene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>c</i> -3-Methyl-2-pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,2-Dimethylpentane	ND	ND	ND	ND	0.07	ND	ND	ND	ND	ND
Methylcyclopentane	0.43	0.61	ND	ND	0.68	0.51	0.22	0.11	0.27	0.15
2,4-Dimethylbutane	ND	0.13	ND	ND	0.19	0.20	ND	ND	ND	ND
2,2,3-Trimethylbutane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Methylcyclopentane	0.06	0.04	ND	ND	0.09	0.07	0.03	0.06	0.03	0.03
Cyclohexane	0.29	0.32	ND	ND	0.25	0.20	0.11	0.07	0.11	0.09
2-Methylhexane	0.57	0.42	ND	ND	0.50	0.61	0.17	0.15	0.22	0.16
2,3-Dimethylpentane	0.27	0.19	ND	ND	0.37	0.41	0.12	ND	0.12	0.12
Cyclohexene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-Methylhexane	0.62	NDR	ND	ND	0.65	0.68	NDR	0.18	NDR	0.22
1-Heptene	ND	0.32	0.64	ND	ND	0.48	ND	ND	ND	ND
2,2,4-Trimethylpentane	0.40	0.33	0.25	0.36	0.68	0.91	0.16	0.15	0.16	0.15
<i>t</i> -3-Heptene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>c</i> -3-Heptene										
Heptane	1.05	0.70	0.37	0.48	0.82	0.81	0.25	0.24	0.36	0.32
<i>t</i> -2-Heptene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>c</i> -2-Heptene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,2-Dimethylhexane	ND	ND	ND	ND	ND	NDR	ND	ND	ND	ND
Methylcyclohexane	0.63	0.34	ND	0.13	0.34	0.33	0.12	0.10	0.16	0.14
2,5-Dimethylhexane	0.16	0.10	ND	ND	0.12	0.17	0.04	0.06	ND	0.04
2,4-Dimethylhexane	0.11	0.09	ND	ND	0.12	0.19	0.06	0.03	ND	0.05
2,3,4-Trimethylpentane	ND	0.11	ND	ND	0.25	0.34	ND	0.04	ND	ND
Toluene	3.20	2.56	1.21	1.37	3.70	3.78	1.10	1.00	1.29	1.19
2-Methylheptane	0.37	0.17	ND	ND	0.28	0.30	ND	0.11	0.13	0.09
1-Methylcyclohexene	ND	ND	ND	ND	ND	ND	ND	0.06	0.05	ND
4-Methylheptane	ND	0.09	ND	ND	0.13	0.12	ND	ND	ND	ND
3-Methylheptane	0.29	0.18	ND	ND	0.29	0.31	ND	0.09	0.12	0.08
<i>c</i> -1,3-Dimethylcyclohexene	0.14	0.05	ND	ND	0.07	0.07	0.02	0.03	0.06	0.04
<i>t</i> -1,4-Dimethylcyclohexane	0.08	0.03	ND	ND	0.05	0.05	ND	ND	0.03	ND
2,2,5-Trimethylhexane	0.04	0.04	ND	ND	0.08	0.08	ND	0.02	ND	ND
1-Octene	ND	0.58	1.27	ND	0.67	0.47	ND	ND	ND	ND

Octane	0.61	0.31	0.27	0.29	0.51	0.48	0.13	0.14	0.17	0.14
<i>t</i> -1,2-Dimethylcyclohexane	0.11	0.05	ND	ND	0.07	0.07	ND	ND	ND	ND
<i>t</i> -2-Octene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>c</i> -1,4-Dimethylcyclohexane/ <i>t</i> -1,3-dimethylcyclohexane	0.04	ND	ND	ND	0.03	0.04	ND	ND	ND	ND
<i>c</i> -2-Octene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethylbenzene	1.33	2.00	0.25	0.26	0.80	0.79	0.23	0.22	0.20	0.21
<i>m</i> -Xylene/ <i>p</i> -xylene	4.89	7.13	0.70	0.77	2.45	2.49	0.56	0.48	0.50	0.49
Styrene	0.10	0.55	ND	ND	0.13	0.09	ND	0.04	0.05	0.05
<i>o</i> -Xylene	1.30	1.54	0.27	0.29	0.87	0.83	0.23	0.20	0.24	0.22
1-Nonene										
<i>n</i> -Nonane	0.77	0.40	ND	0.54	0.61	0.44	0.23	0.11	0.19	0.15
<i>iso</i> -Propylbenzene	0.09	0.07	0.08	0.06	0.08	0.07	0.03	0.03	0.04	0.03
3,6-Dimethyloctane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>n</i> -Propylbenzene	0.24	0.18	0.11	0.12	0.25	0.20	0.08	0.08	0.07	0.06
3-Ethyltoluene	0.49	0.42	0.12	0.20	0.64	0.54	0.13	0.10	0.12	0.10
4-Ethyltoluene	0.30	0.23	0.14	0.16	0.35	0.30	0.09	0.10	0.08	0.07
1,3,5-Trimethylbenzene	0.31	0.32	0.08	0.12	0.34	0.29	0.07	0.05	0.05	0.05
2-Ethyltoluene	0.23	0.20	0.09	0.11	0.30	0.22	0.08	0.06	0.06	0.05
<i>tert</i> -Butylbenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2,4-Trimethylbenzene	0.92	0.72	0.29	0.37	1.07	0.89	0.24	0.19	0.18	0.17
1-Decene										
Decane	0.80	0.45	0.28	0.30	0.77	0.42	0.27	0.13	0.22	0.12
<i>iso</i> -Butylbenzene	0.05	0.03	ND	ND	0.03	0.03	0.02	0.02	0.02	0.02
<i>sec</i> -Butylbenzene	0.04	0.03	ND	0.04	0.04	0.03	0.02	0.02	0.03	0.02
1,2,3-Trimethylbenzene	0.28	0.17	0.12	0.11	0.26	0.20	0.08	0.06	0.06	0.06
<i>p</i> -Cymene	0.21	0.19	ND	ND	0.07	0.10	0.08	0.07	0.08	0.07
1,3-Diethylbenzene	0.08	0.04	0.08	0.06	0.12	0.09	0.03	0.04	0.04	0.02
1,4-Diethylbenzene	0.26	0.14	0.12	0.17	0.31	0.21	0.11	0.10	0.07	0.07
<i>n</i> -Butylbenzene	0.08	0.04	ND	0.08	0.08	0.06	0.04	0.04	0.04	0.03
1,2-Diethylbenzene	0.07	ND	ND	ND	0.05	0.04	0.03	0.04	0.03	ND
Undecane	1.11	0.39	0.20	0.32	1.04	0.40	0.47	0.15	0.20	0.13
Naphthalene	1.18	0.32	0.40	0.30	0.43	0.29	0.19	0.24	0.12	0.12
Dodecane	1.75	0.33	0.30	0.41	1.14	0.36	0.75	0.25	0.22	0.20
“VOC” Total	66.02	60.33	26.62	21.75	56.33	54.35	20.56	19.05	22.43	20.67
Sample date	36032.00	36032.00	36034.00	36034.00	36041.00	36041.00	36047.00	36047.00	36047.00	36047.00
Sample location	DW2B	UW1B	DW2B	UW1B	DW2B	UW1B	DW2B	UW1B	DW2B	UW1B
Miscellaneous information	Boom 1, 1A	Boom 1, 1A	Boom 2	Boom 2	Boom 3	Boom 3	Boom 4	Boom 4	Post-burn	Post-burn
Initial volume (ml)	2755.10	4355.69	1012.79	1296.23	3963.88	4314.00	3680.44	4547.42	5814.56	4272.32
Dilution factor	3.00	2.00	8.00	7.00	2.00	2.00	2.00	2.00	2.00	2.00

^a ND: not detected; NDR: not detected due to incorrect ion ratio; XS: concentration exceeded detector range.

Table 2
Totals for selected VOCs in relevant Summa samples^a

Date	Sampling station	Burn status	Burn number	Adjusted total
26 September 1997	DW3B	ON	2.1	-2.81
26 September 1997	DW2B	ON	2.1	519.50
26 September 1997	DW2B	ON	2.2	15.58
26 September 1997	DW2B	ON	2.3	46.00
1 October 1997	DW2B	ON	4.1	-107.70 ^b
1 October 1997	DW2B	ON	4.2	358.10
1 October 1997	DW2B	ON	4.2	44.76
1 October 1997	DW3B	ON	2.1, 2.2, 2.3, 3.1 ^a	227.50
25 August 1998	DW2B	ON	1.1, 1A.1, 2.3 ^a	5.69
27 August 1998	DW2B	ON	2.1, 2.2 ^a	4.87
3 September 1998	DW2B	ON	3.1, 3.2, 3.3 ^a	1.98
9 September 1998	DW2B	ON	4.1, 4.2, 4.3 ^a	1.53
9 September 1998	DW2B	OFF	4.1, 4.2, 4.3 ^a	1.76

^a Cumulative samples collected over consecutive burn periods.

^b Unusually high background reading, refer to Table 1.

2.2. Infra-red analyzer data

2.2.1. 1997 sample set

Using the data acquired by the internal data logger of the IR detector, two methods of data observation have been used. For one, the portion of the data collected over the exact time periods as those where the Summa canister samples were being collected were observed and compared to the results from the Summa canister analysis. Also, unlike the Summa canister samples, trends throughout the day, including before, during, and after each burn, were observed. Data for 1 October, during which there were three burns, is shown (Fig. 1). With no upwind data in this sample set, this data was not corrected. Average levels during the burn periods were calculated and are shown in Table 3.

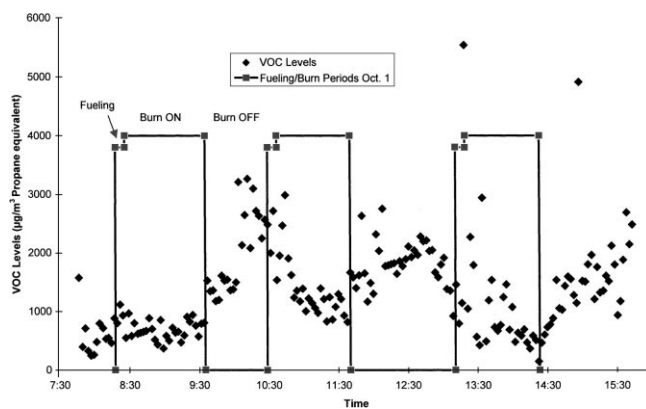


Fig. 1. Raw data from downwind IR detector boom 4, burns 1, 2, 3, 1 October, 1997.

Table 3
Average VOC concentration using IR detector

Date	Burn number	Average VOC concentration ^a (mg/m ³)	Burn status	Sampling station
26 September 1997	2.1	1430	ON	DW3B
26 September 1997	2.2	983	ON	DW3B
26 September 1997	2.3	2010	ON	DW3B
1 October 1997	4.1	707	ON	DW3B
1 October 1997	4.2	1370	ON	DW3B
1 October 1997	4.3	1110	ON	DW3B
25 August 1998	1.1	9	ON	DW2B
25 August 1998	1A.1	34	ON	DW2B
25 August 1998	1A.2	20	ON	DW2B
25 August 1998	1A.3	25	ON	DW2B
27 August 1998	2.1	27	ON	DW2B
9 September 1998	4.1	24	ON	DW2B
9 September 1998	Post 4.1	32	OFF	DW2B
9 September 1998	4.2	16	ON	DW2B
9 September 1998	Post 4.2	28	OFF	DW2B
9 September 1998	4.3	30	ON	DW2B
9 September 1998	Post 4.3	34	OFF	DW2B

^a Propane equivalent.

2.2.2. 1998 sample set

Results generated were done so by taking the differential values between the upwind and downwind stations. A positive result indicates that the downwind station had relatively higher readings than the upwind station. A negative reading is indicative of higher readings at the upwind station, not that unusual since the wind shifted considerably throughout the experiment. The data was recorded by the internal data logger of the IR detectors. Results for the IR detectors during this session were recorded in parts per million (ppm). Examples of the raw data recorded (Figs. 2 and 3) as well the corrected differential data is shown (Figs. 4 and 5). Results shown in Figs. 4 and 5 have been adjusted against the upwind reading and slope corrected. An average VOC concentration over the period of each burn was calculated (Table 3). For the purposes of comparison with the cumulative Summa samples, the results in Table 3 are shown in mg/m³.

3. Discussion

3.1. Experimental conditions

Two changes were made to the experiment in an effort to improve the scientific validity of the results found in the first data set, that is the addition of an upwind (background) IR monitor and side-by-side monitoring with the canister samplers. In that the experimental validity of the data was much better, there were other factors which restricted the

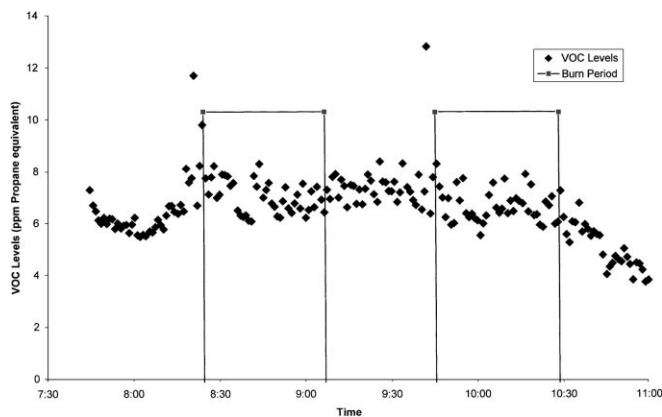


Fig. 2. Raw data from downwind IR detector boom 1A, burns 2, 3, August 26, 1998.

ability to make conclusions based on the gathered data. Although in the preliminary tests we were not able to make a direct comparison between canister sample results and IR data, due to instruments not being side-by-side, the field conditions were favorable. That is to say that, in the earlier test series, the smoke plume being sampled was directed towards the instruments downwind of the burn tank. The stations at which the instruments were placed were deemed to be the prime locations to collect airborne vapors from the test tank, based on predicted wind patterns. These predictions held true in 1997, when the first series of tests took place. These patterns were not consistent while the 1998 samples were being collected. Unfortunately, logistics does not allow the field operators to ideally place all of the equipment prior to each burn, but rather to outline a grid and

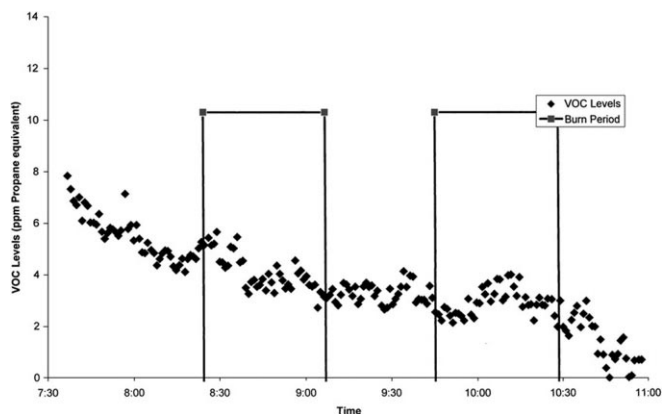


Fig. 3. Raw data from upwind IR detector boom 1A, burns 2, 3, August 26, 1998.

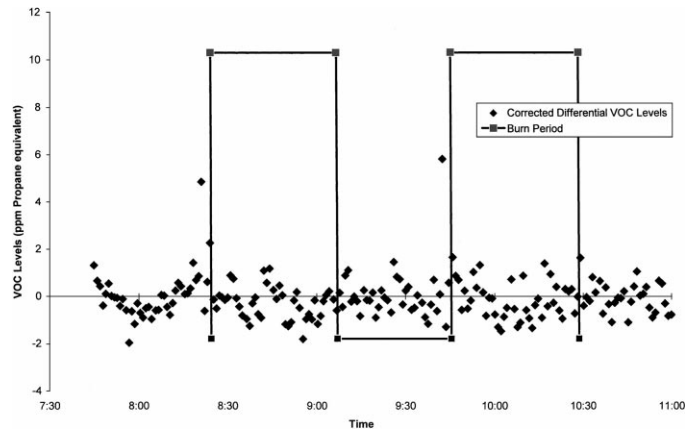


Fig. 4. Slope/baseline corrected differential VOC data from IR detectors boom 1A, burns 2, 3, August 26, 1998.

maintain the instruments at those locations throughout the test period. A number of the tests conducted in this experiment proceeded although the smoke plume did not pass directly over the sampling instruments (placed in the location with the highest likelihood of being beneath the smoke plume). This has a severe effect on the experimental data. For one, in conditions where there was no upwind/downwind bias of the paired IR instruments relative to the smoke plume (in other words, the plume was as likely to swing over the “upwind” station as the “downwind” station), there was no experimental value in sampling. This was the case during the second burn for boom 2 and all of the burns for boom 3. The conditions were so unfavorable towards this portion of the experiment that

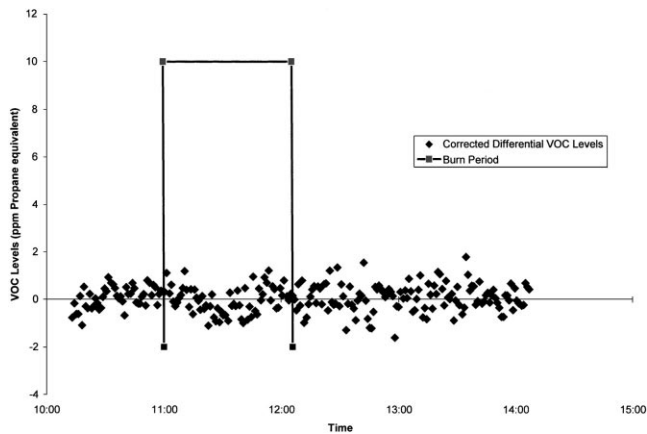


Fig. 5. Slope/baseline corrected differential VOC data from IR detectors boom 4, burn 1, September 8, 1998.

the IR instruments were not used during these burns, even though canister samples were collected.

Secondly, inconsistent sampling conditions during the collection of cumulative samples (with the Summa canisters) leads to potentially lower values as the VOC concentration is averaged to include both favorable and unfavorable sampling situations. For example, a burn for which the conditions are favorable (smoke plume directed over sampler) will produce samples with the highest concentration of airborne vapors due to the burn. A burn for which the conditions are not favorable (smoke directed away from the sampler) will produce samples that are less affected by the burn. When these samples are combined, as with the cumulative samples in this experiment, the quantities are diluted and an average concentration determined by the analysis will be lower than when the conditions are consistently favorable. In comparison with results collected in 1997, the VOC results presented here are consistently lower, due largely to the change in field conditions while the sampling was conducted.

3.2. Direct comparison

When these two detection methods are compared directly (Fig. 6), there are a number of considerations and allowances which must be made. As these methods are both capable of detecting volatile organic compounds, they are using different definitions of the “total VOC”, which we have tried to rectify by eliminating some of the speciated compounds detected by the GC-MSD to more closely approximate what is being detected by the IR detector. However, the IR analyzer is strongly biased towards some compounds and the calibration is made to a single compound (propane) from which the “total” number is derived. For the first data set, most of the comparisons involve samples that were collected 15 m away, over which distance significant differences in actual levels could have been realized. Another factor to be considered in the earlier results is that a common baseline for the entire operating period of the IR detector was used, which is more susceptible

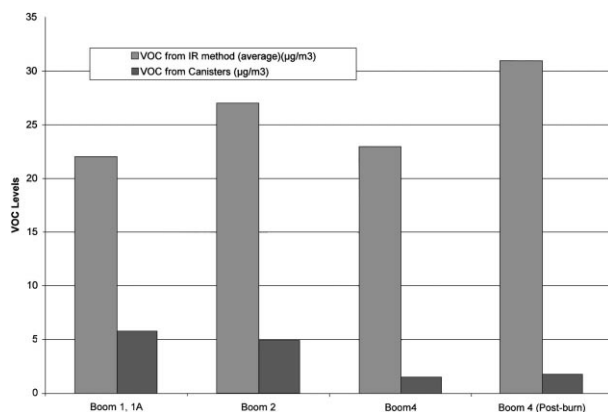


Fig. 6. Direct comparison of IR with Summa samples.

to environmental effects (humidity, temperature) than if baselines were calculated over each segment relevant to one burn period. Also, while the integration software in the IR instrument is designed to compensate for effects of temperature and humidity changes, large variances from calibration parameters can cause deviation in results [7]. There were marked temperature and humidity changes over the course of each day's sampling.

One of the encouraging results from the first sampling set was in the trend in the relative response from burn to burn, that is, when the laboratory result showed a relatively low result, the IR detector also showed a relatively low result. Unfortunately, with results as low as they were in the second set, it is difficult to determine if the results from the IR detectors are reliable, since the values found in the canister samples are below the detection limit for most of the VOC compounds detectable by the IR detectors. In order to better correlate the instrument response with the laboratory analysis, the concentration of hydrocarbons needs to be higher by probably two orders of magnitude, so that the values found would be well above the detection limit. At these levels, it is difficult and ill-advised to derive any direct correlation between these two methods.

3.3. *Observed trends*

Some interesting trends can be observed using the IR detector in continuous sampling mode over the full day, including the monitoring of burn emissions as well as fuelling and pre- and post-burn periods. For one, the concentrations of hydrocarbons measured actually tended to be higher between burns than during the burns themselves. Also, many of the highest spikes were outside the actual burn period. Thirdly, the level during the burn period is relatively consistent. Each of these observations deserves some consideration.

In the first series of tests, using only one IR detector, it was observed that levels were, on average, lower during the burn than in the periods preceding and following the burn period (Fig. 1). When using a background instrument for simultaneous data collection in the 1998 sample set, this trend was less apparent, chiefly due to the lower levels produced, but can be observed in Figs. 4 and 5. Understandably, the highest spikes were often observed while fuelling was taking place prior to the burns. Seen throughout the experiment, during both sample sets, was an apparent drop in the VOC's measured by the IR analyzers during the burn period. It was suggested by trends in the early tests that in the period of time following the burn, there could be some residual emissions due to the inefficient combustion which occurs in the final stage of the burn, when the hot fuel residue which does not get consumed by the open fire is vaporized. Interestingly, the cumulative Summa canister sample collected in the period following the boom 4 burns did show agreement with the trend observed with the IR instruments. Both the uncorrected and background-corrected totals found higher VOC levels in the post-burn cumulative sample than the cumulative sample collected while the burn was taking place, as shown in Table 1.

Short-term elevations in VOC levels which occurred immediately prior to burn periods are likely due to the fuelling which lasted approximately 8 min prior to each burn. Preliminary testing using only the downwind instrument suggested that, since operators were in close proximity, that human activity might be the cause of the elevated levels. In this experiment, the comparison to the upwind level (Fig. 3) shows clearly that the spike is consistently

downwind (Fig. 2) and, since operators were present at both stations, the elevated level can be more clearly linked with the fuelling. Although VOC levels in the post-burn period often fluctuated as much or more than at other times, markedly elevated levels were not consistently observed. Throughout the experiment, other small spikes were observed, but no gross fluctuations from background levels were found.

The advantage of real-time instrumentation is the ability to show short-term changes in the monitoring conditions, should they arise. Overall, the level of hydrocarbons, although low, was seen to be relatively consistent over the burn period, with slightly lower levels during the middle of the burn. This would indicate that emissions from the burn do not vary widely over the burn period. This observation strengthens the confidence in the continued use of Summa canister sampling as a reasonable means to predict the hydrocarbon emissions from a burn of diesel fuel.

All of the observed trends are limited by the low VOC results found during the experiment. What cannot be disputed, however, is that without the IR detector in continuous sampling mode over the full day, including the monitoring of burn emissions as well as fuelling and pre- and post-burn periods, these trends could not have been observed at all.

4. Conclusions

While the aim of this experiment was to determine if IR instrumentation could be used to determine the level of hydrocarbons/VOC in low-level emissions, the levels proved to be too low to adequately postulate a correlation with traditional sampling methods. This lack of experimental control is, unfortunately, a reality when practising field experiments under variable conditions. The experiment was improved greatly by the introduction of a second upwind IR instrument and the differential levels of VOC helped to clarify the trends of VOC emissions, if not to correlate with the laboratory analysis. The indication that the early part of the burn may generate the lowest amount of VOC emissions is interesting, and may suggest that the open fire is hot and efficient enough to consume the majority of the VOCs from the fuel, as well as some of the ambient vapors. This trend would certainly be clarified with more favorable field conditions and more testing.

On a more positive note, this test has shown that the emitted hydrocarbon levels do not appear to change dramatically over the duration of a 1 h burn. This supports the use of a metered grab-type sample as an adequate sampling procedure in fuel/oil burn emission testing for the collection of a representative sample.

With the use of the two methods, we can get a more complete picture of the emission patterns. While with the IR instrument, we can offer near-real-time trends not available with canister sampling, the GC-MSD offers us speciation of compounds which the portable IR instrument cannot do. It may still be possible to formulate a relationship between these two sampling methods and to eventually consider IR detectors for on-site measurement of low-level hydrocarbon emissions. In the interim, these instruments have shown to be reliable in the field and can be used with confidence to show emission patterns and possible anomalies which cannot be determined using traditional sampling methods. When used in support of traditional sampling methods in emission monitoring, the IR detectors can be valuable in providing near-real-time information not previously available.

Appendix A. Compounds detected by laboratory analysis

Chloroform	0.42	0.26
t-2-Hexene	ND	ND
2-Ethyl-1-Butene	ND	0.15
t-3-Methyl-2-Pentene	ND	ND
c-2-Hexene	ND	ND
c-3-Methyl-2-Pentene	ND	ND
2,2-Dimethylpentane	ND	ND
1,2-Dichloroethane	0.05	0.09
Methylcyclopentane	0.43	1.19
2,4-Dimethylpentane	ND	0.33
1,1,1-Trichloroethane	0.32	0.33
2,2,3-Trimethylbutane	ND	ND
1-Methylcyclopentene	0.06	0.14
Benzene	1.19	1.55
Carbontetrachloride	0.53	0.46
Cyclohexane	0.29	0.62
2-Methylhexane	0.57	1.52
2,3-Dimethylpentane	0.27	0.77
Cyclohexene	ND	ND
3-Methylhexane	0.62	1.64
Dibromomethane	0.11	0.07
1,2-Dichloropropane	ND	ND
Bromodichloromethane	NDR	NDR
Trichloroethylene	0.13	0.12
1-Heptene	ND	1.00
2,2,4-Trimethylpentane	0.40	1.62
t-3-Heptene	ND	ND
c-3-Heptene		
Heptane	1.05	1.52
t-2-Heptene	ND	ND
c-2-Heptene	ND	ND
c-1,3-Dichloropropene	ND	ND
2,2-Dimethylhexane	ND	NDR
Methylcyclohexane	0.63	1.28
2-5-Dimethylhexane	0.16	0.36
2,4-Dimethylhexane	0.11	0.43
t-1,3-Dichloropropene	ND	ND
1,1,2-Trichloroethane	ND	ND
Bromotrichloromethane	ND	ND
2,3,4-Trimethylpentane	ND	0.59
Toluene	3.20	6.04
2-Methylheptane	0.37	0.84
1-Methylcyclohexene	ND	0.12
4-Methylheptane	ND	0.44
Dibromochloromethane	0.07	0.04
3-Methylheptane	0.29	0.79
c-1,3-Dimethylcyclohexane	0.14	0.29
t-1,4-Dimethylcyclohexane	0.08	0.15
EDB (1,2-Dibromoethane)	0.28	0.62

Results in µg/m³	25-Aug-98	25-Aug-98	25-Aug-98
Compound Name	DW2B	DW1B	DW3B
1-Propene	1.19	1.89	1.05
1-Propene	11.13	9.89	12.29
Freon 22 (Chlorodifluoromethane)	0.59	0.76	0.59
Freon 12 (Dichlorodifluoromethane)	2.46	2.55	2.46
Propyne			
Chloromethane	4.71	1.74	1.46
Isobutane (2-Methylpropane)	2.30	2.58	2.27
Freon 114 (1,2-Dichlorotetrafluor)	0.16	0.16	0.15
Vinylchloride (Chloroethylene)	0.18	ND	ND
1-Butene/2-Methylpropene	2.01	1.79	1.05
1,3-Butadiene	ND	0.36	0.13
Butane	5.15	5.44	5.31
t-2-Butene	0.13	0.20	0.11
2,2-Dimethylpropane	0.07	0.07	0.08
Bromomethane	0.63	0.11	0.39
1-Butyne	ND	ND	ND
c-2-Butene	0.14	0.18	0.10
Chloroethane	0.80	0.13	0.10
2-Methylbutane	6.18	6.39	6.14
Freon 11 (Trichlorofluoromethane)	2.53	15.48	2.04
1-Pentene	0.28	0.45	0.22
2-Methyl-1-Butene	ND	0.26	ND
Pentane	4.16	4.68	4.39
Isoprene (2-Methyl-1,3-Butadiene)	1.87	2.05	2.07
Ethylbromide	0.09	ND	ND
t-2-Pentene	0.10	0.18	0.06
1,1-Dichloroethylene	0.07	0.08	ND
c-2-Pentene	0.09	0.19	0.10
Dichloromethane	0.93	0.58	0.34
2-Methyl-2-Butene	0.32	0.49	0.23
Freon 113 (1,1,2-Trichlorotrifluor)	0.77	1.08	0.75
2,2-Dimethylbutane	0.26	0.43	0.27
Cyclopentene	0.05	0.08	0.03
t-1,2-Dichloroethylene	0.12	ND	0.07
4-Methyl-1-Pentene	ND	0.15	ND
3-Methyl-1-Pentene	ND	ND	ND
Cyclopentane	0.27	0.38	0.27
1,1-Dichloroethane	ND	ND	ND
2,3-Dimethylbutane	0.36	0.72	0.35
t-4-Methyl-2-Pentene	ND	ND	ND
2-Methylpentane	NDR	NDR	NDR
c-4-Methyl-2-Pentene	ND	ND	ND
3-Methylpentane	0.83	1.81	0.93
1-Hexene/2-Methyl-1-Pentene	ND	0.69	ND
c-1,2-Dichloroethylene	ND	0.07	ND
n-Hexane	1.88	2.29	1.77

2,2,5-Trimethylhexane	0.04	0.19	0.05
1-Octene	ND	0.62	ND
Octane	0.61	1.00	0.58
t-1,2-Dimethylcyclohexane	0.11	0.26	0.13
t-2-Octene	ND	ND	ND
Tetrachloroethene	0.29	0.19	0.40
c-1,4/t-1,3-Dimethylcyclohexane	0.04	0.11	0.04
c-2-Octene	ND	ND	ND
Chlorobenzene	0.42	0.18	0.11
Ethylbenzene	1.33	2.59	1.44
m/p-Xylene	4.89	8.51	5.96
Bromoform	0.08	0.05	0.04
1,4-Dichlorobutane	ND	ND	ND
Styrene	0.10	1.65	0.23
1,1,2,2-Tetrachloroethane	0.07	0.12	0.05
o-Xylene	1.30	2.93	1.62
1-Nonene			
n-Nonane	0.77	1.44	0.48
iso-Propylbenzene	0.09	0.15	0.07
3,6-Dimethyloctane	ND	0.15	ND
n-Propylbenzene	0.24	0.35	0.21
3-Ethyltoluene	0.49	1.10	0.45
4-Ethyltoluene	0.30	0.55	0.25
1,3,5-Trimethylbenzene	0.31	0.95	0.45
2-Ethyltoluene	0.23	0.52	0.18
tert-Butylbenzene	ND	ND	ND
1,2,4-Trimethylbenzene	0.92	2.22	0.79
1-Decene			
Benzylchloride	0.17	ND	ND
1,3-Dichlorobenzene	0.12	0.05	0.04
Decane	0.80	1.71	0.45
1,4-Dichlorobenzene	0.17	0.09	0.07
iso-Butylbenzene	0.05	0.07	0.03
sec-Butylbenzene	0.04	0.07	0.03
1,2,3-Trimethylbenzene	0.28	0.77	0.21
p-Cymene	0.21	0.25	0.17
1,2-Dichlorobenzene	0.19	0.07	0.06
Indan	0.08	0.19	0.07
1,3-Diethylbenzene	0.08	0.14	0.04
1,4-Diethylbenzene	0.26	0.46	0.15
n-Butylbenzene	0.08	0.12	0.05
1,2-Diethylbenzene	0.07	0.05	ND
Undecane	1.11	3.49	0.51
1,2,4-Trichlorobenzene	0.99	0.16	0.12
Naphthalene	1.18	0.79	0.31
Dodecane	1.75	6.50	0.67
Hexachlorobutadiene	0.53	0.05	0.03
Hexylbenzene	0.28	0.22	0.09

The shaded compounds are selected for comparison with IR results. Samples shown for illustration only — full results presented in Table 1.

References

- [1] M.F. Fingas, K. Li, F. Ackerman, J.R.J. Paré, M.C. Bissonnette, P.R. Campagna, R.D. Turpin, M.F. Soleki, S.J. Getty, M.J. Trespalacios, E.J. Tennyson, Emissions from mesoscale in situ oil fires: the Mobile 1991 and 1992 tests, in: *Proceedings of the 16th Arctic and Marine Oil Spill Program (AMOP) Technical Seminar*, Calgary, Environment Canada, Ottawa, Canada, 1993, pp. 749–822.
- [2] W.D. Walton, W.H. Twilley, A.D. Putorti, R.R. Hiltabrand, Smoke measurements using an advanced helicopter transported sampling package with radio telemetry, in: *Proceedings of the 18th Arctic and Marine Oilspill Program (AMOP) Technical Seminar*, Edmonton, Environment Canada, Vol. 2, Ottawa, Canada, 1995, pp. 1053–1074.
- [3] M.D. Goldthorp, P. Lambert, M.F. Fingas, Use of a portable infra-red analyzer for low-level hydrocarbon emissions, in: *Proceedings of the 15th Technical Seminar on Chemical Spills*, Edmonton, Environment Canada, Ottawa, Canada, 1998, pp. 97–113.
- [4] M.D. Goldthorp, P. Lambert, A closer look at the use of a portable infra-red analyzer for low-level hydrocarbon emissions, in: *Proceedings of the 16th Technical Seminar on Chemical Spills*, Calgary, Environment Canada, Ottawa, Canada, 1999, pp. 23–40.
- [5] W.T. Winberry, N.T. Murphy, R.M. Riggan, Method TO-14, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA-600/4-89-017, US Environmental Protection Agency, Research Triangle Park, NC, 1988.
- [6] W.T. Winberry, Method TO-15, *The Determination of Volatile Organic Compounds in Air Collected in Summa Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)*, Final Draft, US Environmental Protection Agency, Research Triangle Park, NC, 1997.
- [7] B.D. Williams, Emission Measurements Research Division, Environment Canada, Ottawa, Ont., 1998, personal communication.