ABSTRACT

CONTINUOUS MONITORING OF VOLATILE ORGANIC COMPOUND EMISSIONS USING MICROTRAP BASED INJECTION TECHNIQUE AND GAS CHROMATOGRAPHY

by
Wenjun Chen

A microtrap is made by packing a small diameter tubing with an adsorbent. The microtrap can be rapidly heated with a pulse of electrical current resulting in a sharp desorption that can act as an injection for GC separation. The microtrap can be used in several configurations to concentrate and inject sample in continuous, on-line monitoring system.

In this research a laboratory scale catalytic incinerator was set up and volatile organic compounds in the incinerator effluents were monitored using the microtrap based injection systems. The detection systems used were gas chromatography and nonmethane organic carbon (NMOC) analyzer. Conventional sample valve, sequential valve microtrap and on-line microtrap in a backflush configuration were studied and compared as on-line injection devices. Figures of merits such as calibration curves, spike recovery and detection limits were studied. The conversion efficiencies of the catalytic incineration process at different operation conditions were also evaluated.

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by
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CHAPTER 1

INTRODUCTION

1.1 VOCs Analysis

Volatile organic compounds (VOCs) have received much attention recently both as air and water pollutants. Within the class of VOCs are straight chain/aromatic hydrocarbons, halogenated organics and molecules containing other heteroatoms. Since these compounds have high vapor pressure, even from water or solid matrix they are eventually volatilized into air. Many of these compounds, specially the aromatic and the halogenated organics are known to be toxic, mutagenic and/or carcinogenic. Even in trace quantities (parts per million/billion) some of these compounds pose a threat to public health. Consequently the VOCs are increasingly being regulated. For example, trichloroethylene (TCE) contamination has been found in ground water and in aquifers and has been a target of much environmental litigation. With the introduction of oxygenated compounds in gasoline, oxygenated VOCs have also become an important class of pollutants. According to new regulation, the organic-bound oxygen such as alcohols, aldehydes and ketones must be added to gasoline at least of 2.7% to reduce CO emissions. This is resulting in oxygenated products in auto emissions. Many VOCs also participate in photochemical reaction with NO_x to generate ozone in the troposphere.

VOCs emissions may come from stationary or mobile sources. Mobile sources, such as automobiles can be controlled by improving the gasoline and engine performance. Stationary sources such as chemical plants, incineration and landfill facilities also emit a variety of VOCs. These sources are regulated and their monitoring is mandatory [1-3]. Consequently, the analysis of VOCs in air has become more important in recent years [4-7]. Monitoring is done with different goals in mind. Workplace air is monitored for immediate danger from exposure to toxic gases. Ambient air is monitored for lower concentrations of VOCs which may cause health effect because of chronic exposures, or result in troposphere ozone formation. Outdoor air may be monitored to study the contribution of sources such as industrial stacks, incinerators, landfills or automobile traffic. Air emission from industrial stacks and vents are also monitored to assure compliance with applicable regulations. Each of these situations put different constraints on sampling and monitoring requirements [8-10]. However, all the methods used to measure VOCs concentrations include three distinct steps: collection, speciation and detection.

Procedures commonly used to collect vapor-phase organic compounds include whole-air samplers, cryogenic collection, sorbent collection and derivatization methods. Whole air sampling involves the capture of an air parcel in a container. Stainless steel canisters or plastic bags constructed from an inert material, such as Teflon or Tedlar, are most commonly used. Each of these container types has advantages and disadvantages. Rigid metal canisters are easier to clean, less prone to leakage, and better for shipping samples from field sites to an analytical laboratory. However, canisters are expensive. In addition, because of their rigid structure, cans are not as useful as bags for the collection of time-integrated samples. In several recent field studies, a combination of bags and canisters has been used. For example, due to their low weight, Teflon bags have been attached to a tethered balloon line and filled at various altitudes in order to define vertical hydrocarbon profiles. Contents of the bags were then transferred to stainless steel canisters for storage and shipment to the laboratory. Cryogenic collection utilizes a glass, Teflon, or stainless steel trap that is cooled to sub-ambient temperatures. The most common sorbent used to collect organic compounds in air is Tenax. The main advantage of the adsorbent method is that large volumes of ambient air can be processed; these large samples lead to very low detection levels for many organic compounds. Derivatization is commonly used to collect polar, oxygenated hydrocarbons. Use of the derivatization methods requires that collection and recovery efficiencies be established for each species.

The method used to resolve a complex air matrix into individual species is dependent on the collection procedure that was used. Gaseous samples are separated into the individual components using gas chromatography, whereas samples in liquid media (derivatized and absorbed) are usually resolved on a liquid or ion chromatography.

Nearly all of the vapor-phase organic compounds show response in a flame ionization detector. Consequently, this detector is most commonly used. Other special-purpose detectors include photoionization, mass spectrometry, atomic emission, ion mobility, mercury oxide reduction, and chemilumiescence detectors. Flame ionization has been proven to be the best detection system for most organic compounds. Its nearly equal carbon response for the true hydrocarbons greatly facilitates calibration. For example, a single hydrocarbon (or a mixture of a few hydrocarbons) can be used to determine the response-versus-concentration curve for calibration of a GC system. Mass spectrometry which uses a quadrupole mass spectrometer as a GC detector for VOCs analysis has come of age in recent years. Development of capillary columns with low carrier gas flows has greatly facilitated the interface of the GC and mass spectrometer (MS). The entire capillary column effluent can be introduced directly into the MS ion source to maximize system sensitivity. GC-MS detection limits are compound-specific but in most cased are similar to those of the flame ionization detector. Quantitation with a mass spectrometer as detector requires calibration curves for individual species. However, total ion chromatogram from a GC-MS is usually very similar to the equivalent FID chromatogram. Consequently, the MS detector can be used to establish hydrocarbon identities and an FID system for quantitation.

Thus traditional monitoring procedure includes collection of a sample from a process or waste stream, then transporting it to a central laboratory for analysis. Adsorbent trapping is one method which concentrates the desired materials as the sample air is passed through a trap or cartridge containing an appropriate adsorbent. The VOCs adsorb on the surface of the packing, and are thus separated from the bulk of the air. The cartridges or traps are then returned to the laboratory, and the analyte is removed either by raising the temperature of the trap to release the adsorbed compounds, or by washing them from the trap with an appropriate solvent. Samples of air can also be collected in the field in containers, and these can be returned to the laboratory for analysis. The primary requirement for an air sampling container is that it must neither add nor remove analytes from the sample. For low level ambient air samples, the most commonly used containers are low pressure stainless steel canisters, with an internal surface which has been electrolytically deactivated.

The GC analysis is done using either packed or, more frequently, capillary columns. EPA and other regulatory agencies have published methods, recommending particular columns for each class of VOCs. Packed columns are somewhat easier to use, with larger sample capacities, but are not suitable for the analysis of ambient samples, where a very large number of compounds at similar levels are expected. Usually, analysis is done hours or days after a sample is collected. EPA methods which have approved to analyze for VOCs in ambient air and stack emissions use either whole air samplers such as Tedlar bags and canisters (EPA method TO 14) or sorbent cartridges (EPA method T 01). The analysis is usually done using a GC with flame ionization detector (FID) or a mass spectrometer (GC/MS) [11-14].

These EPA methods are very useful in routine analysis of VOCs in air sample. However, they can not be used for continuous or real-time monitoring. Continuous monitoring has become more popular in chemical process control and environmental monitoring. Continuous monitoring offers many advantages. Real-time or near real-time information about a process can be obtained [15]. This real-time information can be fed back to process so that the chemical process can be optimized. A continuous monitoring system is an automatic, unattended system. Sampling, sample conditioning and injection are done on-line. No delay occurs between sampling and analysis so as to eliminate cross contamination and sample loss.

1.2 Continuous On-line Monitoring

In an ideal process analyzer, the sample should flow continuously through the system. This system can extract the sample, condition it, and present it to an analytical instrument for measurement. The process analyzer should have a fast response to reflect real-time information about the process. Infrared methods and mass spectrometry have been used in real-time monitoring of organics in wastewater and stack gas [16-17]. For example, infrared analyzers using narrow bandpass interference filters have been used for ambient air and process stream monitoring [18]. IR provides fast response, a rugged instrument and both qualitative and quantitative information. However, moisture interference and band overlap are very serious problems in IR analysis of complicated environmental samples. The sensitivity is not high enough for compliance with today's environmental regulations.

On-line mass spectrometers have been used for detecting VOCs in emissions [19]. Mass spectrometry provides fast response, and excellent quantitative and qualitative information. But direct injection only can detect middle ppm (parts per million) level of VOCs. Membrane introduction mass spectrometry (MIMS) has bee developed and applied to continuous monitoring organics in water and gas streams. MIMS is an analytical technique based on the selective transport of analyte molecules of interest across a semipermeable membrane into a mass spectrometer. The analyte matrix, such as water, is excluded from passage through the membrane to varying degrees depending on the membrane material used. This provides a degree of enrichment of the analyte molecules entering the mass spectrometer and allows lower levels of detection than can be obtained using other direct-sampling systems. Most of applications of MIMS focus on VOCs analysis in water. However, many parameters, such as temperature, pressure and flowrate etc., will affect membrane-based enrichment of analytes. The enrichment factor and recovery depend on the molecular properties of analytes. Furthermore, lag time and memory effects will significantly affect the precision and accuracy of analytical results. On other hand, a typical environmental sample may contain dozens of compounds. Without any separation it is not easy to detect the analytes, even though single ion monitoring (SIM) technique is used.

Gas Chromatography has been used in continuous monitoring applications such as process stream analysis since the 1950s [20]. A crucial part of process GC is the injection device, which can extract, condition and inject sample into the GC column. Sample valves have used as injectors of the process GC for continuous monitoring. These types of injectors are commercially available and are routinely used in industry. But the injection volume of a sample valve is limited and a typical sample volume for capillary column is about 100 μl. Thus a small detector response is generated, due to the small injection volume. If a large sample volume is injected using a sample valve, the peaks are broad and the resolution is poor. So the sample valve is inadequate to analyze trace level samples. Analysis of trace concentrations of sample at sub parts per billion levels is usually done by sampling a large quantity of air and concentrating the pollutants. Sorbent traps are often used to extract analytes from a large sample. Sorbent trap characteristics have been studied and particular attention has been given to their sample trapping characteristics[29-31]. After sampling, the traps are transported to the laboratory, where the pollutants are desorbed and analyzed by GC or GC/MS. However, these techniques cannot be used in continuous, on-line analysis.

1.3 On-line Microtrap System

On-line microtrap (OLMT) has been used as an injection device for continuous monitoring of VOCs in gas stream [21-28]. The typical microtrap is made by packing a short metallic tubing with an adsorbent. The microtrap is placed in front of GC column instead of a conventional injection port. When VOCs pass through the microtrap, they are trapped and concentrated. The VOCs are released and injected into the GC column by rapid electrical heating. It can make reproducible injections. It is rugged, and exhibits long term stability. It has several advantages over an injection valve. Unlike an injection valve, it acts as an injection device as well as a sample preconcentrator. Thus much lower detection limits are obtained using on-line microtrap compared to a sample valve. This method has the potential advantage over valves in term of faster operation, smaller band width and lower detection limit.

The microtrap can be configured in different ways with a gas sampling valve. In what has been referred to as sequential valve microtrap (SVM), a microtrap is connected in series with a gas sample valve [21]. In this technique, a large volume injection (several milliliters) or several small volume (e. g., multiple 100 μl) injections are made by the sample valve. The analytes are trapped by the microtrap. Then the microtrap is heated to inject the analytes into the GC. The microtrap can be also be configured in a way that it can make injection in a backflush mode. This is referred as OLMT-BF. Here a microtrap replaces the sample loop of an injection valve. In sampling mode, a sample stream passes through the microtrap. The analytes are trapped by the microtrap, and the matrix gases such as moisture and air are vented out. When the valve is switched to the injection mode, inlet carrier gas (e.g., He) passes through microtrap. The flow direction is reversed to backflush the microtrap. Then the microtrap is heated and analytes are desorbed/injected into the GC column.

Injection devices based on microtrap have shown advantages in continuous, on-line monitoring of VOCs in air low detection limits have been achieved and the device is simple and can be operated automatically.

1.4 Nonmethane Organic Carbon Analysis

Nonmethane organic carbon (NMOC) is the measure of total carbon except methane in source emissions. NMOC analysis is the measurement of volatile organic compounds as total gaseous nonmethane organics as carbon in air sample..

Method 25 [32-36] was developed in the mid 1970's as a means of quantifying volatile organic compound (VOC) emissions from stationary sources. After a stack sample is collected, the analysis is performed on a unit known as the nonmethane organic (NMOC) analyzer. Since the analyzer does not speciate the hydrocarbons, the instrument must respond equivalently to all hydrocarbons. The equivalent response is achieved by catalytically oxidizing all organics to CO_2 and then reducing the reducing the resultant CO_2 to methane which is measured by a flame ionization detector (FID). The simplified schematic of EPA method 25 of non-methane organic analyzer is shown in Figure 1. The NMOC analyzer consists of an injection loop and valve, a separation column, an oxidation catalyst, a reduction catalyst, and a flame ionization detector. The sample is loaded in the sample loop using a vacuum pump. Then the sample is injected into the GC column, in which nonmethane organics are separated from CO, CO_2 and CH_4. Once the permanent gases have eluted, the column is backflushed so that the organics are injected into the NMOC detector. Oxygen is added to the helium carrier gas before the oxidation catalyst. Hydrogen is added before the reduction catalyst. Thus carbon-containing compounds are oxidized to CO_2 first, and then reduced to methane. The effluent from the reduction catalyst is monitored by FID. Figure 2 is a typical chromatogram of the NMOC analyzer.

In our experiment the microtrap based system was used as an injector. As the sample containing VOCs, CO_2, CH_4, H_2O and N_2 is passed through the injection system, the microtrap selectively traps the VOCs but allows CO_2 ,CH_4, N_2 and H_2O to pass through. Thus, the microtrap served as a separator as well as an on-line preconcentrator. Then the microtrap is heated to inject the VOCs into the NMOC detector.

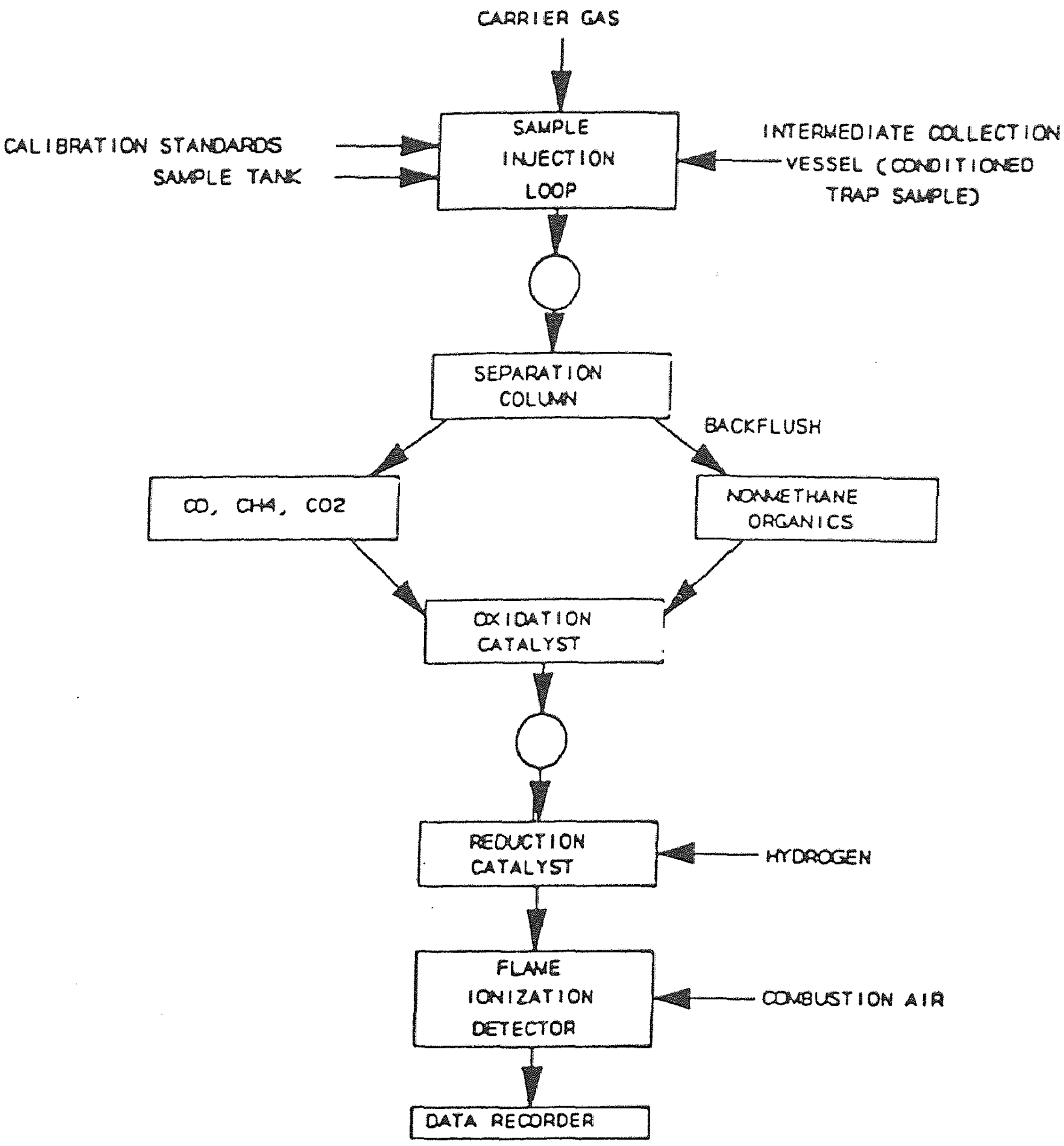

Figure 1 Simplified schematic of nonmethane organic analyzer

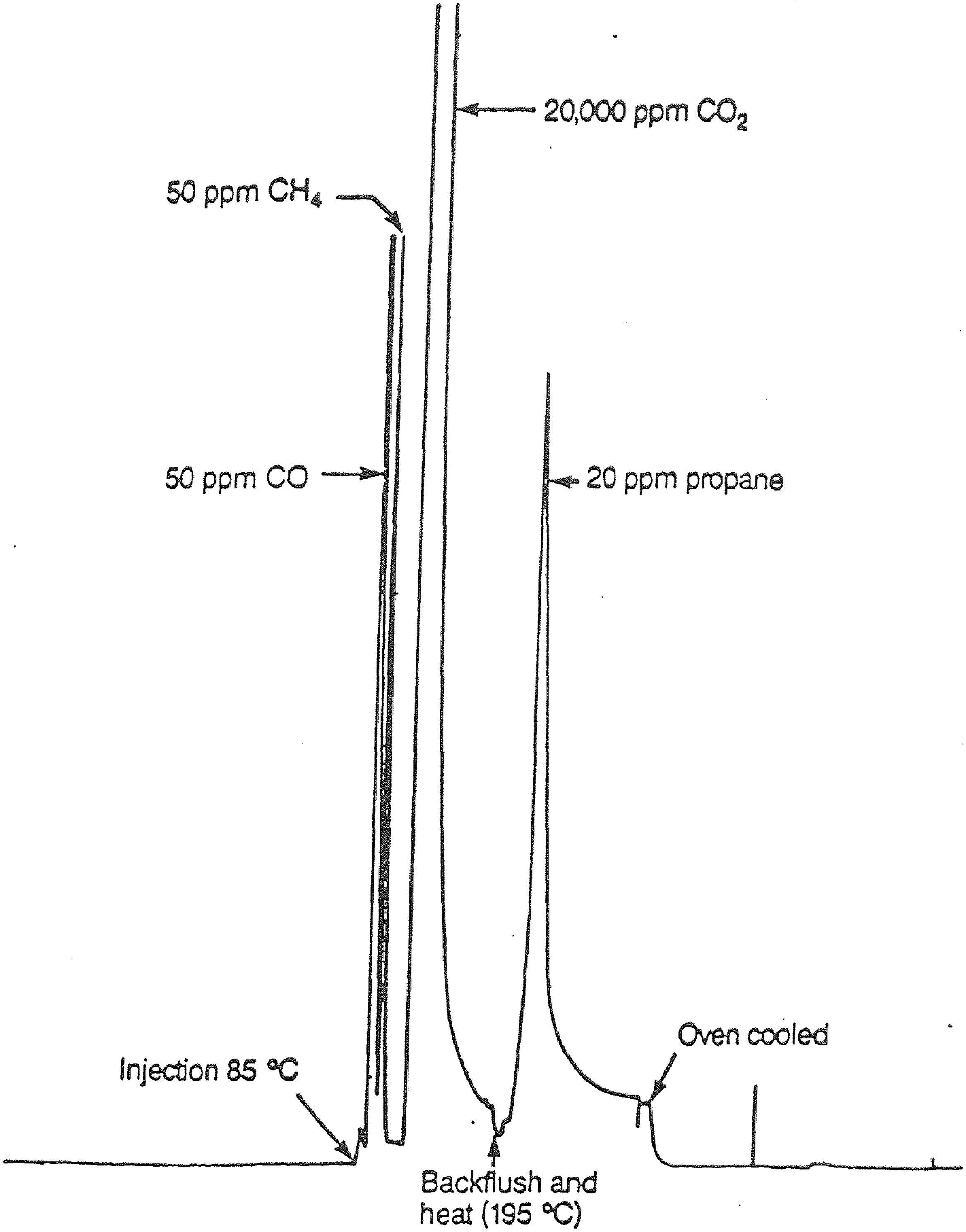

Figure 2 Typical chromatogram of NMOC using method 25

CHAPTER 2

RESEARCH OBJECTIVE

The objectives of this research are to use a microtrap based system for continuous, on-line monitoring of VOCs and NMOC in the stack gas of a catalytic incinerator; to evaluate conversion efficiency of catalytic incinerator using microtrap based analytical system. Different configurations of the microtrap based system will be used for comparison purposes.

CHAPTER 3

EXPERIMENTAL

3.1 Instruments and Reagents

3.1.1 VOCs Monitoring System

The experimental system used in continuous monitoring of VOCs in emissions from catalytic incinerator is shown in Figure 3. The catalytic incinerator contains a 2.5 cm o.d. diameter quartz tube reactor (Kontes Scientific Glassware, Inc.) residing in a horizontal furnace (Lindberg, Watertown, WI). The catalysts used in this research were provided by Engelhard Corporation. The catalysts were 1.5% platinum deposited on ϒ-alumina washcoat and carried on a 400 (or 200) cells per square inch cordierite honeycomb [37-38]. The thickness of catalyst layer in this experiment was 0.5 cm.

Three injection systems were used in this research: a multiport gas sample valve, SVM system and OLMT-BF system. An air activated electronically controlled automatic gas sampling valve (Model VIII, Valco Instruments Co., College Station, Texas) was used. A 100 μl sample loop was used for injection when only the valve was used for injection. In the SVM mode, the volume of the sample loop was 8 ml. The microtrap was made using a 0.53 mm i.d silica lined stainless steel tubing (Restek Co. Bellefonte, PA) packed with 60 mesh Carbotrap C. The length of the microtrap was 9 cm. In the OLMT-BF mode, a microtrap replaced the sample loop in the valve. This microtrap was made by packing a 1.5 mm i.d. stainless steel tubing with 20-40 mesh Carbotrap C. The length of microtrap was 5 cm. A microprocessor controlled device was designed and fabricated in house to control the valve switching and the microtrap injections.

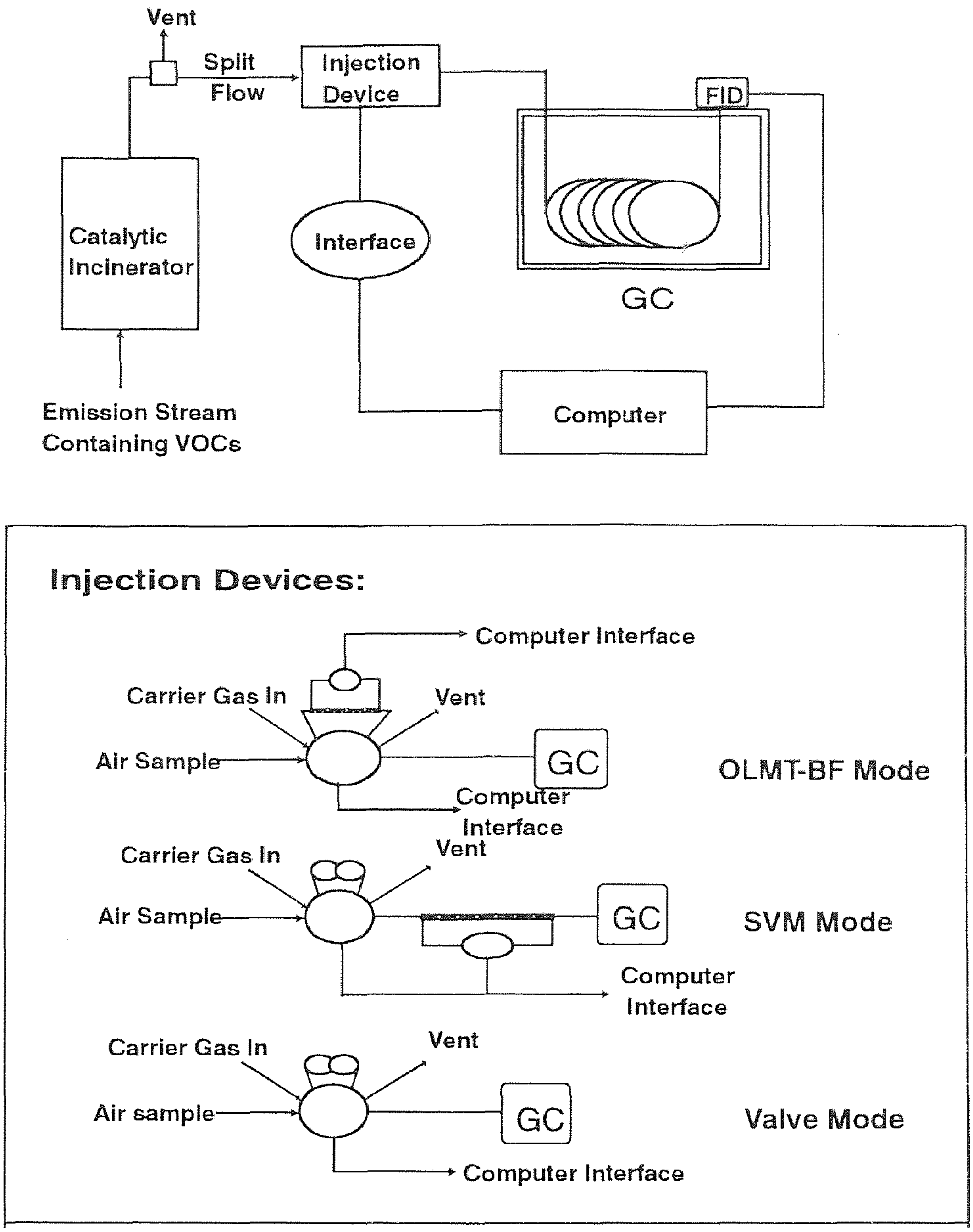

Figure 3 Instrumentation for continuous monitoring system of VOCs in incinerator effluent using gas chromatography

A Hewlett Packard 5890 series II gas chromatograph (Hewlett Packard Company, Avondale, PA) equipped with a 0.53 mm i.d. 30 m long DB 624 capillary column (J&W Scientific, Folsom, CA) and a flame ionization detector was used for analysis. HP 3365 Chemstation was used for data acquisition and analysis.. The operation conditions of the GC are shown in Table 1.

A gas standard containing ppm levels of benzene, toluene, trichloroethylene and ethylbenzene was made in the laboratory. An empty 52.73 L tank was evacuated and then flushed with zero grade air. This process was repeated several times to clean the tank. Then a predetermined quantity of each of the four compounds was injected into the tank. The tank was then filled with zero grade air to about 800 psi and was left to stand for a week to allow proper mixing. A 1 ppm certified standard gas containing benzene, toluene, trichloroethane and ethylbenzene was used to verify the concentration of the gas standard. The concentrations of this standard gas is listed in Table 2.

Table 2. Composition of Standard Gas

Compounds	concentration (ppm_v)
Benzene	80.5
Trichloroethane	96.2
Toluene	75.5
Ethylbenzene	68.2
Air	balance

Table 1. Gas Chromatograph Operating Conditions

GC	HP 5980 Series II with HP 3365 Chemstation	
Injector	Sample valve SVM or OLMT-BF	Room temperature
Column	0.53 mm i.d. DB 624, 30 meter (J&W Scientific)	
	Temperature	100 °C
	Carrier Gas N_2	6 ml/min
Detector	Flame Ionization Detector (FID)	
	Temperature	280 °C
	Attenuation	0-1
	Range	0
	H_2	30 ml/min
	Made up gas N_2	25 ml/min
	Air	300 ml/min

3.1.2 NMOC Analytical System

Figure 4 presents a schematic diagram of NMOC analytical system. The catalytic incinerator was the same as that in VOCs monitoring system. The oxidation unit was a 4 inch long, 1/4 inch stainless steel tubing packed with Chrome Alumna. This oxidation unit was put in a furnace at 550 °C (Lindberg, Watertown, WI). The reduction unit was a 1/4 inch i.d. quartz tube packed with 10% nickel nitrate on Chromosorb G AW 100/120 (Varian, CA) about 4 cm. This reduction unit was installed in a GC injection port at 350 °C. All transfer lines were heated and maintained at 100 °C to prevent the condensation of analytes.

Simulated stack gas containing 1 ppm of benzene, trichloroethane, toluene and ethyl benzene was obtained from Liquid Air Corporation Morrisville, PA). Its composition is shown in Table 3. The gas supply of whole experimental system and the GC was zero grade (Spectra Gases Inc., Newark, NJ, USA). All other chemical reagents were chromatographic grade from Fisher.

Table 3. Composition of 1 ppm Standard Gas

Compound	Specification	Actual
Oxygen	11%	10.9%
Carbon dioxide	9%	9.27%
Sulfur dioxide	150 ppm	164 ppm
Carbon monoxide	80 ppm	75 ppm
Benzene	1	1
Toluene	1	1
Ethylbenzene	1	1
Trichloroethylene	1	1
Nitrogen	Balance	Balance

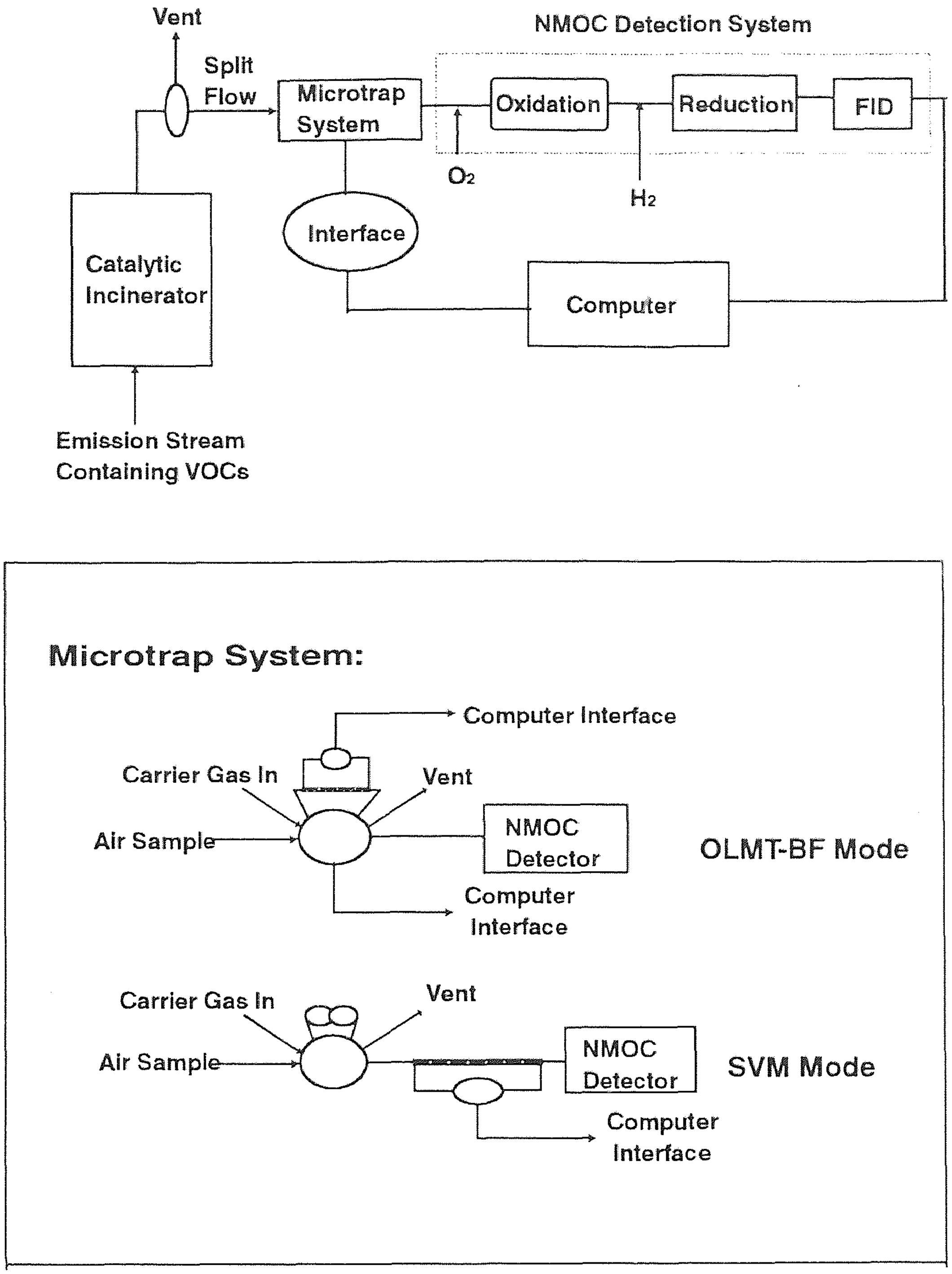

Figure 4 Continuous on-line NMOC analyzer

3.2 System Operation

An air stream containing VOCs continuously flowed through the catalytic incinerator at space velocities of 4000 to 24000v/v/hr. Typical reactor temperature was between 350 °C and 600°C. A vacuum pump was used to draw a portion of effluent gas from incinerator exit into the injection system. In the OLMT-BF system, when the valve was in loading mode, the VOCs were trapped by the microtrap, while the permanent gases, including moisture, flowed through.. Then the valve was switched to the injection mode and the microtrap was heated to release the VOCs. In the SVM system, when the valve was in loading status, the sample filled the large sample loop. Then the valve injected the sample onto the microtrap. The microtrap selectively trapped and concentrated the VOCs. Then the trap was heated to inject the VOCs into the GC. The analytes were separated by capillary column and detected by FID.

In NMOC analysis, a portion of stack gas from catalytic incinerator was introduced into microtrap system using a vacuum pump. The VOCs released from microtrap system went directly into the NMOC analyzer. The VOCs were first oxidized to carbon dioxide by the oxidation reactor which was packed with chrome alumina. The typical flow rate of oxygen gas was 6 ml/min. Then the sample stream passed through the reduction reactor to convert the carbon dioxide into methane by hydrogen. The flow rate of hydrogen was 40 ml/min. Finally FID detected methane.

An external calibration method was used to quantitate the concentration of VOCs and NMOC in the emission sample with 1 ppm of standard gas.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Performance of the Microtrap Based Injection System for Monitoring of VOCs in Emissions from Catalytic Incinerator

In this study, different injection systems, namely the valve, SVM and OLMT-BF were compared. Chromatograms from these three systems are presented in Figure 5A, B and C. As mentioned before, sample valves have been used as on-line injectors in process GCs. These types of injectors are commercially available and are routinely used in industry. Typical sample loop volume used with capillary column is 100 μl. If a large sample loop is used, band broadening occurs, which reduces chromatographic resolution. On the other hand, a small injection volume contains a small quantity of analyte, which generates a small detector response. As a result detection limits are high. In our experiment the gas sample valve with 100 μl sample loop was controlled such that sample loop was loaded for 350s and injection was for 10s. A typical chromatogram of continuous monitoring of VOCs by the valve system is shown in Figure 5C.

In the SVM, system an 8 ml sample loop was used to inject into the microtrap. The peaks using SVM were much higher than those using a valve because a larger sample volume was injected (Figure 5B). Figure 5A presents the chromatograms of continuous monitoring of VOCs in simulated stack gas using OLMT-BF. The response from the OLMT-BF system was even higher than the SVM because 20 ml sample was injected into the GC. Thus it can be concluded that for a given injection interval OLMT-BF system provides the highest sensitivity followed by the SVM. The valve showed the lowest sensitivity. It can also be seen that the peaks from the SVM and OLMT-BF systems were sharp and exhibited high precision.

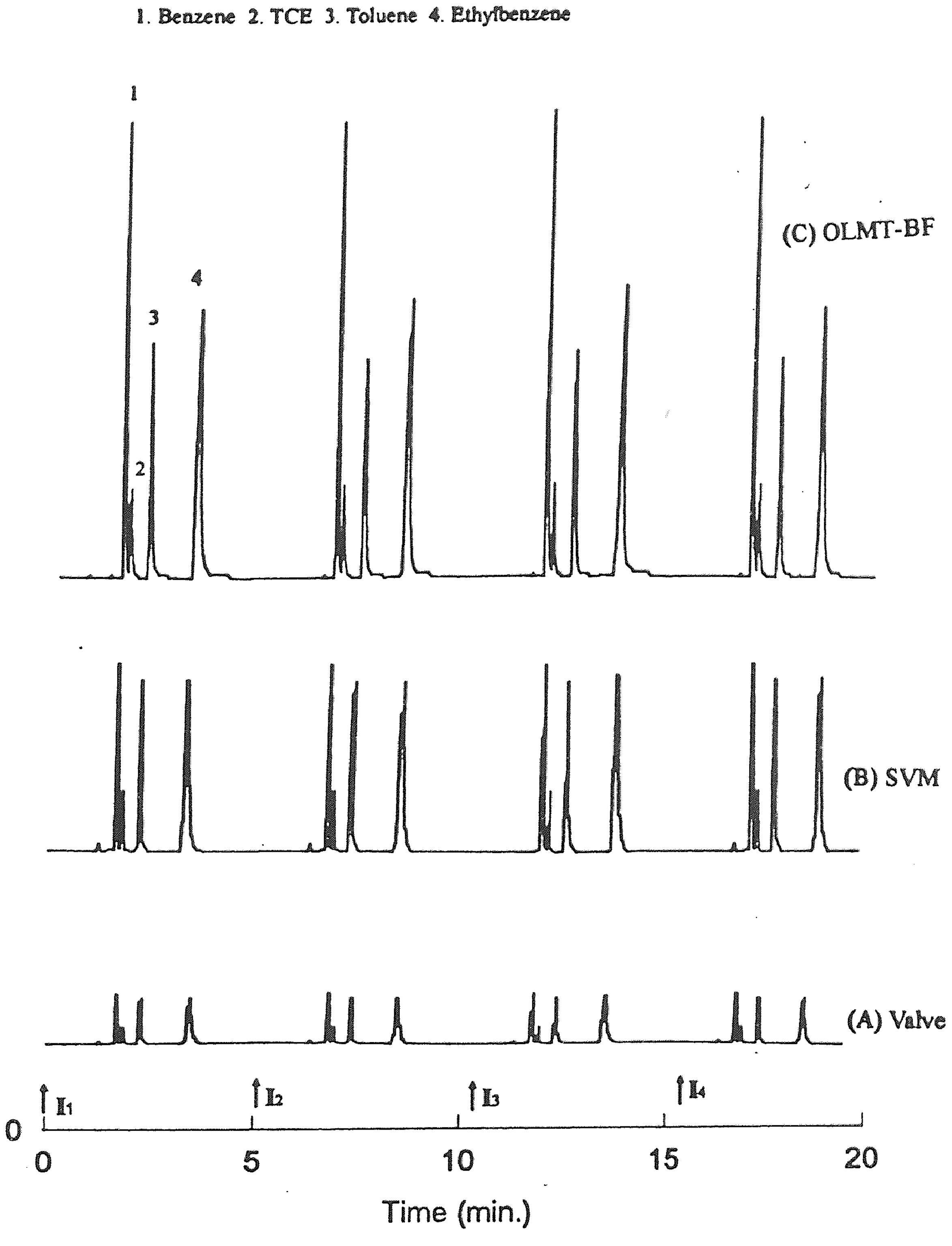

Figure 5 Series of chromatograms from a gas standard containing 1 ppm of benzene, TCE, toluene and ethylbenzene. The valve was equipped with a 100 µl sample loop. An 8 ml sample loop was used in the SVM system. In the OLMT-BF mode, sampling time was 6 minutes at a flowrate of 15 ml/min.

4.1.1 Detection Limits and Calibration Curve

Detection limit is defined as the concentration at three times the signal to noise ratio [39]. Table 4 lists the detection limits of benzene, TCE, toluene and ethylbenzene by using the three different injection techniques. The OLMT-BF and SVM systems had low detection limits all the way to sub-ppb level. OLMT-BF had lowest detection limits. However, SVM was operationally simpler than OLMT-BF because precise flow rate control is necessary in OLMT-BF mode.

Linearity of calibration curves is important for quantitative analysis. Figure 6, 7 and 8 show the calibration curves of typical VOCs using Valve, SVM and OLMT-BF systems. In this experimental range, calibration curves were linear. Figure 9 is a comparison of the calibration curves for toluene using different injection systems. It is evident that at the same concentration, the response from the SVM system is larger than the valve, and the response from the OLMT-BF system is higher than that from the SVM system. The calibration sensitivity, defined as the slope of the calibration curve, was also an order of magnitude higher for the OLMT-BF mode than the SVM mode. A higher calibration sensitivity provides better discrimination between sample of similar concentration.

4.1.2 Spike Recovery

To test the accuracy of the analytical system, and to see if there was any sample loss in sampling system, the effluent from the incinerator was spiked with a standard of known concentration. The experimental diagram of spike recovery test is shown in Figure 10. The spike was added just before the sample entered the microtrap system. In the spike recovery, the inlet concentrations at the catalytic incinerator were benzene 80.5 ppm, toluene 75.5 ppm, ethylbenzene 68.2 ppm and TCE 96.2 ppm at a flowrate of 75.0 ml/min. The catalytic incinerator was at 350 °C when tested with benzene, toluene and ethylbenzene and at 450 °C when tested

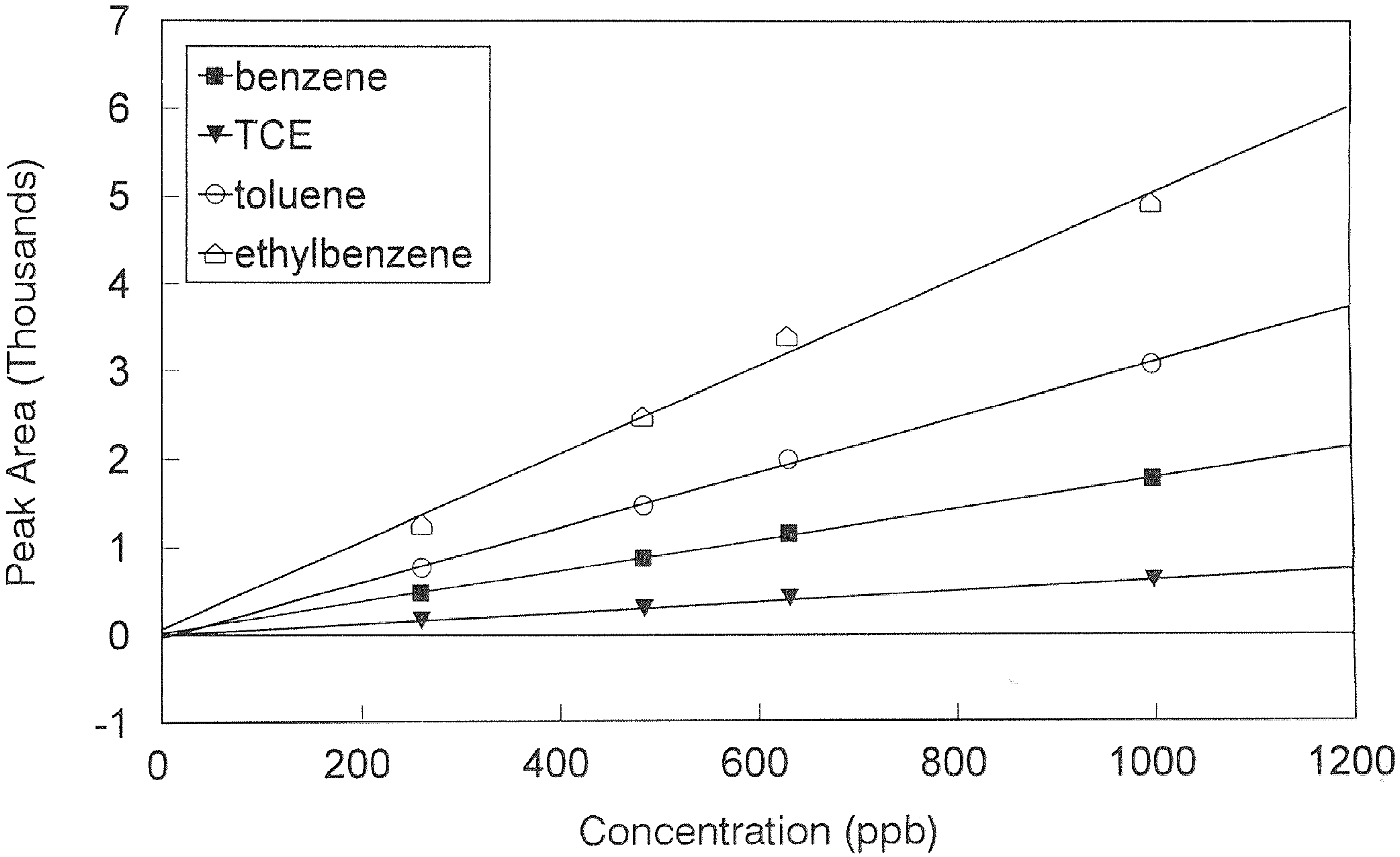

Figure 6 Calibration curve using a valve with 0.1 ml sample loop

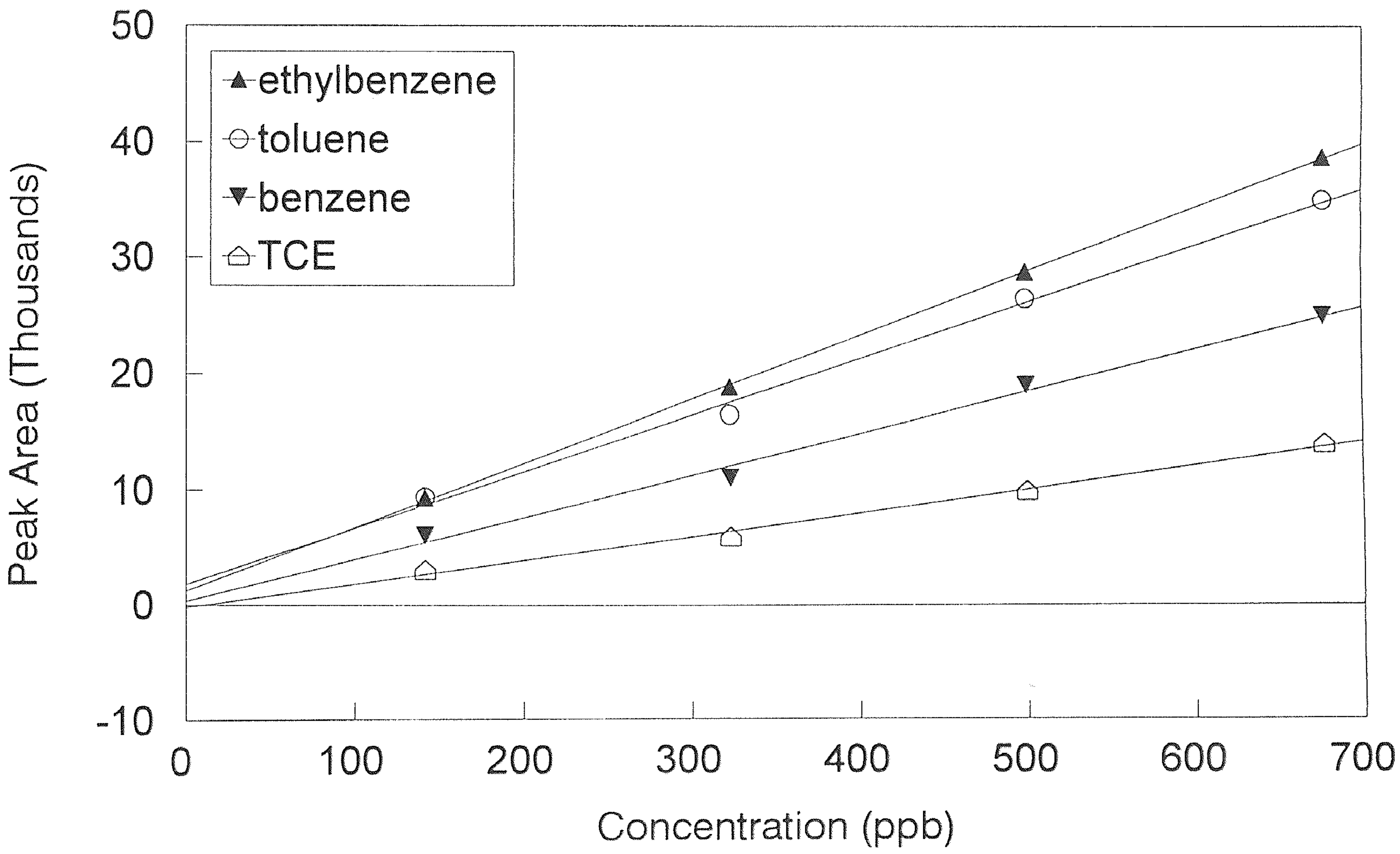

Figure 7 Calibration curve using the sequential valve microtrap system with an 8 ml sample loop

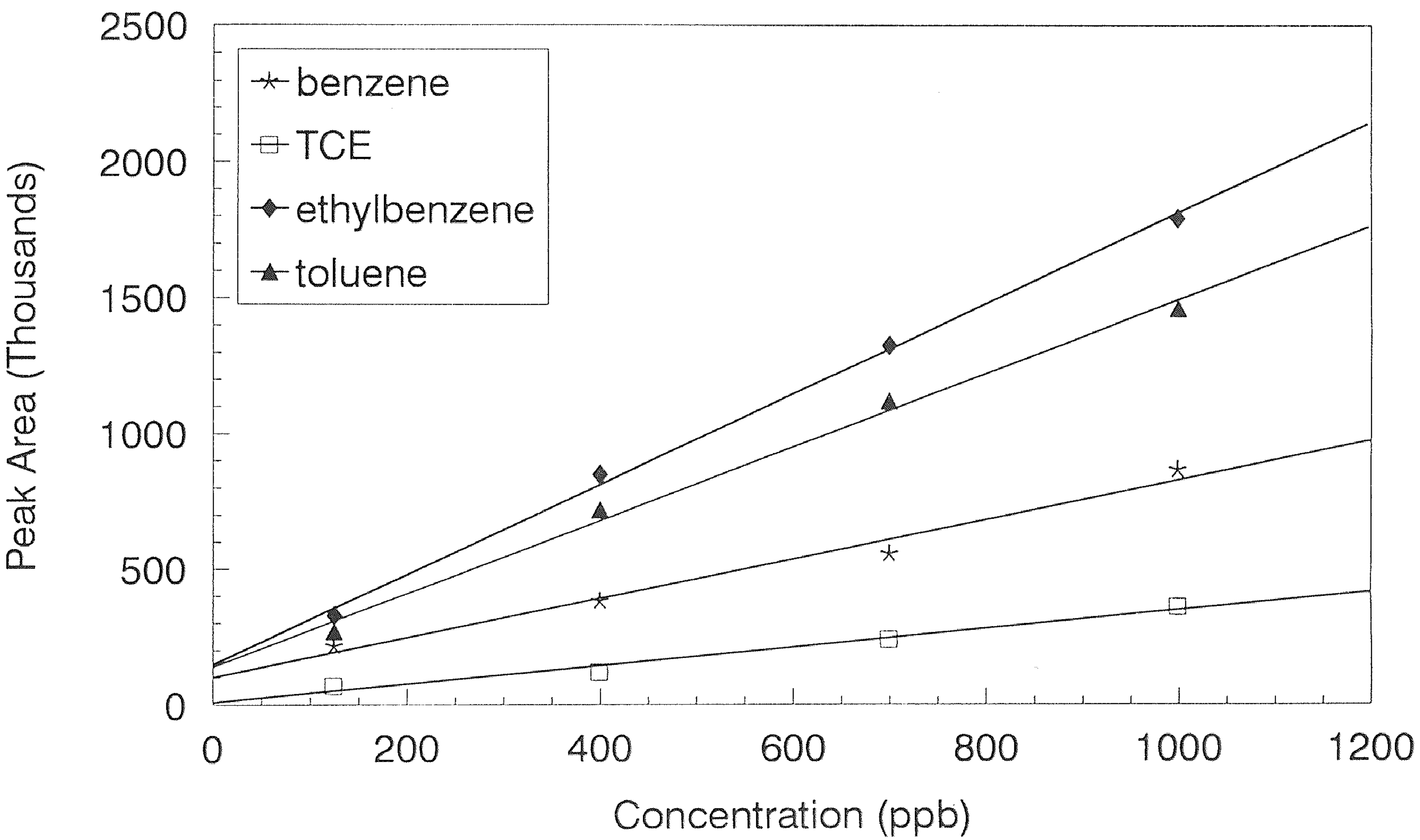

Figure 8 Calibration curve using the OLMT-BF system. The sampling time was 6 minutes at a flowrate of 15 ml/min.

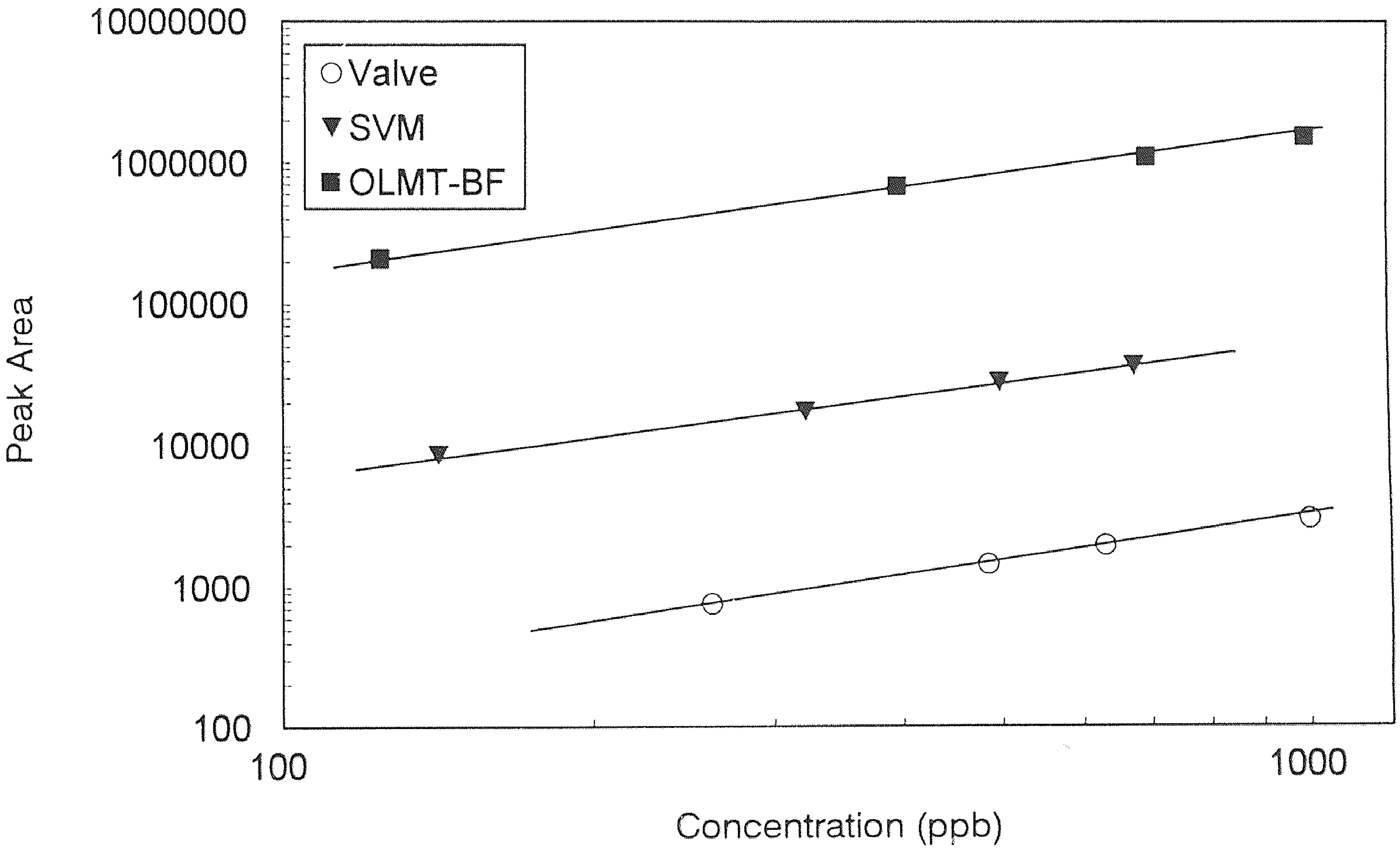

Figure 9 Calibration curves for toluene using the different injection modes. In the valve mode, a 0.1 ml sample loop was used. In the SVM mode, an 8 ml loop was used. In the OLMT-BF mode, the sampling time was 6 minutes at a flowrate of 15 ml/min.

TCE. Under these conditions the destruction efficiencies for all the compounds were close to 99.9 % such that outlet concentrations among 1 and 3 ppm were similar to that in the spike standard. The spike standard gas contained 1 ppm of benzene, TCE, toluene and ethylbenzene. Spike recovery was quantitated as:

$$\text{Spike recovery (\%)} = \frac{\text{Csp(measured)}}{\text{C' sp(spiked)}} \bullet 100$$

Here $C_{sp(measured)}$ is the recovered concentration of spiked analyte, and $C'_{sp(spiked)}$ is the spike concentration of analyte. The results of spike recovery were shown in Table 5. The results here are an average of five repeat runs.

The spike recovery study produced excellent results. Recoveries of all the compounds were close to 100% (from 91 to 106 %). This showed that the measurements were accurate and the sampling system loss was minimal. The relative standard deviations were high for toluene, but still within acceptable limits.

Table 4. Detection Limits of Three Systems

Compounds	Detection Limits $(ppb_v)^1$		
	Valve^2	SVM^3	OLMT-BF^4
Benzene	17.14	0.46	0.064
TCE	48.46	0.99	0.33
Toluene	9.63	0.47	0.02
Ethylbenzene	6.10	0.56	0.03

1. The detection limits were calculated at a signal to noise ratio of 3.
2. The volume of sample loop was 100 μl.
3. The volume of sample loop was 8 ml and a 0.53 mm i.d, 9 cm long microtrap was used.
4. A 1.5 mm i.d, 5 cm long microtrap packed with 20-40 mesh Carbotrap C was used.

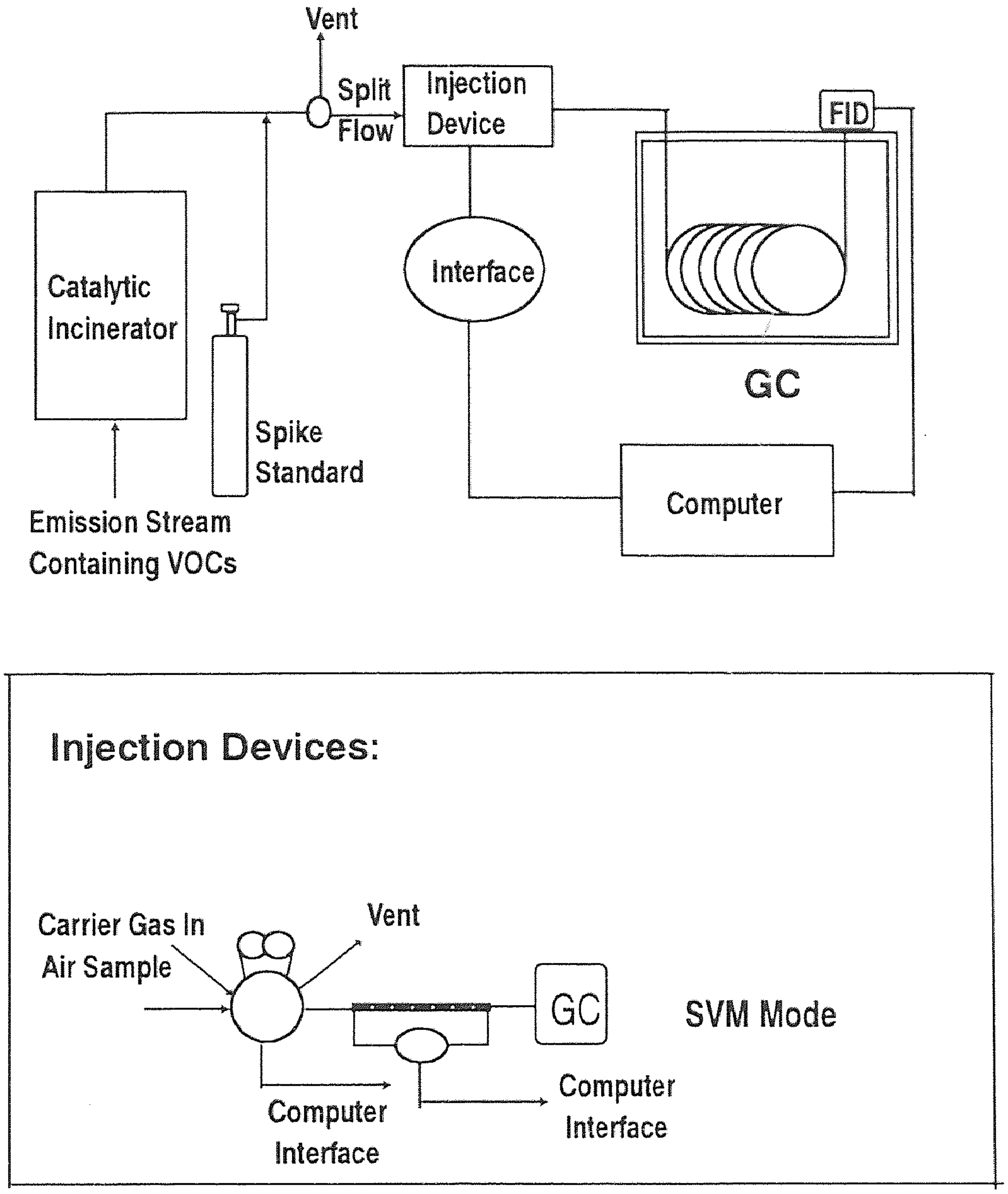

Figure 10 Spike recovery of VOCs

Table 5 Spike Recovery of VOCs [1]

	Conc. at incinerator outlet (ppm)	Spike conc. (ppm)	Calculated total conc. (ppm)	Measured total conc. (ppm)	Spike recovery(%)	RSD (%)
Benzene [2]	2.52	1.00	1.76	1.79	106.4	2.45
TCE [3]	1.95	1.00	1.48	1.41	91.8	5.01
Toluene [2]	1.15	1.00	1.08	1.07	98.2	14.15
Ethylbenzene [2]	2.26	1.00	1.63	1.66	106.4	9.29

1. The SVM system was used in this spike recovery experiment.
2. Spike recovery of benzene, toluene and ethylbenzene at an incinerator temperature of 350°C.
3. Spike recovery of TCE was studied at 450°C.

4.1.3 Effect of Moisture

Moisture is known to cause problems in a chromatographic system. It can cause problems such as deterioration of GC column, baseline and retention time shifts. Moreover, if moisture accumulates in the microtrap, it changes the trapping characteristics of the trap. So it is necessary to prevent moisture from either accumulating in the trap or being injected into the GC. In case of SVM, moisture from an 8 ml equivalent sample goes into the column. The microtrap being hydrophobic in nature allows the moisture to pass through. The moisture from this injection volume did not appear to interfere with GC analysis. When the microtrap injection was made, it was done in a moisture-free environment. During sampling. in the OLMT-BF mode the moisture passes through the trap and is vented out. Once again the microtrap is heated in presence of a carrier gas and the injection occurs in moisture free environment. On the whole, the OLMT-BF mode was more effective in eliminating moisture.

In order to test if moisture effected the system response, moisture was added at the inlet of the catalytic incinerator. The experimental system is presented in Figure 11. The inlet stream was bubbled through an impinger containing water. The moisture content in inlet stream was controlled by setting the temperature of the impinger. The water temperature was controlled between 0 °C and 90 °C to obtain various concentrations of water [40]. In this experiment the reactor temperature, was set at 350 °C. The OLMT-BF system was used as the injection device. The effect of moisture concentration to system response is shown in Figure 12. The moisture did not affect the system response. The OLMT-BF system was able to effectively eliminate moisture from the sample.

4.1.4 Evaluating Catalytic Incineration Using Microtrap-GC

The fraction of inlet VOCs oxidized to carbon dioxide is an important parameter used to evaluate the efficiency of catalytic incineration. When the VOC containing

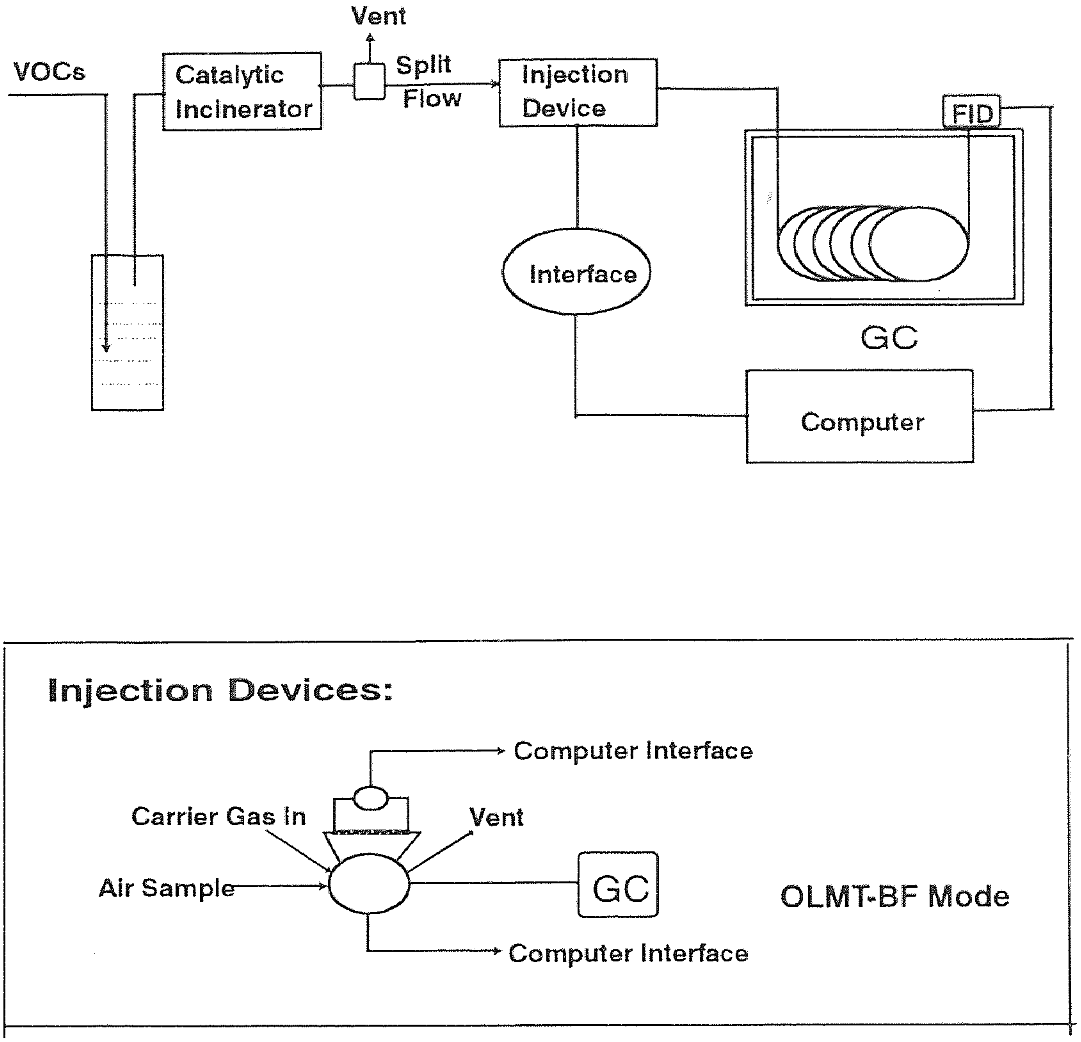

Figure 11 Experimental system to study the effect of moisture

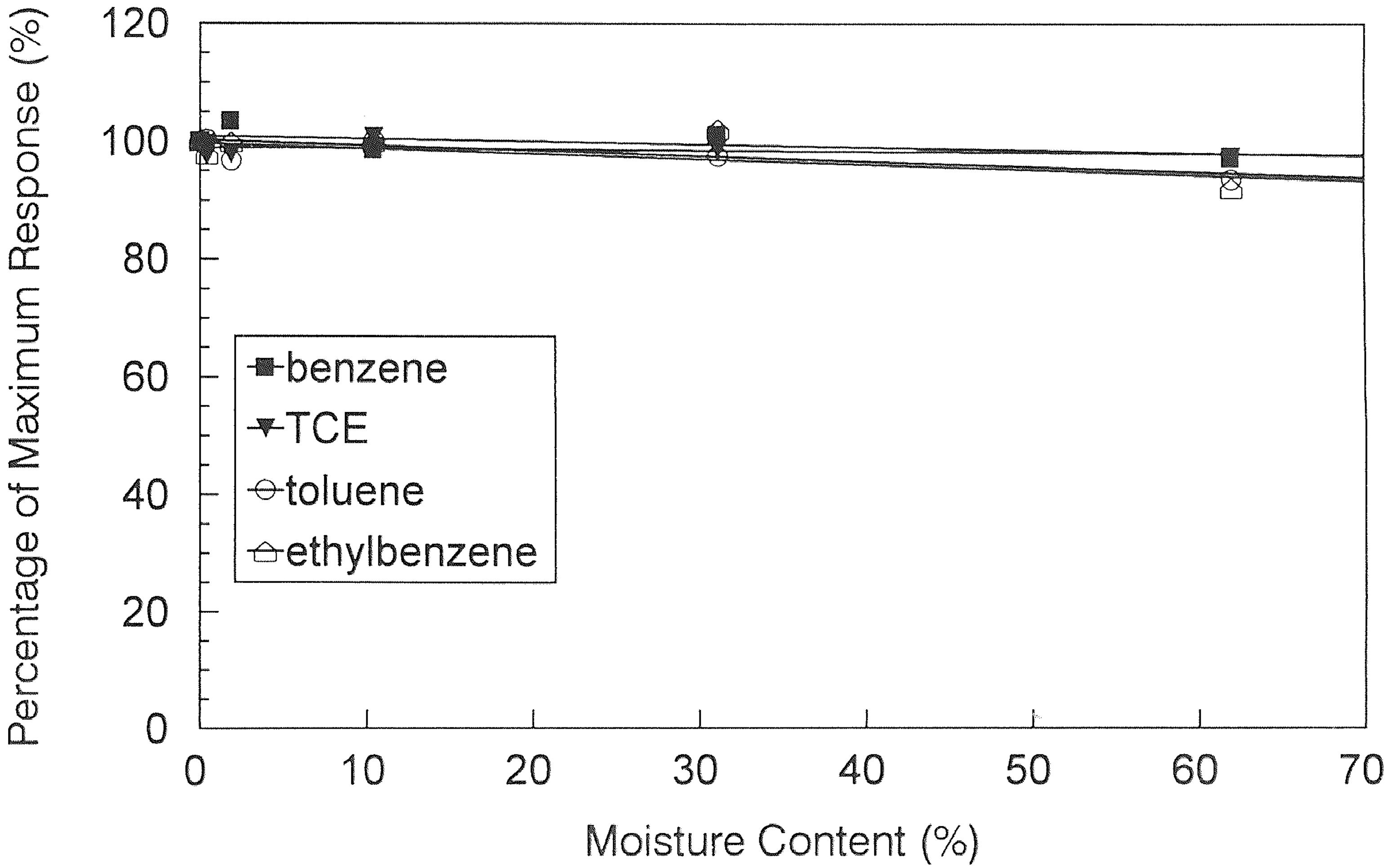

Figure 12 Effect of moisture content on system response. The temperature of the catalytic incinerator was 623 K and an OLMT-BF mode was used for this test.

stream passes through the catalytic incinerator, the conversion of VOCs depends up on the temperature of the catalytic incinerator. Conversion efficiency as high as 99.99% was achieved. The outlet concentration having monitored can very can be changeling. For example, at an inlet concentration of 1 ppm and 99.99% conversion efficiency, the corresponding outlet concentration can be as low as 0.1 ppb. Since the microtrap based systems are able to handle low ppb level samples, they were effective in monitoring effluent from the catalytic incinerator.

The destruction efficiency of a catalytic incinerator is a function of temperature. Figure 13 and 14 shows the conversion as a function of reaction temperatures. The inlet stream contained 80.5 ppm benzene, 96.2 ppm TCE, 75.5 ppm toluene and 68.2 ppm ethylbenzene. A SVM system was used to continuously monitor the outlet gas stream.. We can see that the SVM system was able to monitor low ppb levels of VOCs.

Typical chromatograms of VOCs at ppb level in catalytic incinerator effluents using a valve, SVM and OLMT-BF system are shown in Figure 15, 16, 17, 18A, B and C at an incinerator temperature of 550 °C. At this temperature, the conversion reached 99% for benzene, toluene and ethylbenzene and 95% for TCE. When the inlet gas stream contains 1 ppm of benzene, toluene, TCE and ethylbenzene, the VOC concentration in outlet of incinerator was only a few ppb. Figure 18C shows a typical chromatogram of VOCs at low ppb levels using the gas sampling valve. It was difficult to determine the concentration of components as they are close to detection limits. In Figure 18A and 18B using SVM and OLMT-BF systems, we were able to identify and quantitate the VOC concentration. In this case, outlet concentrations of four compounds were determined to be 12.5 ppb, 134.0 ppb, 12.3 ppb and 4.3 ppb for benzene, TCE, toluene and ethylbenzene, respectively.

An important finding was that the inlet concentration of VOCs can affect conversion at a given temperature. At a reactor temperature of 350 °C, the inlet

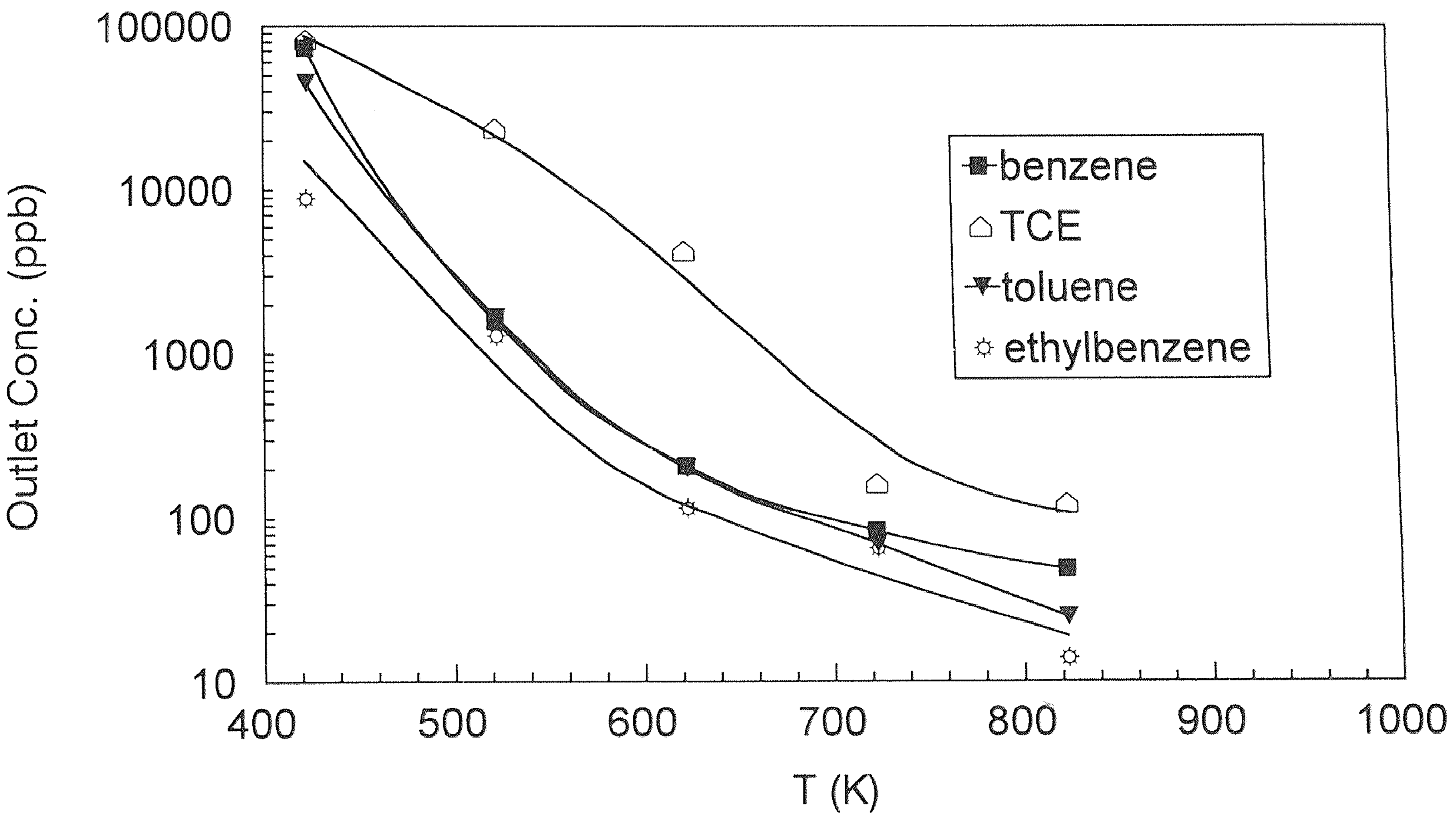

Figure 13 Outlet concentration as a function of the incinerator temperature. Inlet concentrations were 80.5 ppm of benzene, 75.5 ppm of toluene, 96.2 ppm of TCE and 68.2 ppm of ethylbenzene. A SVM system with an 8 ml sample loop was used for monitoring.

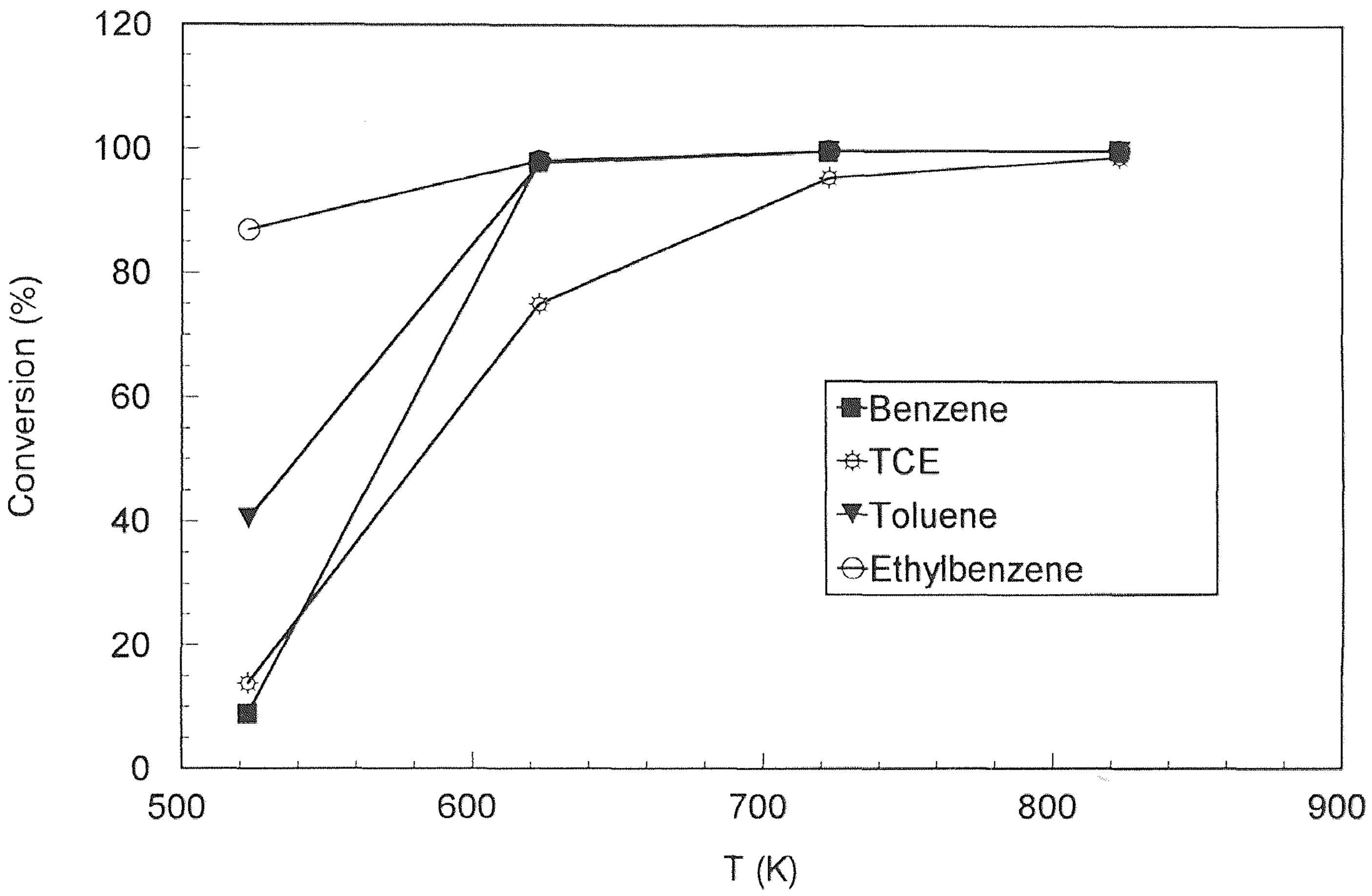

Figure 14 Conversion as a function of the incinerator temperature. Inlet concentrations were 80.5 ppm of benzene, 75.5 ppm of toluene, 96.2 ppm of TCE and 68.2 ppm of ethylbenzene. A SVM system with an 8 ml sample loop was used for monitoring.

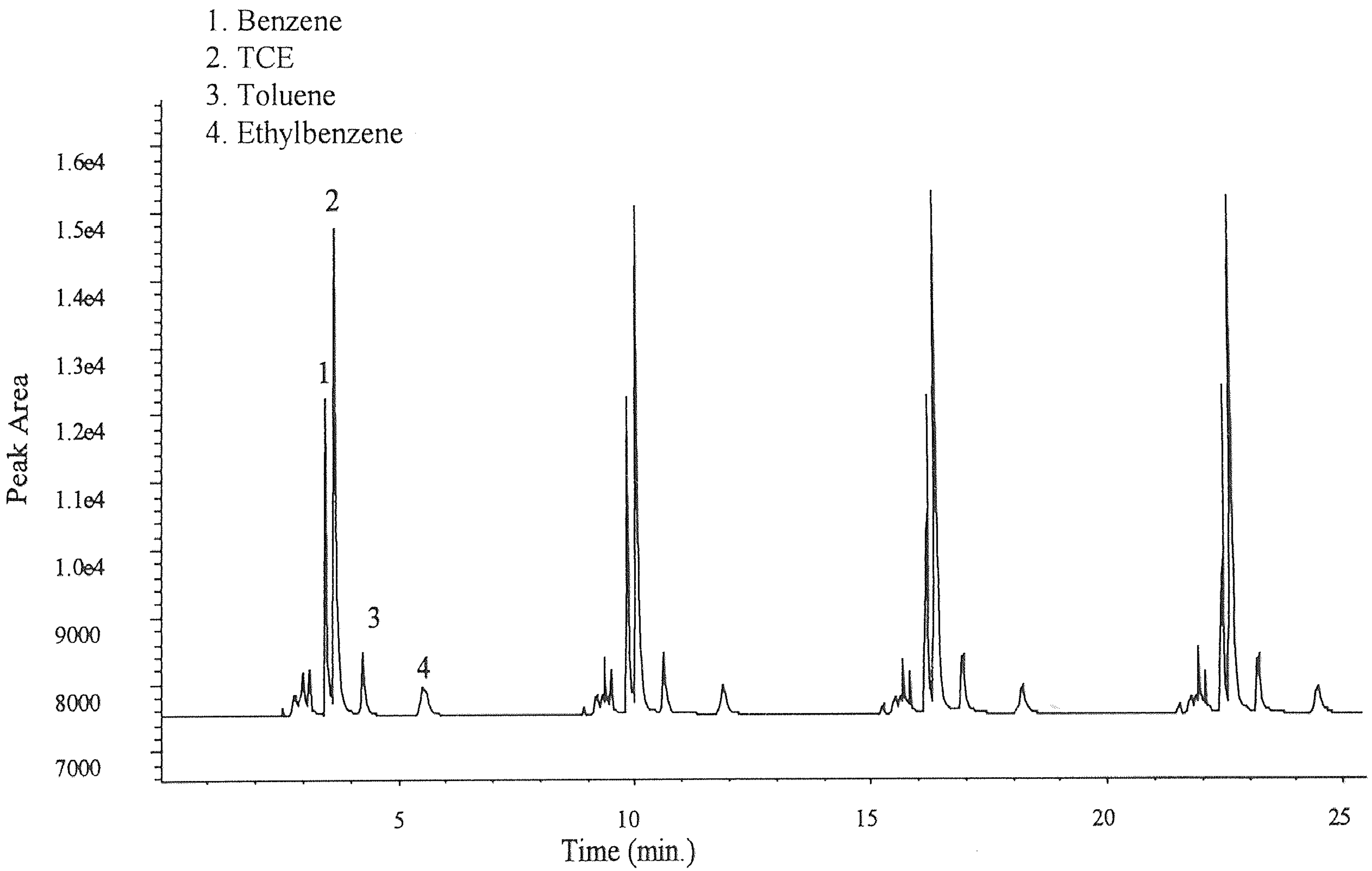

Figure 15 Chromatogram of ppb level VOCs at incinerator outlet using OLMT-BT mode. The inlet concentrations were 1 ppm of benzene, TCE, toluene and ethylbenzene. The incinerator temperature was 823K.

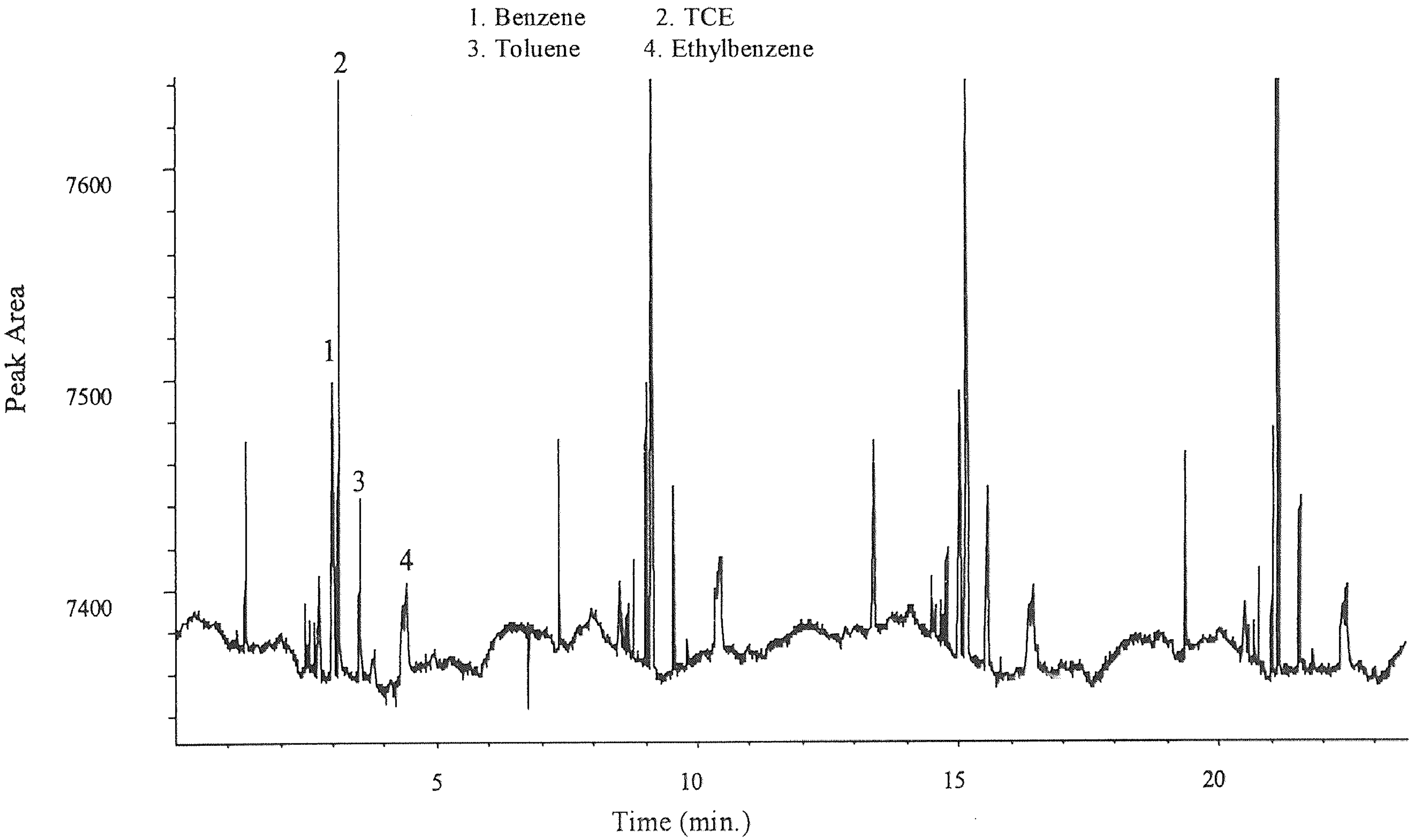

Figure 16 Chromatogram of ppb level VOCs at incinerator outlet using SVM mode with an 8 ml sample loop. The inlet concentrations were 1 ppm of benzene, TCE, toluene and ethylbenzene. The incinerator temperature was 823K.

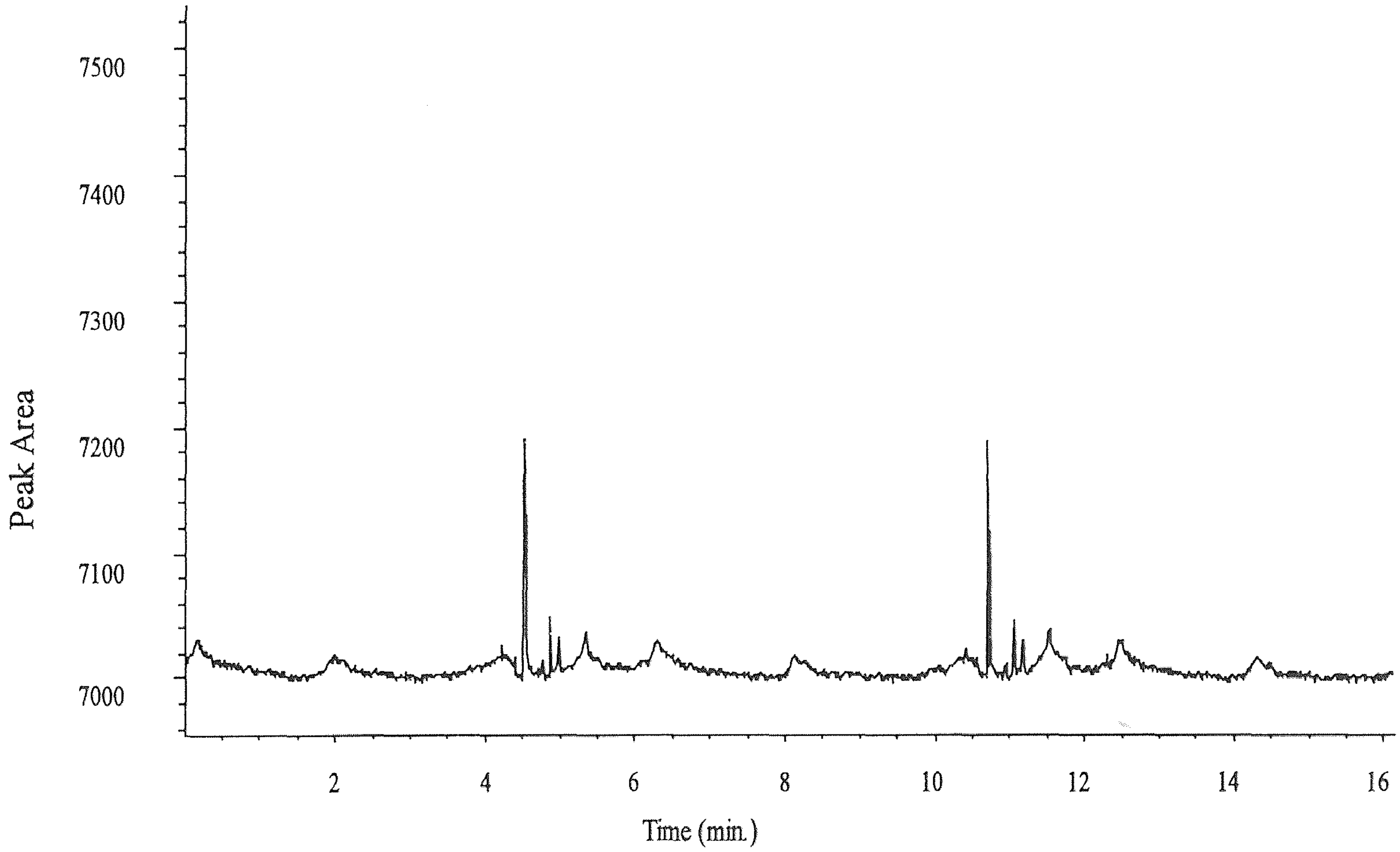

Figure 17 Chromatogram of ppb level VOCs at incinerator outlet using a 0.1 ml sample loop valve. The inlet concentrations were 1 ppm of benzene, TCE, toluene and ethylbenzene. The incinerator temperature was 823K.

Concentration was changed from 0.05 ppm to 100 ppm. The conversion efficiency and outlet concentration profile are shown in Figure 19 and 20. These measurements were made using the SVM mode. The conversion can be defined as following:

$$\text{Conversion (\%)} = 1 - \frac{\text{outlet concentration}}{\text{inlet concentration}} \bullet 100$$

It is easily seen that the conversion of the four compounds had the same trend in these figures. The conversion of TCE was low compared to toluene. The results were expected because TCE is chlorinated compound and is not easily oxidized.

4.2 Monitoring NMOC at the Outlet of Catalytic Incinerator

In a NMOC analyzer, every organic carbon is expected to produce equal response no matter what is the structure of the molecule. Thus organics are first oxidized to CO_2, and then the CO_2 is reduced into methane which produces a response in the FID. Permanent gases such CO_2, CO and CH_4 in air sample interfere in the NMOC analysis. In the conventional NMOC analyzer, a packed column is used to separate NMOC from permanent gases. In microtrap based injection NMOC system (Figure 4), the microtrap not only serves as a concentrator for VOCs, but also a separator for permanent gases. The microtrap can selectively concentrate NMOC from gas stream and vent out the matrix gases such as CO_2, CH_4 and H_2O.

Both SVM and OLMT-BF systems were used for NMOC monitoring. Figure 21 shows a series of peaks from continuous monitoring of NMOC in a simulated stack gas using OLMT-BF system. The simulated stack gas contained 1 ppm of benzene, TCE, toluene and ethylbenzene, 9.27% of CO_2, 10.9 % O_2, 164 ppm of SO_2 and 75 ppm of CO. In this OLMT system, sample stream passed through a microtrap. The microtrap trapped the VOCs and permanent gases vented out from system since they have very small breakthrough volumes. As a result, the VOCs were concentrated on the microtrap. In injection mode of OLMT-BF, the trapped VOCs were released into NMOC detector by heating the microtrap. As

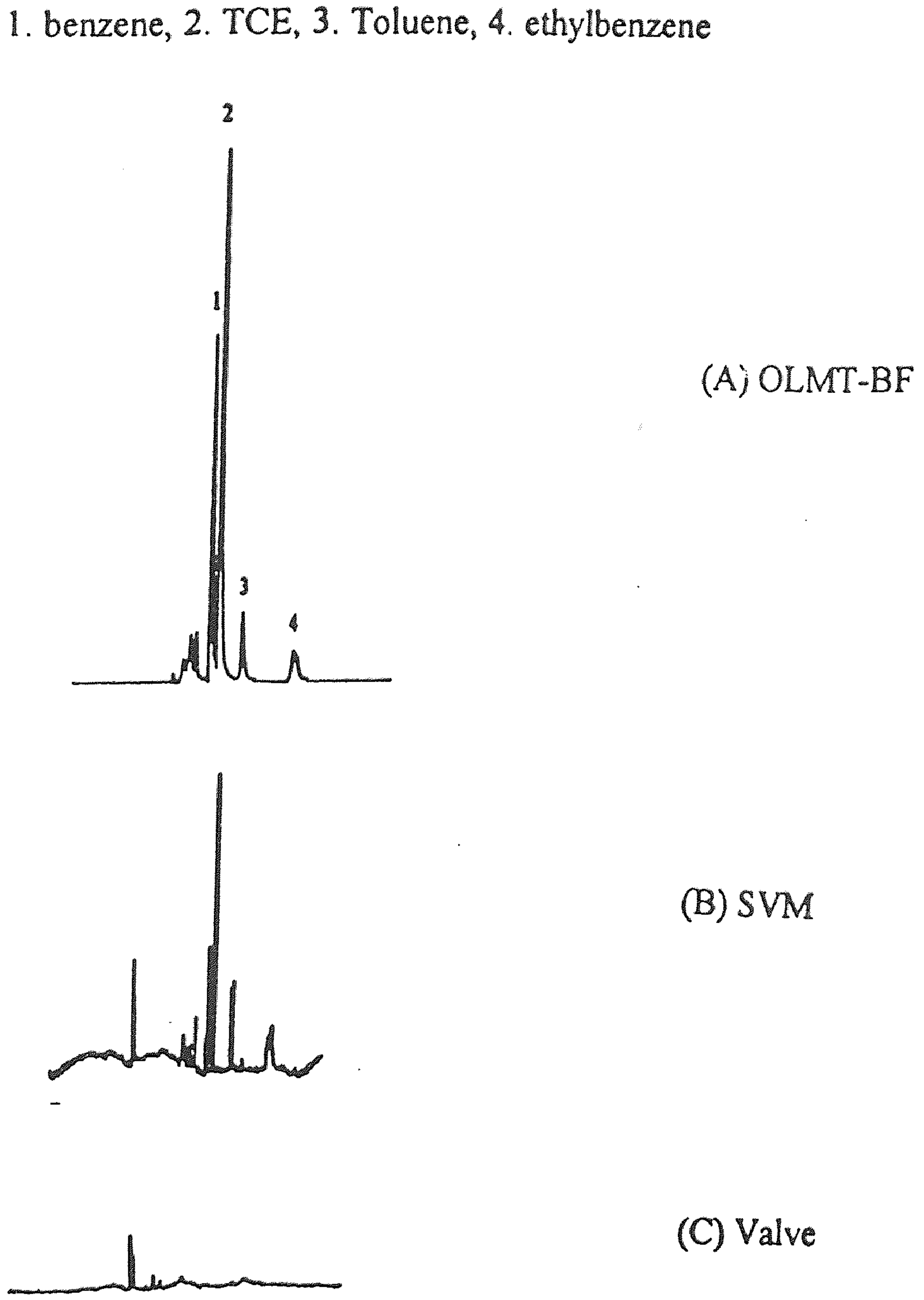

Figure 18 Chromatograms of ppb level VOCs at incinerator outlet. The inlet concentrations were 1 ppm of benzene, TCE, toluene and ethylbenzene. The incinerator temperature was 550 °C. In the valve system, a 100 μl sample loop was used. In the SVM system, an 8 ml sample loop was used. In OLMT-BF system, sampling time was 6 minutes at a flowrate of 15 ml/min.

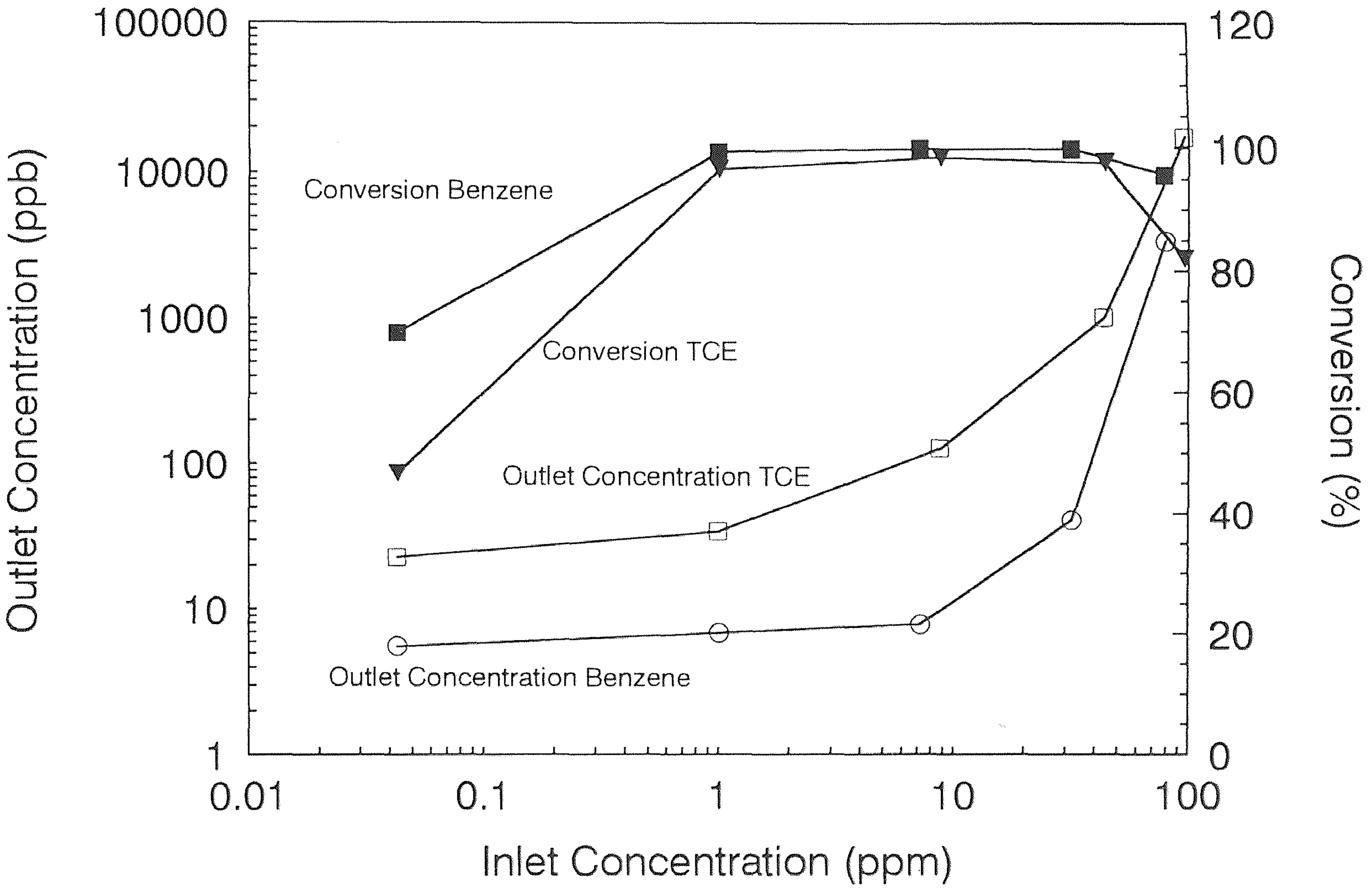

Figure 19 Conversion of benzene and TCE. The temperature of the catalytic incinerator was 623 K and the SVM mode was used.

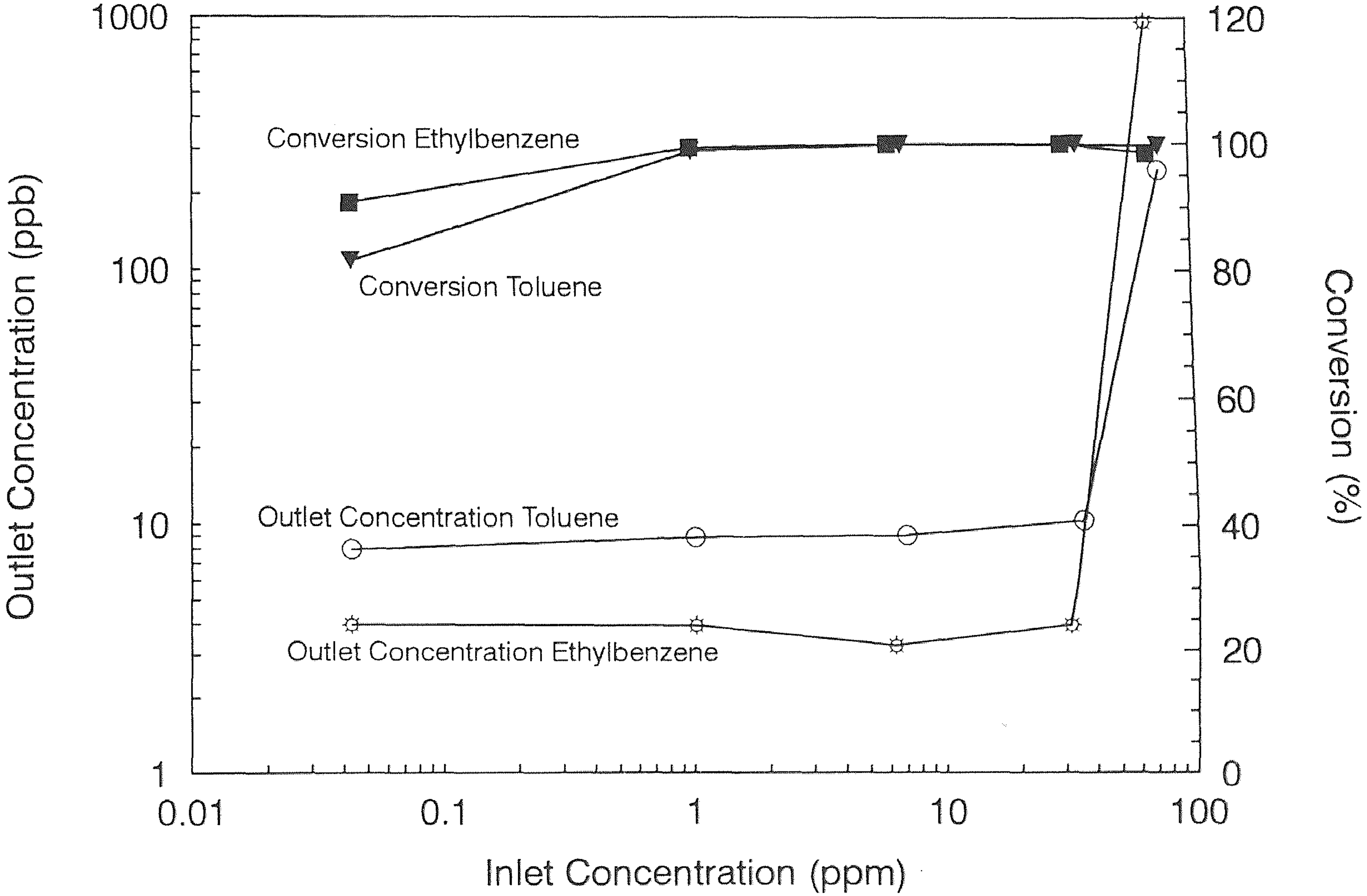

Figure 20 Conversion of toluene and ethylbenzene. The temperature of the catalytic incinerator was 623 K and the SVM mode was used.

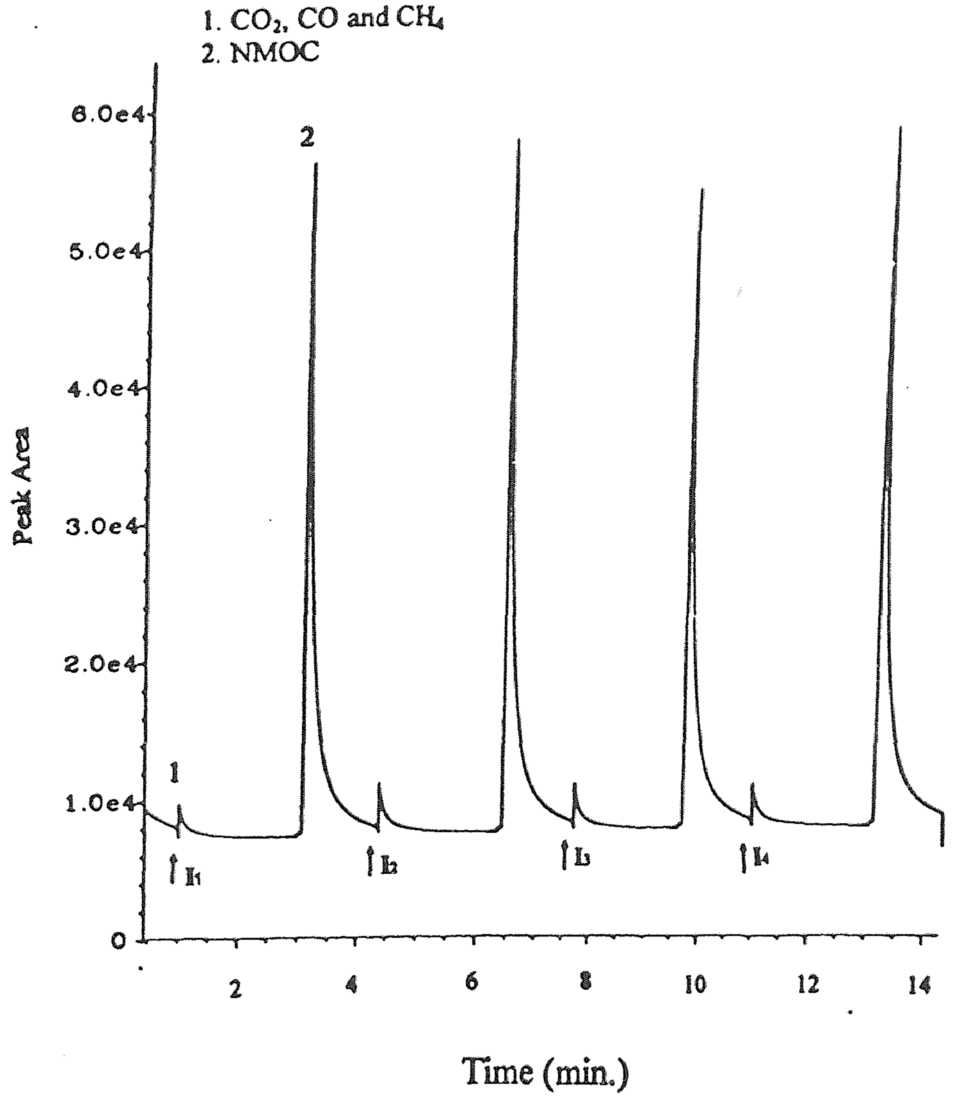

Figure 21 NMOC monitoring of a simulated stack gas using the OLMT-BF system. The simulated stack gas contained 1 ppm of benzene, TCE, toluene and ethylbenzene, 9.27% CO_2, 10.9% O_2, 75 ppm of CO and 164 ppm of sulfur dioxide. Injection were made every 4 minutes and sample flowrate was 15 ml/min.

expected, the NMOC peak was much larger than the permanent gas peak even though concentration of permanent gas was over 9.25 %. Therefore, the microtrap can effectively accumulate the NMOC while eliminating the permanent gases. Figure 22 shows NMOC monitoring the simulated stack using the SVM system. In this case, when an 8 ml sample loop injected the organics into the microtrap, which trapped the VOCs. CO_2 and other permanent gases that were not retained flowed into the NMOC detector. Thus a large permanent gas peak appeared. After the elution of these gases, the microtrap was pulsed and the VOCs were injected into the NMOC system. Thus, the NMOC peak appeared after the permanent gas peak. Figure 23 and Figure 24 show typical chromatograms of NMOC in real emission sample from a catalytic incinerator using OLMT-BF and SVM systems.

4.2.1 Spike Recovery of NMOC

To ensure that the system produced reliable quantitative results and there was no loss in the sampling system, VOCs were spiked at the outlet of the incinerator and then measured using the microtrap system. The experimental system for spike recovery is shown in Figure 25. The concentration at the inlet of the incinerator was 1749.5 ppm carbon and the flowrate was 75.0 ml/min. The incineration reactor was at 450 °C. A 23.0 ppm carbon flowed continuously into the analytical system at a flow rate of 75 ml/min. The results here are an average of five repeat runs. The results of spike recovery were shown in Table 6.

Table 6 Spike Recovery of NMOC

	C_{NMOC}[1]	Spike conc.(ppm)	Calculated conc.(ppm)	Measured conc.(ppm)	Spike recovery (%)	RSD (%)
NMOC	21.2	23.0	22.1	21.9	98.3	5.23

1. C_{NMOC} is the concentration of NMOC at the outlet of incinerator

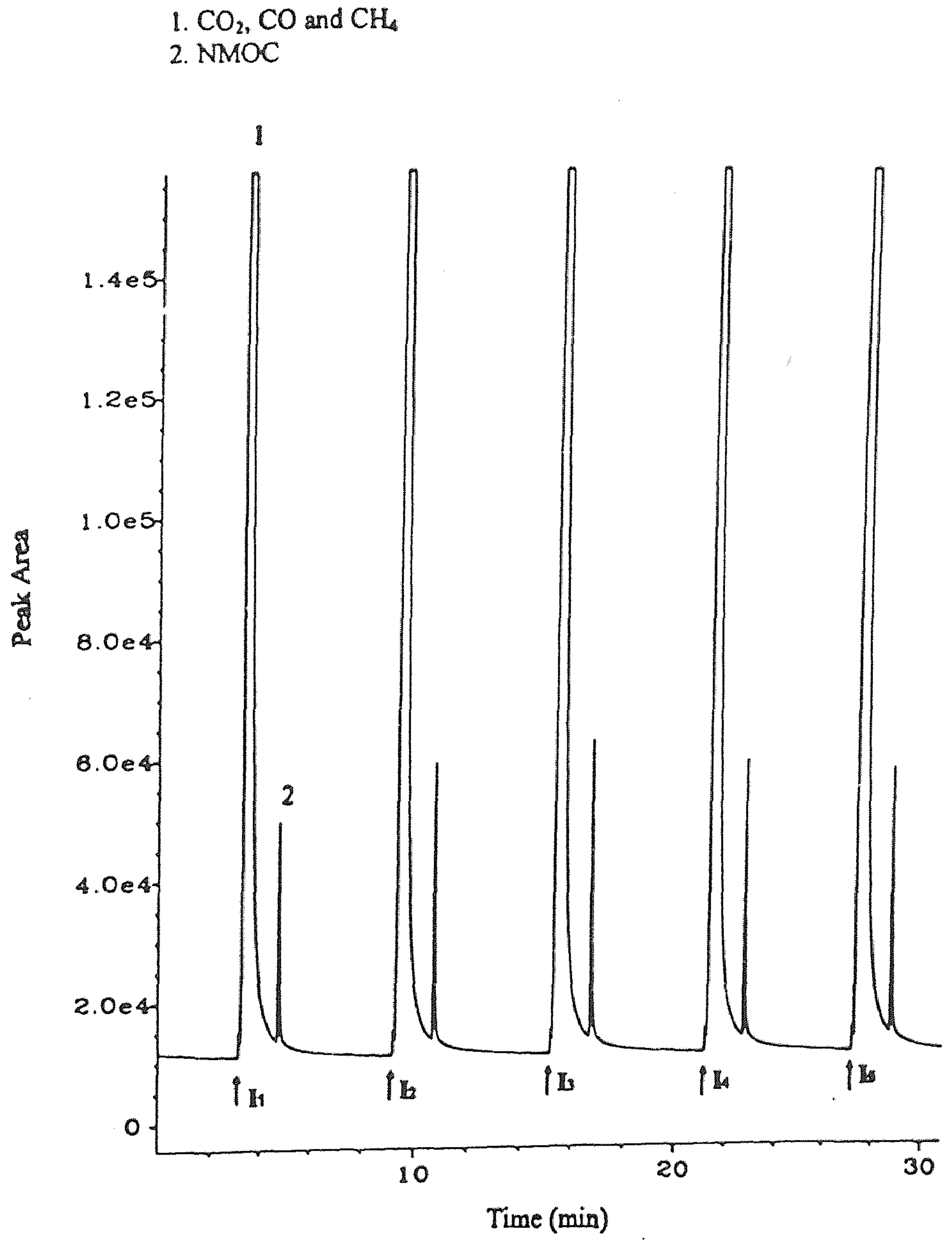

Figure 22 NMOC monitoring of a simulated stack gas using the SVM system. The simulated stack gas contained 1 ppm of benzene, TCE, toluene and ethylbenzene, 9.27% CO_2, 10.9% O_2, 75 ppm of CO and 164 ppm of sulfur dioxide. The volume of the sample loop was 8 ml.

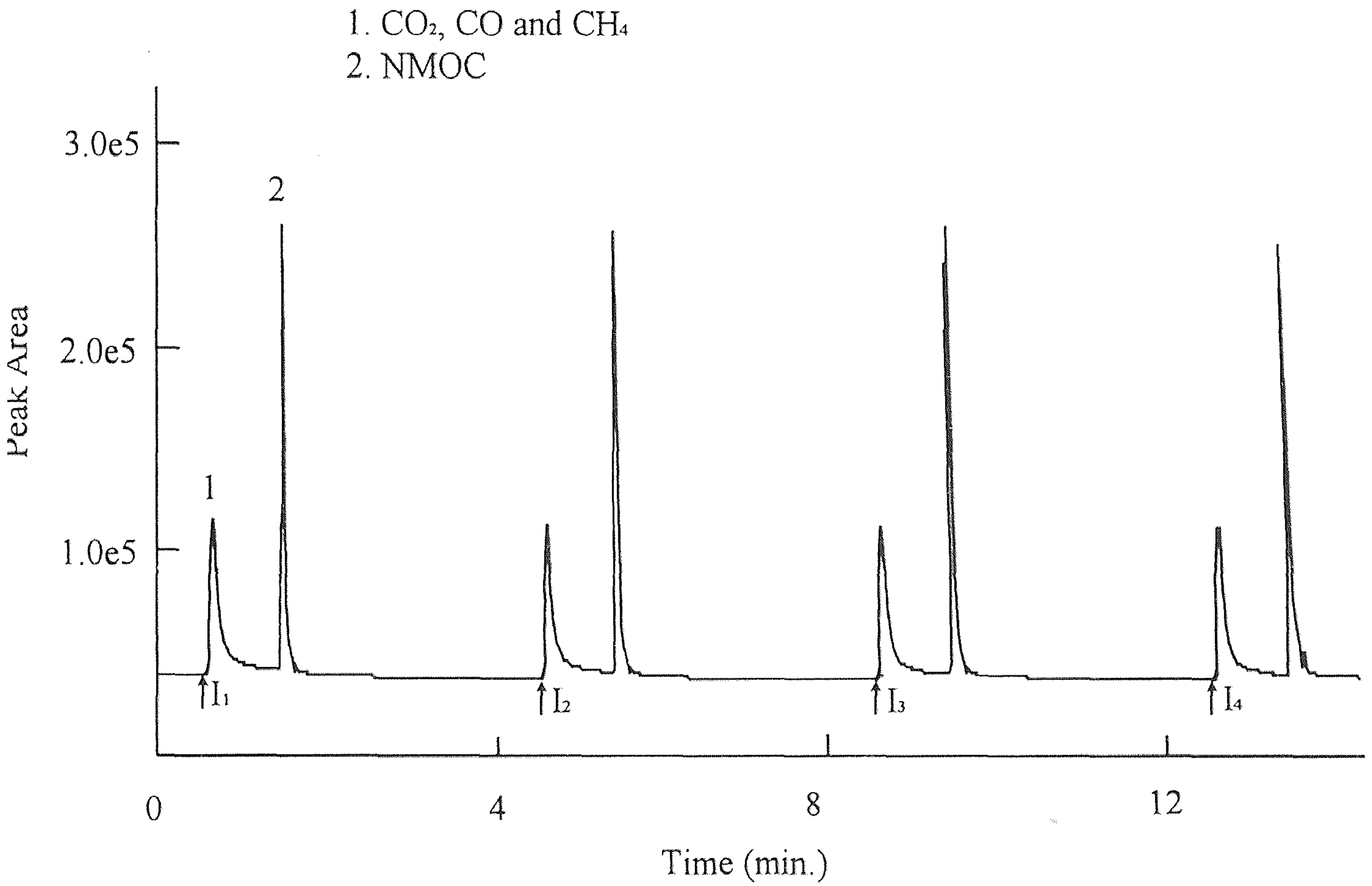

Figure 23 NMOC monitoring of emission gas from the catalytic incinerator using OLMT-BF system. The temperature of catalytic incinerator was 623 K. The inlet concentration of NMOC was 1749.5 ppm. Injections were made every 4 minutes and the sample flowrate was 15 ml/min.

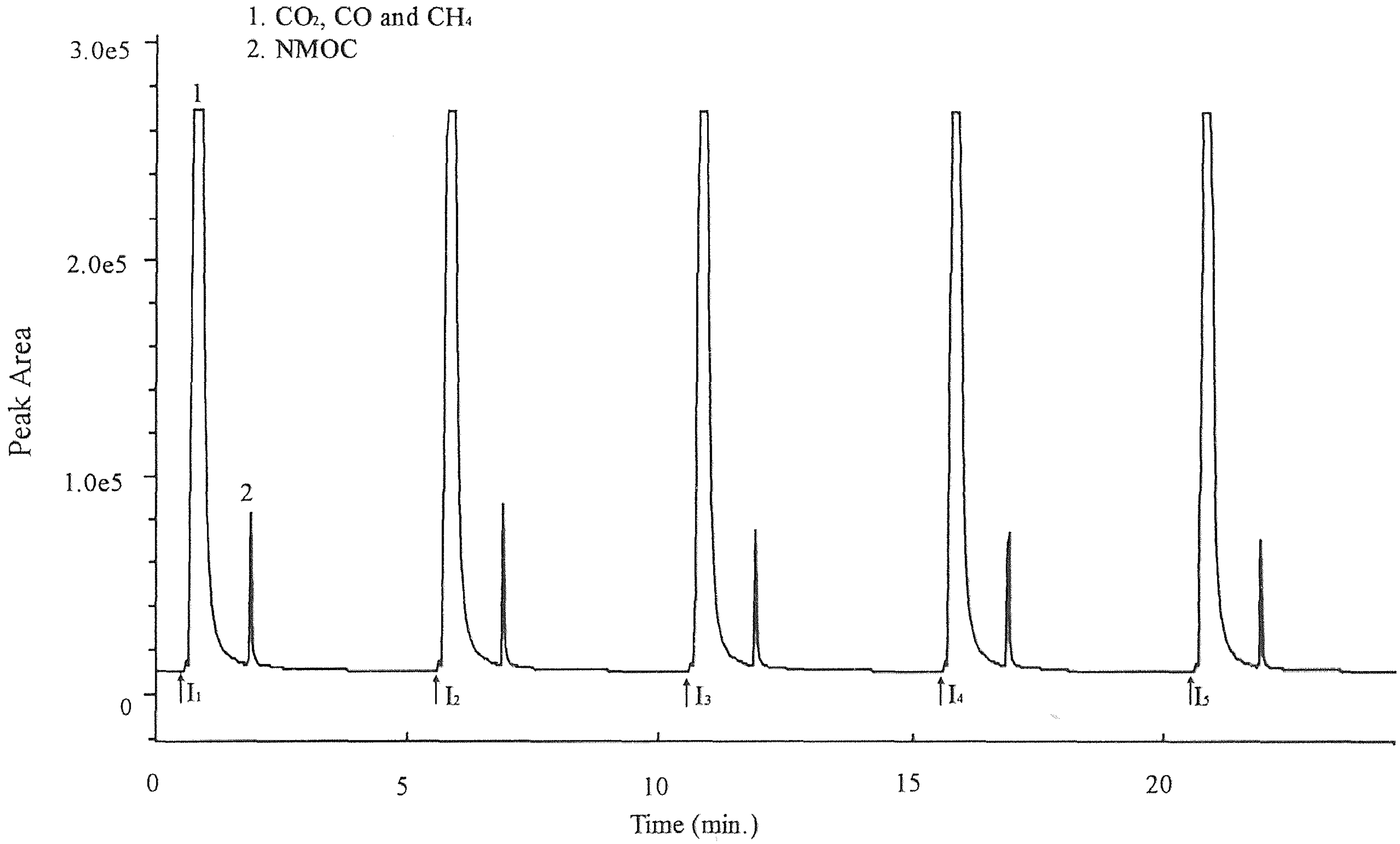

Figure 24 NMOC monitoring of emission gas from the catalytic incinerator using SVM system. The temperature of catalytic incinerator was 573 K. The inlet concentration of NMOC was 1749.5 ppm. The volume of sample loop was 8 ml.

4.2.2 Effect of Moisture

In the conventional NMOC analyzer, when carbon dioxide (CO_2) and water vapor are present together in the sample, they can produce a positive bias [29]. To test the effect of moisture on the NMOC response, the gas stream was passed through an impinger containing water which added the moisture to the stream. The moisture content was varied by altering the temperature of the impinger. The experimental diagram is presented in Figure 26. The water temperature in the impinger was varied from 0 °C to 75 °C, respectively. In this experiment, the SVM system was used to monitor NMOC and the incineration temperature was set at 350 °C. The inlet concentration of VOCs was kept constant. The results are shown in Figure 27. The result showed that the moisture did not significantly affect the NMOC response.

4.2.3 Evaluation of Catalytic Incinerator

Here continuous monitoring of NMOC was done using SVM and OLMT-BF as injection system. As temperature of catalytic incinerator was increased, the destruction efficiency increases which lowered the concentration at the outlet of the catalytic incinerator. In Figure 28 and 29, the NMOC concentration is presented as a function of reactor temperature. It can be seen that as temperature was raised NMOC concentration decreased.

Based on previous experiments, the inlet concentration of VOCs could affect the conversion efficiency. In this experiment, various inlet concentrations of VOCs were feed into the incinerator. The NMOC concentration at the outlet was monitored using the NMOC analyzer. The results were shown in Figure 30. When the inlet concentration of carbon increased, the outlet NMOC concentration also increased.

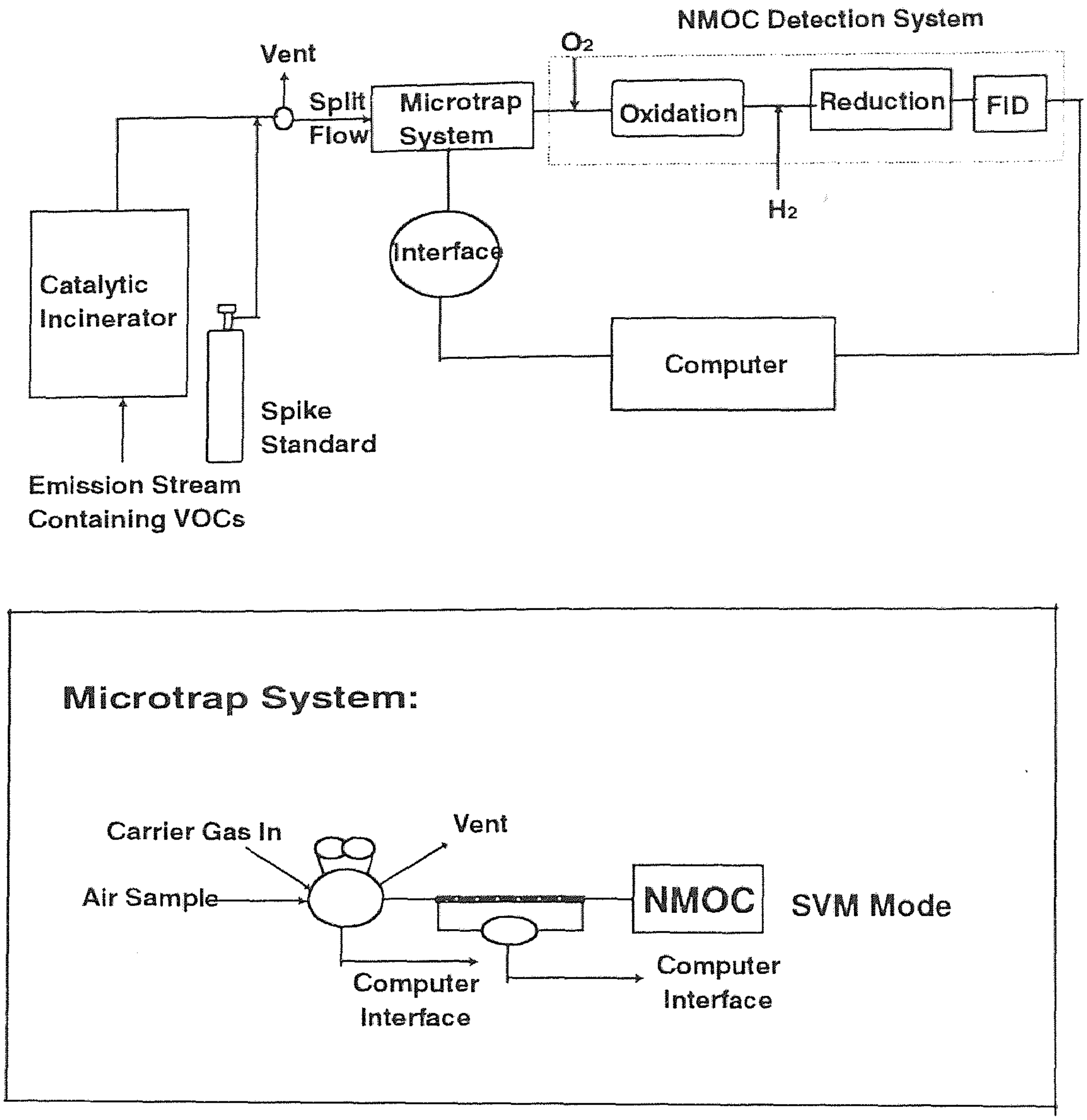

Figure 25 Experimental system for spike recovery of NMOC

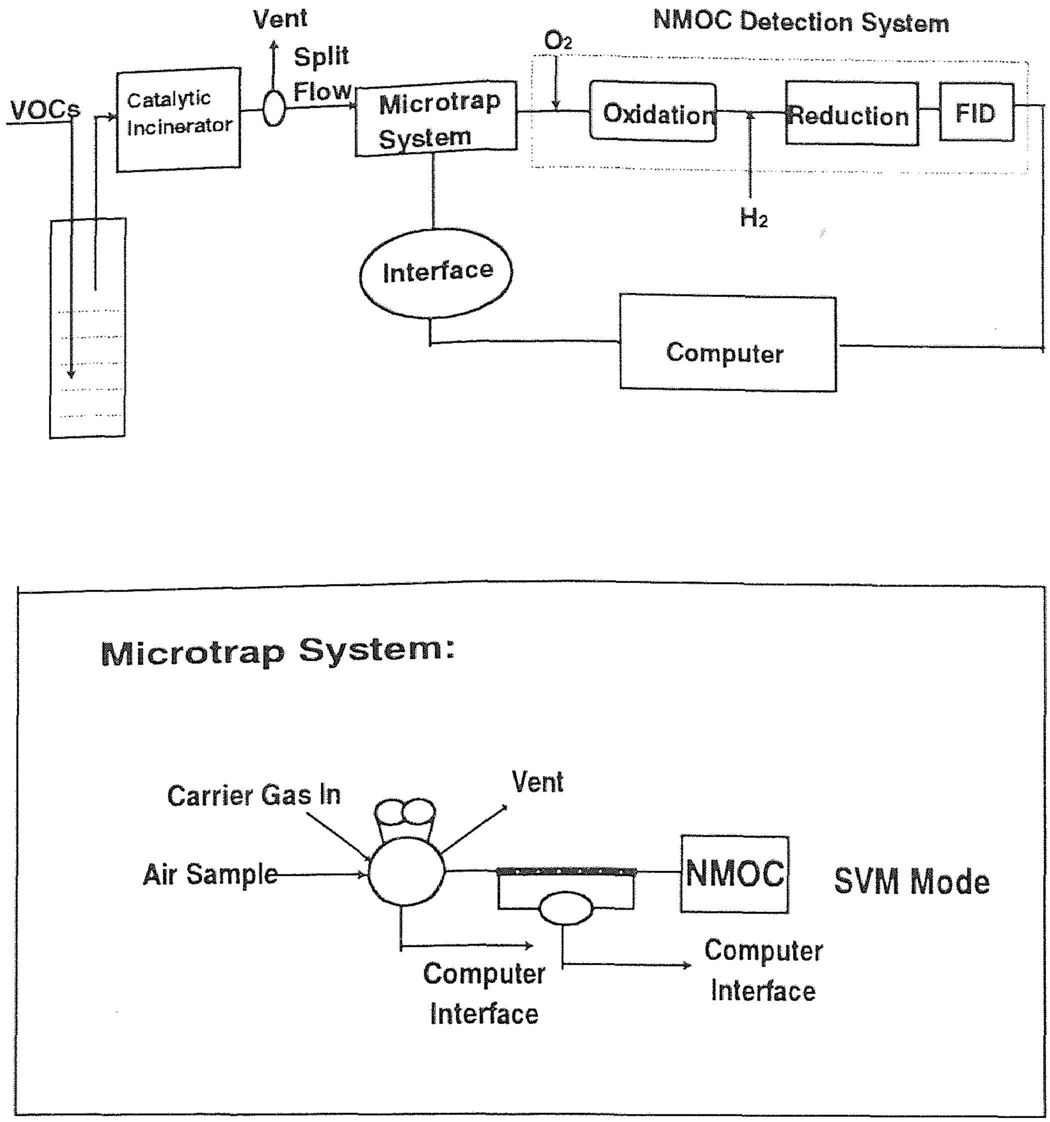

Figure 26 Experimental setup to study the effect of moisture

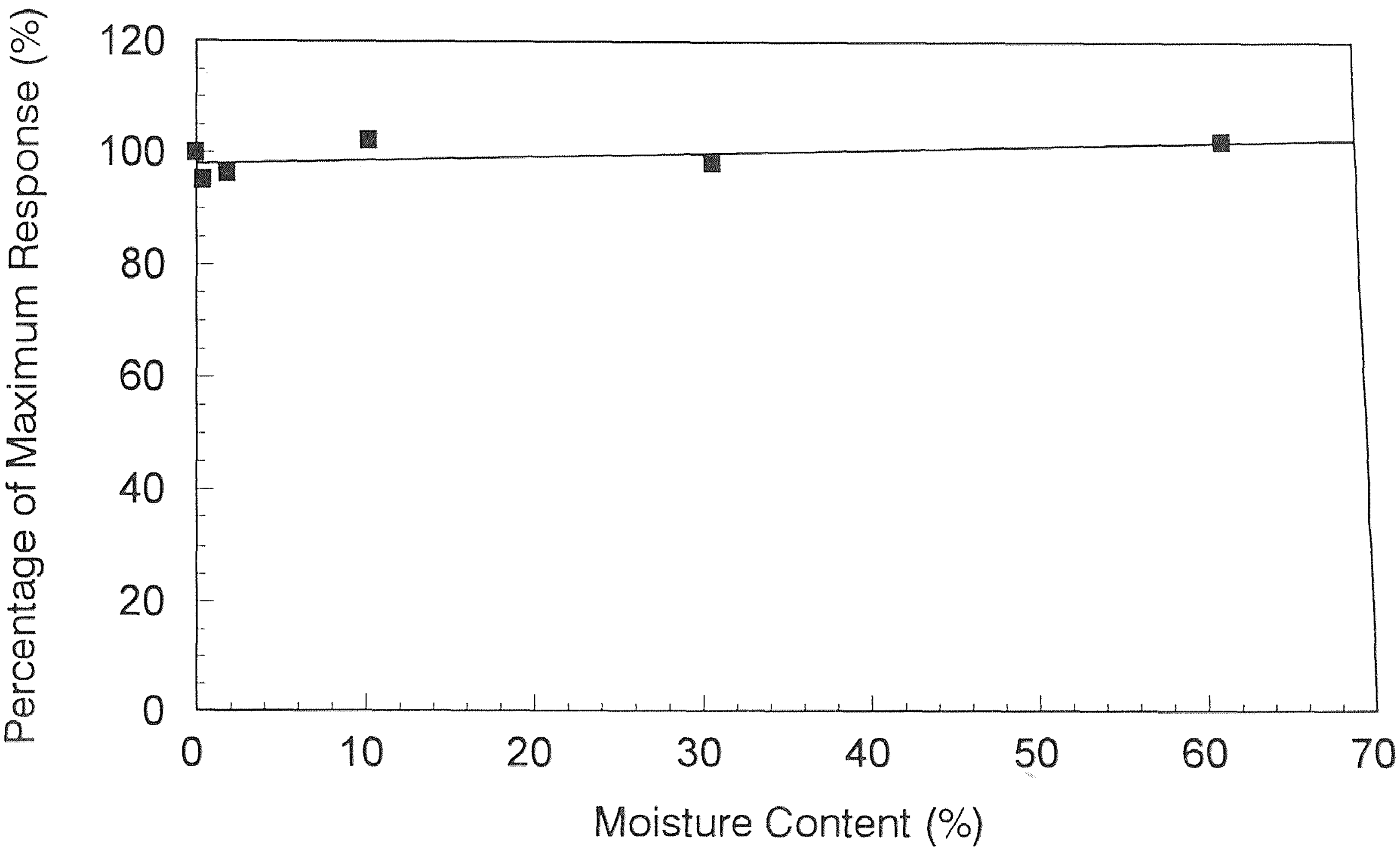

Figure 27 System response as a function of moisture concentration. Inlet NMOC concentration was 1749.5 ppm and the temperature of the incinerator was 623 K. A SVM system was used.

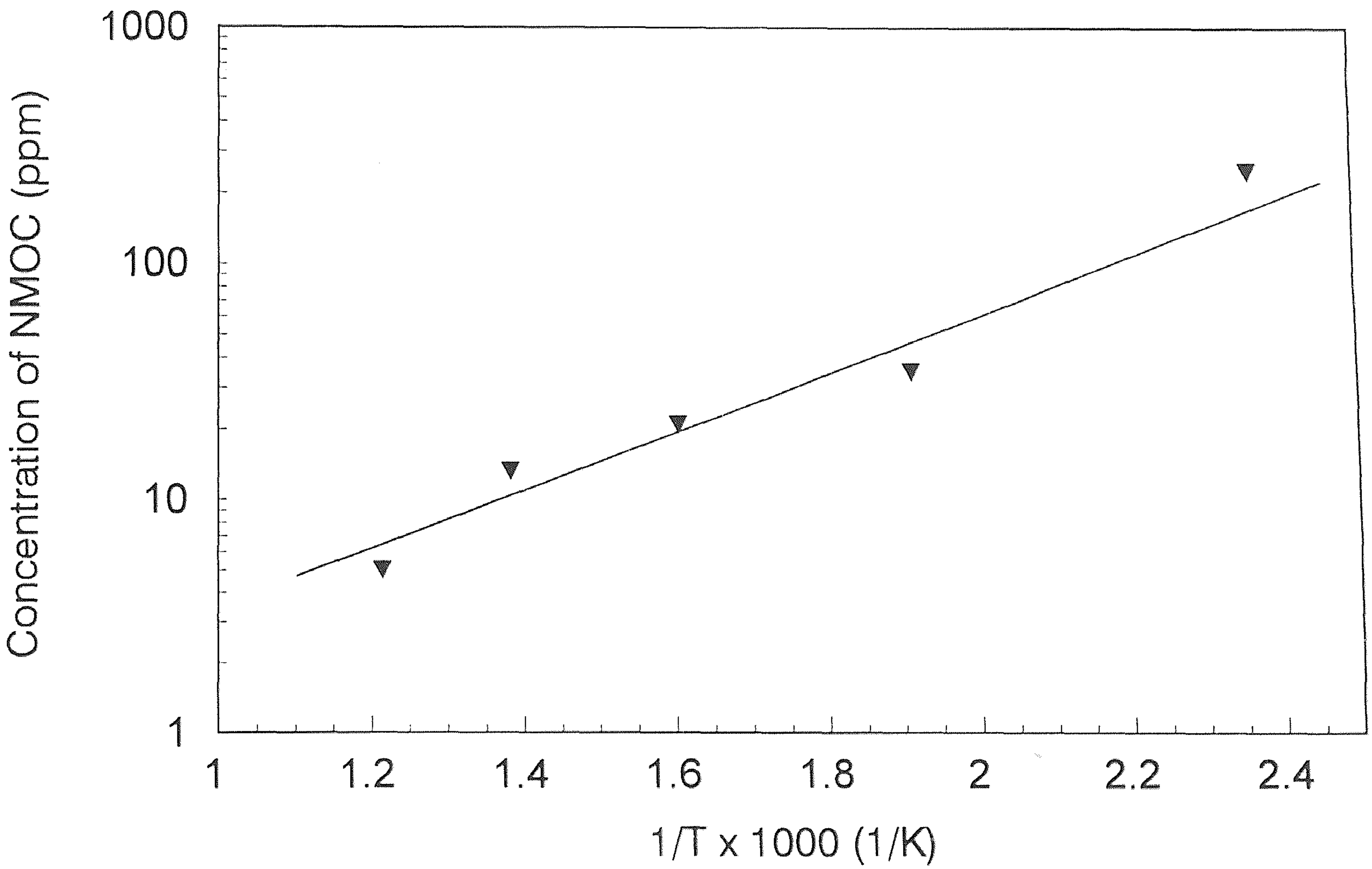

Figure 28 Outlet NMOC concentration at incinerator as a function of temperature. Inlet concentration was 1749.5 ppm.

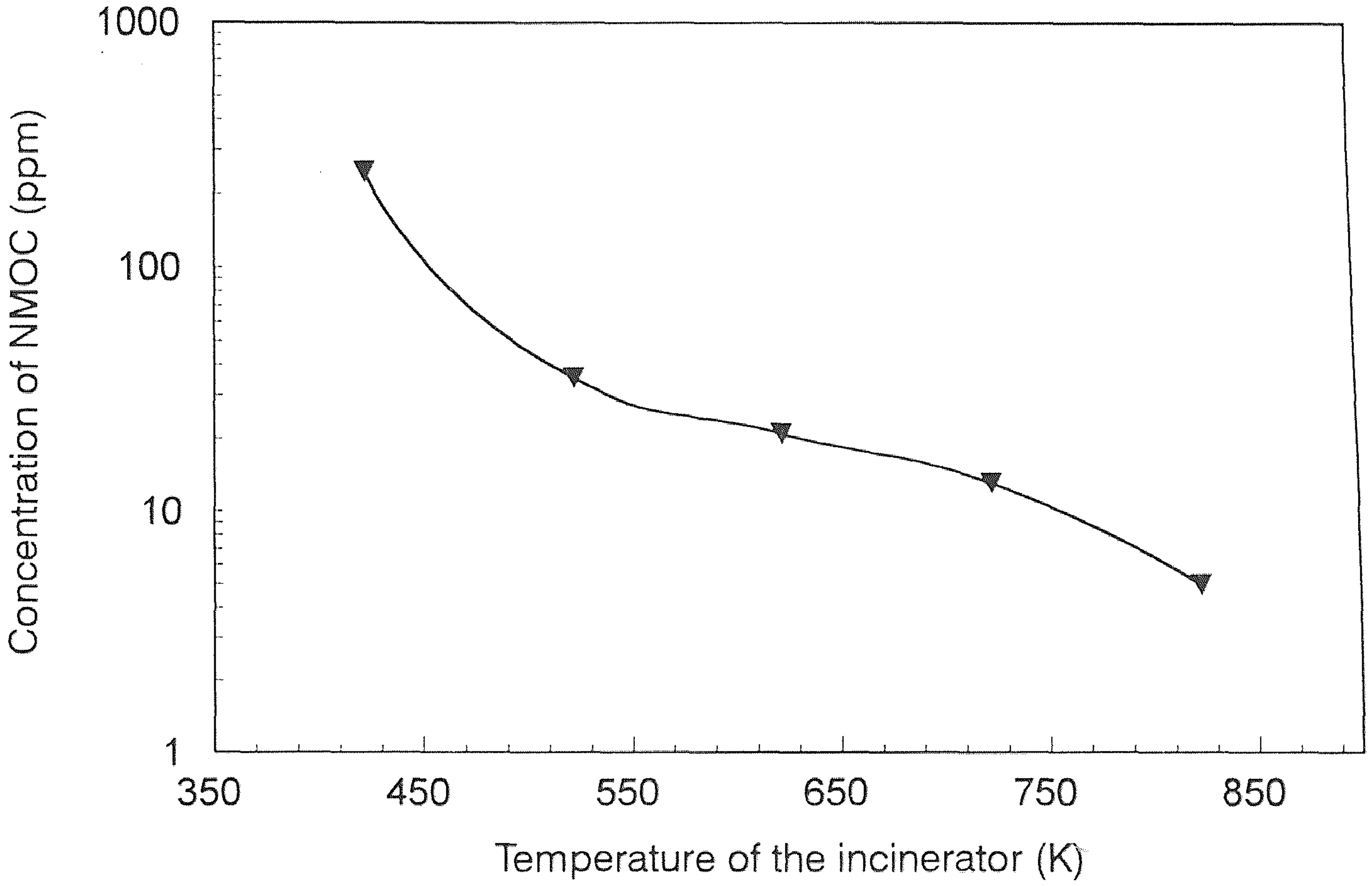

Figure 29 Relationship between outlet NMOC concentration and temperature of incinerator. Inlet carbon concentration was 1749.5 ppm..

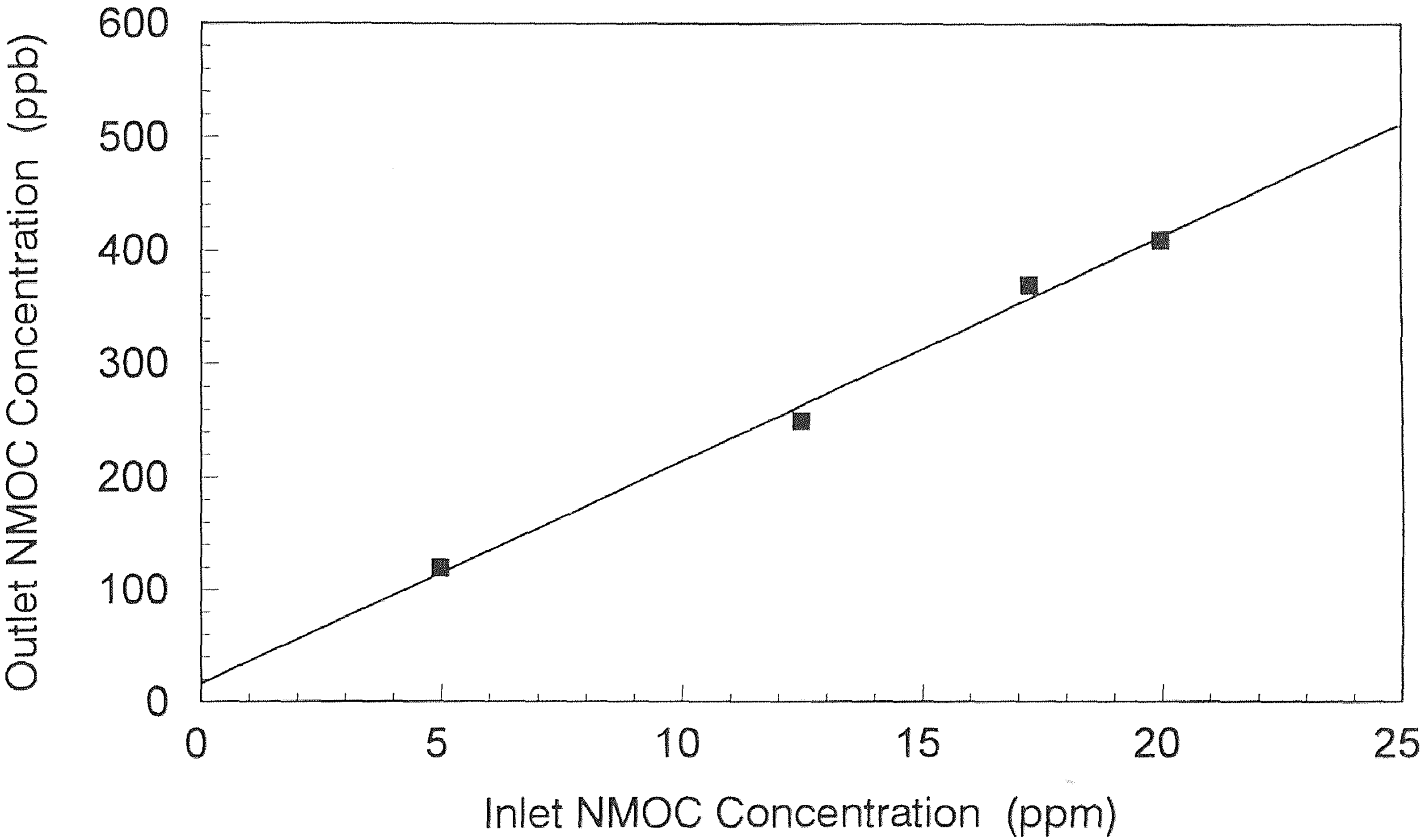

Figure 30 Outlet NMOC concentration as a function of inlet concentration. The temperature of incinerator was 623 K. The inlet stream contained benzene, TCE, toluene and ethylbenzene. Analysis was performed in the SVM mode.

CHAPTER 5

CONCLUSION

In this research, microtrap based injection system was investigated for continuous on-line monitoring method for VOCs in the effluents from a catalytic incinerator. Three injection systems namely gas sampling valve, SVM and OLMT-BF were evaluated and compared. From this research, it is clear by established that both the SVM and OLMT-BF systems are very sensitive and have low detection limits. The OLMT-BF system has lower detection limits than the SVM system because of larger sampling volume. However, the SVM system is operationally simpler. Quantitative spike recovery was possible for the VOCs tested using the GC and the NMOC detector.

The catalytic incinerator was evaluated using microtrap GC system as well as the NMOC system. The concentration of VOCs and NMOC in exhaust gas decreased with the increase of reactor temperature. The conversion efficiencies for benzene, toluene and ethyl benzene were over 99% when reactor temperature was over 350°C. The conversion efficiency of TCE was only 95% at 350°C since chlorinated compounds are more difficult to be oxidized. The inlet concentration of VOCs was seen to affect the destruction efficiency of VOCs.

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