

Ambient air monitoring of a SARA Title III facility using the TAGA[®] 6000E MS/MS[☆]

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Abstract

SARA Title III legislation requires facilities to report the quantities of regulated chemicals that are used on site in an effort to determine the chemicals' fate. One pathway by which a chemical may leave a facility is through volatilization into the atmosphere. These chemical emissions pollute the environment and may be a potential health problem. The TAGA[®] 6000E was used to investigate a specific site for chemical losses due to volatilization by analyzing the ambient air on and off the facility's property.

Keywords: Trace atmospheric gas analyzer; Mass spectrometer/mass spectrometer; SARA Title III facility; Ambient air monitoring

1. Introduction

In 1986, the Emergency Planning and Community Right-to-Know Act, also known as Title III, was established. This act has four major sections, with Section 313 providing regulations for toxic chemical release reporting. Facilities subject to this reporting are required to complete Toxic Chemical Release Form (Form R) for specified chemicals. Information necessary to complete this form includes the quantity of the chemical entering air, land, and water annually.

In 1989, the US EPA Environmental Response Team (ERT) was requested to provide analytical support to US EPA Region I in its efforts to conduct an air

[☆] Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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monitoring study in the vicinity of a Title III facility. Monitoring was being conducted by Region I to determine if this facility was introducing regulated chemicals into the air. The study was designed to monitor off-site locations on the perimeter of the facility for compounds whose presence in the ambient air would strongly suggest origination at the facility. The air study also included the performance of on-site analyses for compounds to locate their sources.

2. Experimental methods

Eight target compounds (Table 1) were selected for continuous monitoring by the Trace Atmospheric Gas Analyzer (TAGA®) 6000E (Fig. 1). Five of these compounds were selected based on their identification in the facility's Title III report. The other three compounds were selected because they represent common solvents, and because one is an indicator of target compound contribution due to vehicular exhaust. The sampling was performed during periods when it was believed that the meteorological conditions would permit observation of the maximum concentrations of the targeted compounds.

The 6000E mass spectrometer/mass spectrometer (MS/MS) is a real-time, direct-air sampling, laboratory instrument which is mounted in a vehicle [1, 2]. The general theory of the TAGA® 6000E MS/MS utilizes the technique of triple quadrupole MS/MS to differentiate and quantitate compounds. The analysis procedure involves multiple sequential steps. The initial step in the MS/MS process involves simultaneous chemical ionization of the compounds present in a sample of ambient air. The ionization produces either positive or negative ions by donating or removing one or more electrons. The chemical ionization is a "soft" ionization technique, which allows ions to be formed with little or no structural fragmentation. These ions are called parent ions.

The parent ions with different mass-to-charge (m/z) ratios are separated by the first quadrupole (the first MS of the MS/MS system). The quadrupole scans for selected m/z ratios allowing only the parent ions with these ratios to pass through the quadrupole. Parent ions with m/z ratios different than those selected are discriminated electronically and fail to pass through the quadrupole.

The parent ions selected in the first quadrupole are accelerated through a cloud of uncharged argon atoms which are introduced normal to the ion path in the second quadrupole. A portion of the parent ions entering the second quadrupole fragment as they collide with the argon atoms. These fragmented ions are called daughter ions. This process, in the second quadrupole, is called collision induced dissociation (CID).

The daughter ions are separated according to their m/z ratios by the third quadrupole (the second MS of the MS/MS system). The quadrupole scans for selected m/z ratios allowing only the daughter ions with these ratios to pass through the quadrupole. Daughter ions with m/z ratios different than those selected are discriminated electronically and fail to pass through the quadrupole. Daughter ions with the selected m/z ratios are then counted by an electron multiplier. The resulting signals

Table 1
Target compound list

Benzene ^a
Chlorobenzene ^a
1,2-Dichloroethane ^a
1,4-Dioxane
Methylene chloride ^a
1,1,1-Trichloroethane
Toluene ^a
Xylene (total)

^a Identified from facility's Title III report.

are measured in ion counts per second (ICPS) for each parent/daughter ion pair selected. The intensity of the ICPS for each parent/daughter ion pair is directly proportional to the ambient air concentration of the organic compound that produced the ion pair.

If all of the ions are singly charged, the m/z ratios of the ions are equal to the ion masses (atomic mass units). Therefore, the terms parent and daughter masses are synonymous with parent and daughter ion m/z ratios.

The TAGA[®] performs mobile, ambient air monitoring using a direct-air sampling system along roads adjacent to suspected sources to detect emissions originating from these locations. Outside ambient air is continuously drawn through a port in the wall of the TAGA[®] bus at a flow rate of approximately 1.5 l/s.

The air then passes through a glass splitter where the pressure gradient between the mass spectrometer core and the atmosphere causes a sample flow of approximately 10 ml/min into the ionization source through a heated transfer line. The flow into the low pressure chemical ionization (LPCI) source is manually controlled and adjusted so that the ionization source pressure is maintained at an optimum value, which is about 1 torr. The remaining air flow is drawn through the air motor and vented from the bus.

The TAGA[®] performs mobile monitoring in the parent ion or parent ion/daughter ion monitoring mode. As the mobile monitoring proceeds, the operator presses the letter keys (flags) sequentially to denote events or locations during the monitoring. This information is also recorded on the operator's log sheet. The intensity of each parent ion or parent/daughter ion pair monitored by the TAGA[®] is recorded by the Plessey computer in a file on the hard disk. One set of measurements for each ion is called a sequence.

While continuously analyzing for the target compounds, mobile monitoring was performed along public roads and over lanes around the commercial facilities surrounding the Title III plant (Fig. 2). As the mobile monitoring proceeded, the computer was flagged with a letter to denote an event or a location; these flags were also recorded on the TAGA[®] operator's log sheet. The flags are indicated on the ion profiles (Fig. 3) and correspond to the map locations associated with that file. Figs. 2 and 3 are illustrative examples of the 38 mobile monitoring events conducted

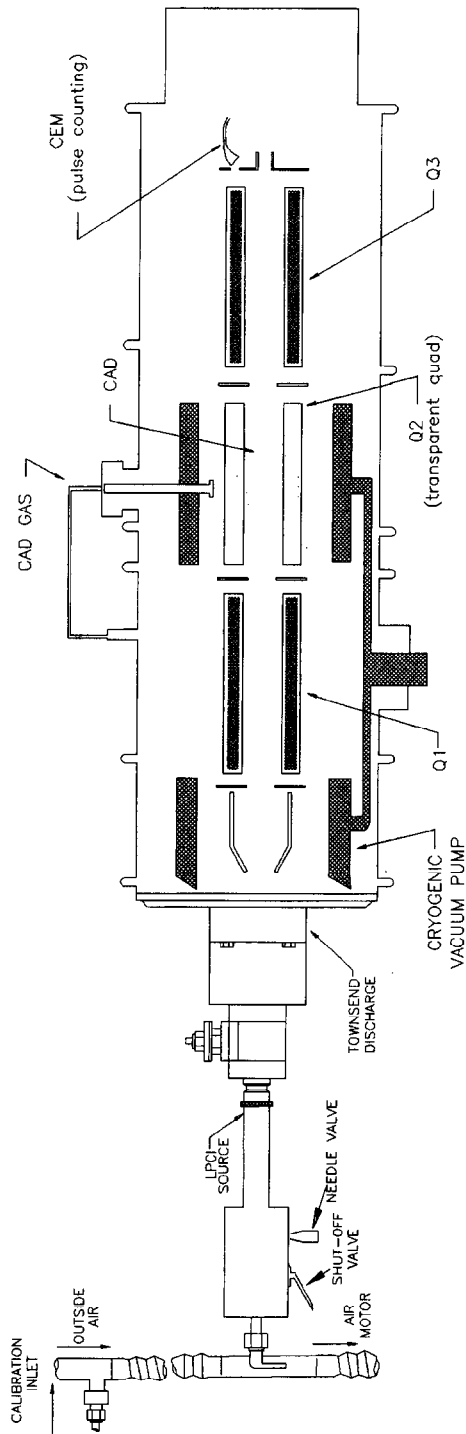


Fig. 1. The TAGA 6000E triple quadrupole mass spectrometer.

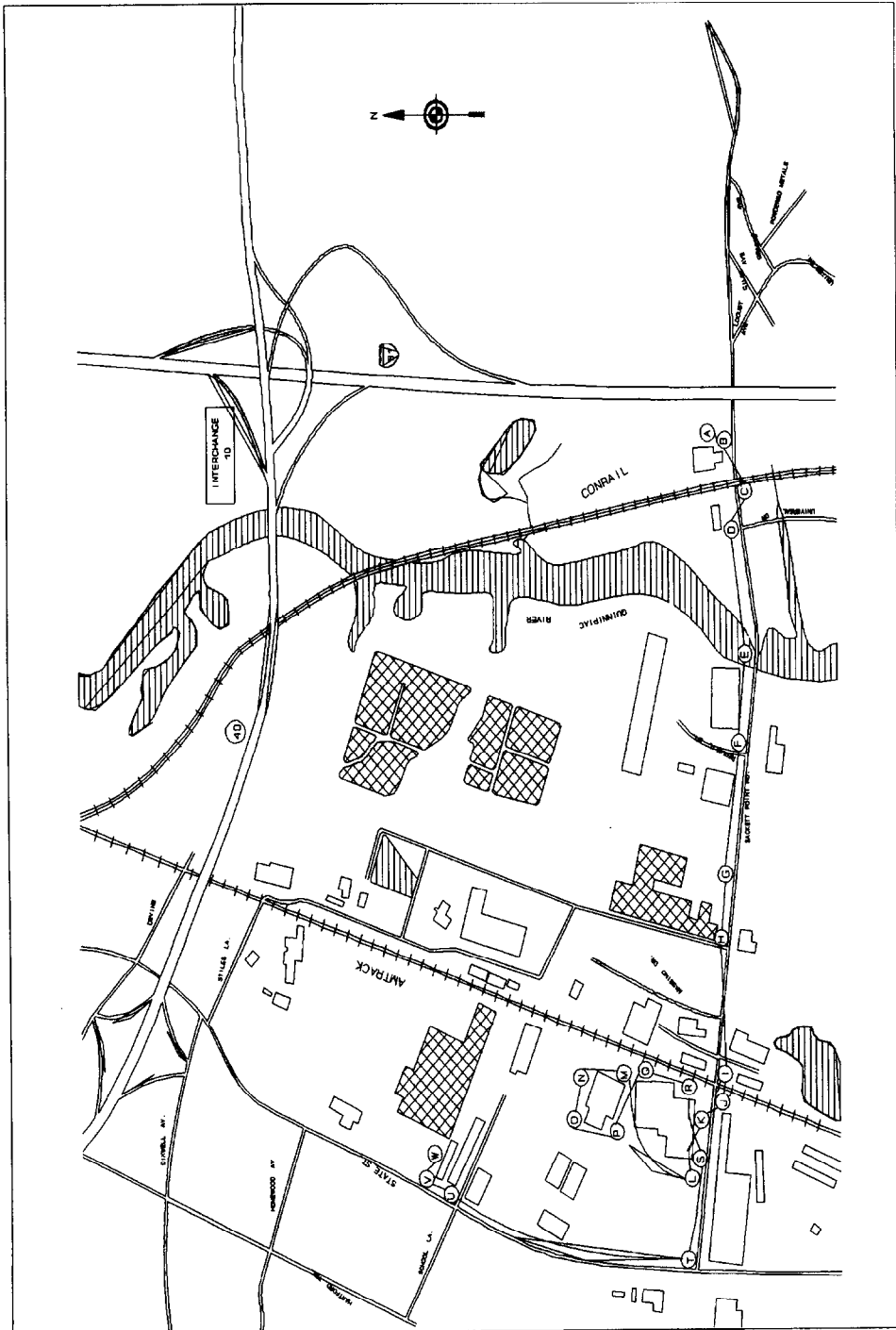


Fig. 2. Route traversed to perform air monitoring.

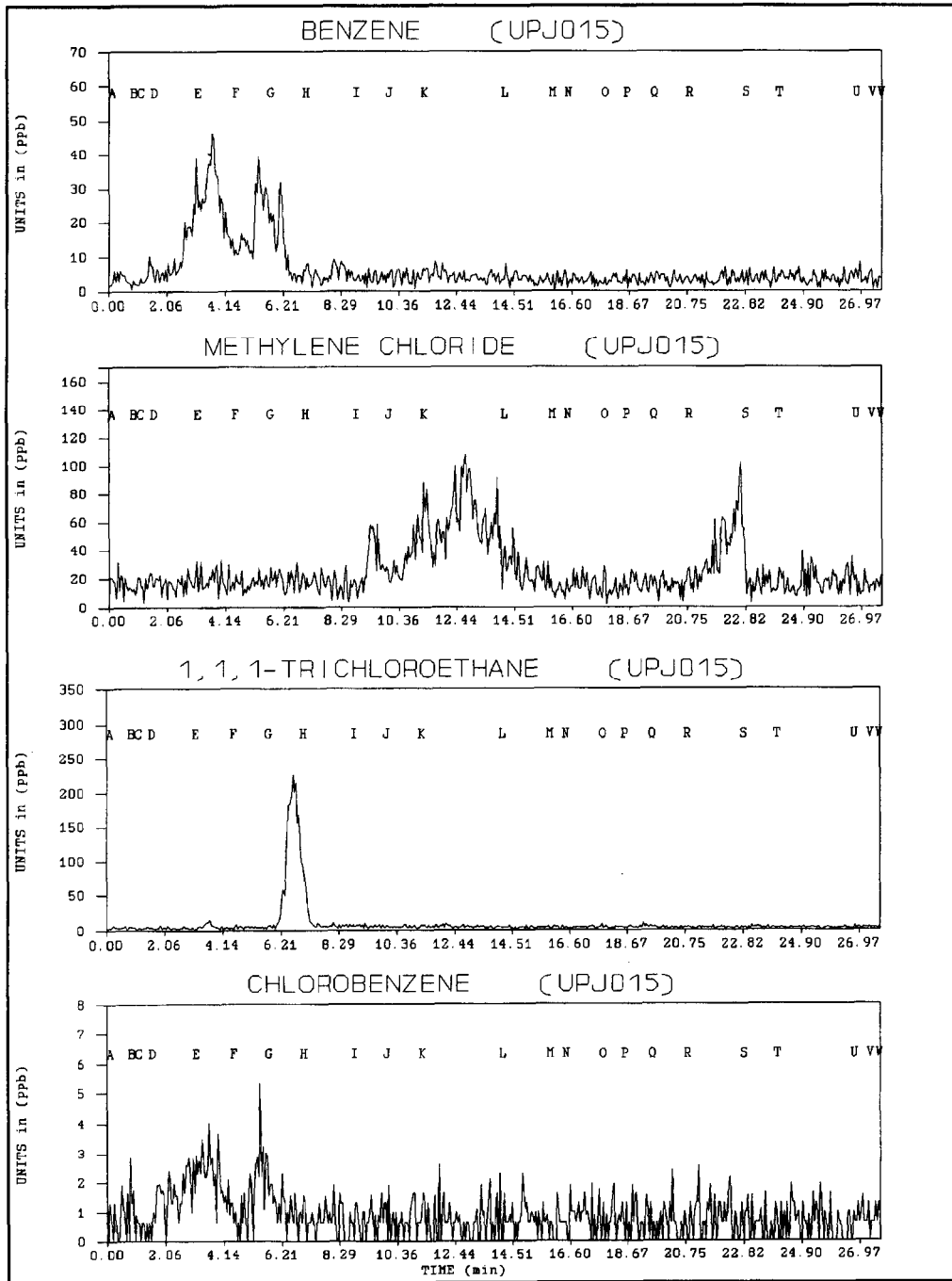


Fig. 3. Ion profiles for target compounds.

during the project. Once a plume was located, an effort to isolate the source was conducted by monitoring around the suspected source to determine if any upwind contributions existed.

A SUMMA[®] canister is a stainless steel collection vessel for air samples, which has a proprietary process and electroplating solution applied to the inside surface. The SUMMA[®] passivation process is used to reduce the surface effects associated with the sampling and storage of gas samples. SUMMA[®] canister sampling is applicable to specific volatile organic compounds (VOCs) that have been tested and determined to be stable when stored in pressurized canisters. The organic compounds that have been successfully collected in pressurized canisters by this method are listed in the US EPA Toxic Organic Compounds in Ambient Air Method TO-14 [The Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA[®] Passivated Canister Sampling and Gas Chromatographic Analysis] [3, 4].

SUMMA[®] canisters were used as the medium to collect grab, whole-air samples. The canisters utilized for this field activity had been cleaned and certified to ensure that no target compounds were present at detectable levels prior to release to the sampling crew [5]. Before any sample was collected, each canister was checked for leaks with a pressure gauge to ensure that a proper vacuum existed (less than 0.05 mm Hg). The SUMMA[®] canister samples were collected to confirm the TAGA[®] analysis and to provide additional information for compounds not on the TAGA[®] target compound list.

The TAGA[®] monitoring and subsequent SUMMA[®] canister sampling was performed by initially monitoring with the TAGA[®] and then once the TAGA[®] identified a plume, a sample was collected in the SUMMA[®]. The collection was accomplished by connecting a SUMMA[®] to the TAGA[®] sample air flow tubing via a glass splitter and a section of Teflon tubing [6]. No attempt was made to regulate the flow rate into the canister. After the canister had reached ambient pressure, the valve was closed, the tubing was disconnected, and both the canister and the glass splitter were capped. The time, and location of sampling were noted on the canister, and also included on the TAGA[®] operator's log sheet.

The SUMMA[®] canisters were returned to Edison, NJ, where each canister's pressure was recorded; ultra-high purity nitrogen was added until the canister's final pressure was twice its initial pressure; and the canister's contents were analyzed by gas chromatograph/mass spectrometer (GC/MS) for targeted and non-targeted compounds. The SUMMA[®] canisters were also analyzed by the TAGA[®] for the targeted compounds.

3. Results and discussion

This investigation had three goals: (1) identify off-site plumes using target compounds; (2) attempt to locate the sources of plumes, using meteorological data collected concurrently with sampling; and (3) collect whole-air samples using SUMMA[®] canisters for target and non-target compound analysis at a later date using conventional methods.

Sampling was conducted during periods when it was believed that the meteorological conditions would produce an atmospheric inversion, resulting in observation of maximum concentrations of target compounds. These sampling periods were:

Sampling period I	8 August 1989	04:29-07:42
Sampling period II	8 August 1989	20:17-23:52
Sampling period III	9 August 1989	12:34-16:55
Sampling period IV	10-11 August 1989	23:40-03:19

Four distinct plumes were observed off site. One contained the target compounds benzene, toluene, and chlorobenzene. This plume is believed to have originated from the Title III facility. Another plume contained the target compound 1,1,1-trichloroethane. This plume is believed to have originated from an electrical part manufacturing plant. The third plume contained methylene chloride and is believed to have originated from a parcel delivery service. The fourth plume is suspected to have originated from a graphic arts building and contained the target compounds, methylene chloride and 1,4-dioxane. Over the course of the project, the maximum concentration, in parts per billion by volume (ppb), observed off site for the target compounds were:

Benzene	300 ppb
Chlorobenzene	30 ppb
Methylene chloride	120 ppb
1,1,1-Trichloroethane	1100 ppb
Toluene	180 ppb
Xylene	80 ppb
1,4-Dioxane	18J ppb

No 1,2-dichloroethane was detected off site. The *J* associated with the 1,4-dioxane concentration denotes that the value is above the detection limit but below its quantitation limit. The maximum concentration observed on site for the target compounds were:

Benzene	5500 ppb
Chlorobenzene	350 ppb
1,2-Dichloroethane	70 ppb
Toluene	1700 ppb

No methylene chloride, 1,4-dioxane, 1,1,1-trichloroethane, or xylene was detected on site.

A meteorological station was provided for the examination of the micro-meteorology at various locations near the Title III facility. There was considerable variation between the US EPA/ERT data generated off site and the on-site data available from the facility. The differences in the meteorological conditions were believed attributable to local topographical features, which allowed channelling and eddy formation. The meteorological data generated at the facility was used to correlate the wind conditions and locations of the source of the plumes.

SUMMA[®] canister samples were taken in several plumes so analyses for targeted and non-targeted compounds could be performed by conventional GC/MS methods. The canisters were also analyzed by the TAGA[®] 6000E. The results of these analyses are located in Table 2. The results between the two techniques exhibited good agreement for the target compounds, particularly when concentrations were elevated.

Table 2
SUMMA[®] canister analytical results (concentrations in ppb)

Compound	SUMMA [®] #41		SUMMA [®] #69		SUMMA [®] #67	
	GC/MS	TAGA [®]	GC/MS	TAGA [®]	GC/MS	TAGA [®]
1,2-Dichloroethane	ND ^a	DL ^b = 4	ND	7J ^c	ND	6J
Benzene	QL ^d = 10	DL = 6	95	74	QL = 10	DL = 6
Methylene chloride	ND	DL = 28	ND	DL = 28	ND	30J
1,4-Dioxane	ND	DL = 6	ND	10J	ND	8J
Toluene	QL = 10	DL = 13	18	22J	QL = 10	DL = 13
1,1,1-Trichloroethane	QL = 10	DL = 4	QL = 10	9J	39	42
Xylene	QL = 10	DL = 8	QL = 10	10J	QL = 10	9J
Chlorobenzene	ND	DL = 2	9J	6	ND	DL = 2
Compound	SUMMA [®] #52		SUMMA [®] #1		SUMMA [®] #48	
	GC/MS	TAGA [®]	GC/MS	TAGA [®]	GC/MS	TAGA [®]
1,2-Dichloroethane	ND	6J	ND	6J	ND	6J
Benzene	QL = 10	DL = 6	117	139	235	229
Methylene chloride	49	71J	QL = 8	DL = 28	QL = 10	DL = 28
1,4-Dioxane	ND	8J	ND	DL = 6	ND	8J
Toluene	QL = 10	DL = 13	154	197	92	86
1,1,1-Trichloroethane	ND	5J	QL = 8	5J	QL = 10	5J
Xylene	QL = 10	10J	ND	DL = 8	QL = 10	9J
Chlorobenzene	ND	DL = 2	13	17	27	19
Compound	SUMMA [®] #12		TAGA [®]		SUMMA [®] #58	
	GC/MS	GC/MS DUP ^e	GC/MS	GC/MS	GC/MS	TAGA [®]
1,2-Dichloroethane	ND	ND	6	ND	ND	6J
Benzene	20	20	22	QL = 10	QL = 10	DL = 6
Methylene chloride	QL = 10	QL = 10	35J	QL = 10	QL = 10	32J
1,4-Dioxane	ND	ND	8J	ND	ND	10J
Toluene	18	17	26J	QL = 10	QL = 10	14J
1,1,1-Trichloroethane	ND	ND	9J	QL = 10	QL = 10	10J
Xylene	QL = 10	QL = 10	9J	QL = 10	QL = 10	10J
Chlorobenzene	3J	ND	4J	ND	ND	DL = 2

^a Not detected.

^b Detection Limits.

^c Value between detection limits and quantitation limits.

^d Quantitation limits.

^e Duplicate.

4. Conclusion

The goals of this investigation were successfully met. The TAGA[®] 6000E identified off-site plumes using target compounds; the sources of these plumes were located using meteorological data collected concurrently with the sampling; and the TAGA[®] 6000E located plumes enabling whole-air samples to be collected in SUMMA[®]

canisters for target and non-target compounds analyses using conventional GC/MS methodology. Furthermore, the SUMMA[®] canister analysis for target compounds by both the GC/MS and the TAGA[®] exhibited good agreement.

References

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