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Original Research

Parameter Optimization for the Measurement of VOCs by Canister System

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Abstract

With growing concern for quality of the environment, demand for reliable and sensitive monitoring techniques for organic compounds in the atmosphere has increased recently. Canister sampling and analysis is becoming a widely accepted choice for the measurement of volatile organic compounds (VOCs). Before carrying out any measurement it is necessary to optimize parameters in order to get reproducible results. In view of this, a canister sampling technique was optimized for efficient measurement of various VOCs, including sulfur and chlorinated compounds. For all studied compounds the optimum trap desorption temperature was found to be 225°C, while for CCl_4 the optimum temperature was lower and this compound shows a decrease in response with the increase in trap desorption temperature. Other chloro compounds like chloroform and 1, 2-dichloroethane showed the same behavior as other organic compounds. Furthermore, cold trap desorption temperature and cryo injection time and moisture control system (MCS) were also optimized.

Keywords: VOCs, optimization of desorption parameters, canister, GC/MS, sulfur & chloro compounds.

Introduction

The collection of air samples for the analysis of trace-level constituents, however, demands highly skillful approaches relative to those contained in other environmental media [1]. This is especially the case when highly reactive or unstable, gaseous components like volatile organic compounds (VOCs) are concerned [2]. Although VOCs occur in ambient air in trace concentrations, they nevertheless remain important air pollutants. In addition to being photochemical smog precursors, some VOCs can pose significant risks to human health, particularly the so-called “air toxics,” some of which are known or suspected carcinogens or known to result in other adverse human health and/or environmental effects [3-4].

Organic compounds that have a chlorine atom in their molecule and their by-products are also suspected to cause a number of environmental and human health problems. Chloro compounds like DDT, PCB, CFC, etc., are well known for their threat to the environment and human health [5-8]. Some chloro compounds (CFCs, HCFC substitutes, halons, carbon tetrachloride and methyl chloroform) contribute to stratospheric ozone depletion, tropospheric photochemical ozone formation and toxic and carcinogenic human health effects [9-12].

Harmful contamination of the air can be reached very quickly upon the evaporation of some compounds like carbon tetrachloride at 20°C. On contact with hot surfaces or flames this substance decomposes, forming toxic and corrosive fumes (hydrogen chloride, chlorine fumes and phosgene). In the work of risk estimation, Wallace [13] reported that six VOCs (benzene, vinyl chloride, p-dichlorobenzene, chloroform, methylene chloride and carbon

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tetrachloride) exceeded the negligible lifetime risk level of 10^{-6} (one chance in a million of contracting cancer) by a factor of 10 or more. In spite of being banned from consumer products by U.S. Consumer Product Safety Commission and thus being no longer an indoor source of pollution, carbon tetrachloride is still a threat because of its huge accumulation and long lifetime in the atmosphere [14].

A canister sampling system and analysis technique was employed for the measurement of various volatile organic compounds, including sulfur and chlorinated compounds. The collection of air samples for the analysis of trace-level constituents demands highly skillful approaches compared to other environmental media [1]. This is especially the case when highly reactive, unstable gaseous components like VOCs are concerned [2]. Among various sampling techniques canister sampling is used in a variety of air monitoring programmes and forms the basis of USEPA TO-14 [15-16]. One of the advantages of canister samples is that they do not need any refrigeration or special handling until they are analyzed.

During analysis the sample is transferred from canister into cryo trap. To achieve acceptable sensitivity the sample needs to be concentrated using either a cryo trap (cold trap) or a cryofocusing device if trace components have to be monitored [17-18]. By the process of thermal desorption analytes are transferred from cryo trap to the GC-column. In some specific cases a second cryogenic trap is placed ahead of the capillary column to provide narrow chromatographic bands [15, 19]. While collecting the sample into the canister as a method of whole air sampling we must take into consideration all parts of the air matrix. The most important is the water from humidity in ambient air [16, 20-23].

Setting up analytical parameters/conditions is quite essential before making any measurement. Sometimes, compounds of similar composition behave in a very different manner. In view of this, the present study was undertaken to optimize various parameters of canister sampling and analysis technique in order to measure organic compounds efficiently.

Experimental

Preparation of Standard Gas Mixtures

Two standard gas mixtures were prepared. The first mixture was prepared using n-pentane, benzene, 1-propanol, dimethylsulphide, dimethyldisulphide, tetrahydothiophene and carbon tetrachloride. Another standard gas mixture was prepared using carbon tetrachloride, chloroform, 1.2-dichloroethane and toluene. All the compounds were of GC analytical reagent grade obtained from Lachema, Brno, Czech Republic with purity above 99%. The details about the compounds in standard mixture are given in Table 1. Intermediate gas standards were prepared by injecting a calculated amount of liquid standards into a 6-liter SUMMA Canister (Tekmar – Dohrman, USA) filled with a known volume of zero-grade nitrogen as the diluting gas. Concentration of intermediate standard was around 1.00 mg/m^3 for each compound.

The concentration of compounds in the gas mixture was calculated (24) from equation 1:

$$C_{ppmv} = 22.4 \times 10^6 (\rho.V_1 / MV) (T / 273) (760/P) \quad (1)$$

...where C_{ppmv} is the concentration of the VOC sample (ppmv), 22.4 is the molar volume of gas at STP (l/mol), ρ is the density of the liquid sample injected (g/ml), V_1 is the volume of liquid sample injected (ml), M is the molecular weight of the analyte (g/mol), V is the total volume of the dilution gas (l), T is the temperature (K) and P is pressure (Torr).

Table 1. List of compounds in standard mixture and their properties.

Compounds	CAS no.	Molar weight (g/mol)	Density (g/ml)	Vapor pressure (mmHg at 25°C)	Intermediate concentration (mg/m^3)	Final canister concentration (µg/m^3)
n-Pentane	109-66-0	72.20	0.66	514	990.00	577.50
Benzene	71-43-2	78.10	0.88	95	990.00	577.50
1Ppropanol	71-23-8	60.10	0.80	20	998.75	582.60
Dimethylsulphide	75-18-3	62.13	0.85	439.8 (20°C)	951.75	555.19
Dimethyldisulphide	624-92-0	94.18	1.06	28	915.25	533.90
Tetrahydothiophene	110-01-0	88.17	1.00	18	875.00	510.42
Carbon tetrachloride	56-23-5	153.80	1.59	110	993.75	579.69
Chloroform	67-66-3	119.4	1.48	190	992.25	578.81
1,2 Dicholoroethane	107-06-2	98.96	1.235	82	1000	583.33
Toluene	108-88-3	92.10	0.87	30	990	577.50

Final standard gas mixture was prepared in a 6-liter SUMMA stainless steel canister. The canister was connected to zero-grade nitrogen through a tee piece as shown in Fig. 1. One opening of the tee was closed with a septum and a gas-tight syringe was used to inject the primary standard into the tee. Stock standard (intermediate standard) gas mixture was injected into 6 liter SUMMA stainless steel canister with the help of a gas-tight syringe (Hamilton gas-tight syringe). Dilution gas (zero grade nitrogen) was flowing during the injection process. The gas sweeps the VOCs into the humidified canister and prevents them from being adsorbed to the tee or the lines. Final concentration of standard gas mixture prepared in 6-liter canisters was around 600μg/m^3. Exact concentration appears in Table 1.

Canister Method

Canisters were cleaned by evacuation and pressurization cycles with humidified pure nitrogen as in compendium method TO-14. An aliquot of canister content was transferred to Gas Chromatograph/Mass Spectrometer via automatic cryofocusing unit (Autocan Tekmar, USA). The sample was transferred at a flow rate of 100 ml/min to a cryotrap (glass bead trap) maintained at -165°C by liquid nitrogen. The trapped analytes were then flash-heated to be transferred to a capillary cryofocusing unit via a transfer line maintained at 200°C (Fig.2). The temperature of the second cryofocusing unit was also kept at -165°C to trap all the analytes. Finally this cryofocusing unit is flash-heated to transfer all the analytes to a GC column.

Gas Chromatography / Mass Spectrometry Parameters

Gas Chromatography (Fisons instruments GC 8000 series) separations were performed using a capillary column Vocol (Supelco, USA) with dimensions 60m × 0.32mm × 3μm. GC oven temperature was programmed as follows: initial oven temperature was set to 40°C for two minutes, and then ramped by 10°C/min to 230°C for a hold time of 10 minutes. Mass Spectrometry measurements were performed on Fison MD 800 instrument. Source and interface temperature were set to 180°C and 220°C, respectively. Electron ionization conditions were as follows: ion energy – 70eV, scan range from 10 to 300 AMU (atomic mass unit), scan rate 0.5 scan/sec, tune reference compound was heptacosa (perfluorotributylamine).

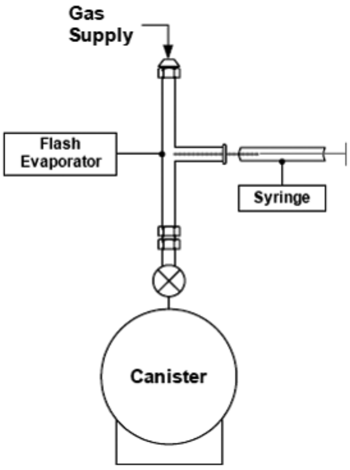


Fig. 1. Preparation of standard gas mixture in canister.

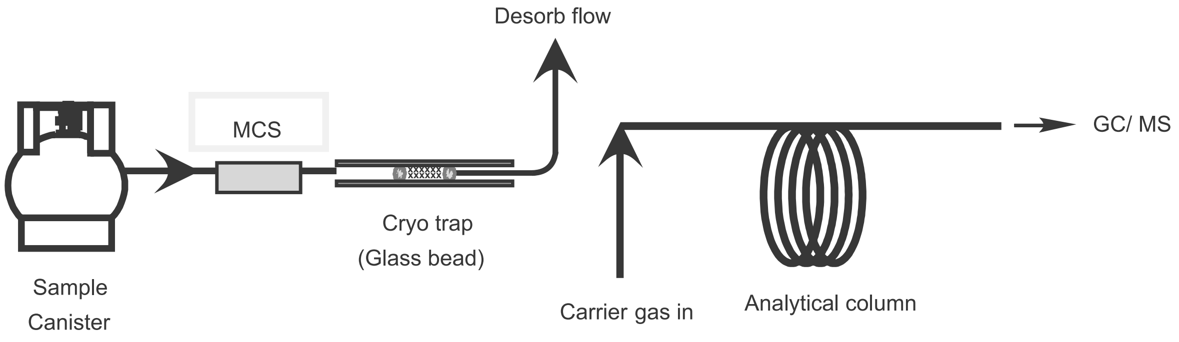
Results and Discussion

The present study was undertaken to optimize the method for canister sample analyses. Standard gas mixture containing aromatic and aliphatic hydrocarbons (benzene and pentane, respectively), sulfur compounds (dimethylsulphide, dimethyldisulphide, tetrahydothiophene), chloro compound (carbon tetrachloride) and alcohol compound (1-propanol) was applied for optimization work.

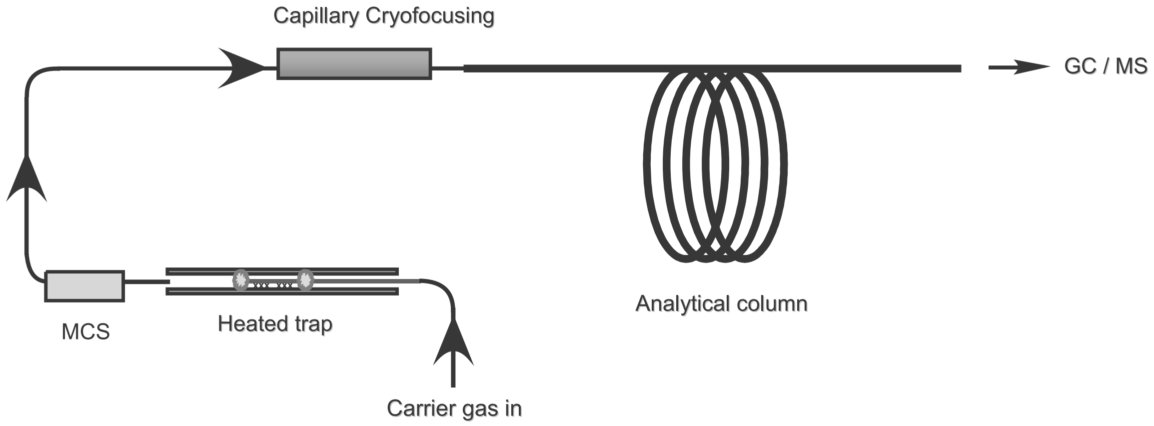
The appropriate cryo trap desorption temperature was evaluated in the range of 200 to 300°C. Optimum cryo trap desorption temperature was found to be 225°C for all the analytes except for carbon tetrachloride as shown in Fig. 3. Carbon tetrachloride recovery decreased considerably as the trap temperature was raised. The rest of the analytes shows slightly decreasing recovery if the desorption temperature is increased above 275°C. To confirm the unusual behavior of carbon tetrachloride, another standard gas mixture containing carbon tetrachloride, chloroform, dichloroethane and toluene was examined in the temperature range of 150°C to 275°C. The optimum desorption temperature for carbon tetrachloride was observed to be 200°C or less as shown in Fig. 4. Carbon tetrachloride recovery decreased sharply with the increase in trap desorption temperature. Other chloro compounds like chloroform and dichloroethane do not exhibit similar behavior.

Fig. 5 shows the dependence of analyte recovery on trap desorption time. The trap desorption time of 5 minutes was found to be suitable for the recovery of all analytes. In less than 5 minutes of desorption time not all the analytes may be recovered completely. Cryotrap contains glass beads to hold analytes at sufficiently low temperature (-165°C), so heating of the trap from -165°C to +225°C also takes 1-2 minutes. Increasing the trap desorption time above 5 minutes does not have any effects.

Cryo-injection time also showed little dependence on analyte recovery. It is clear from Fig. 6 that 3 minutes of cryo-injection time was sufficient to ensure the best results. The probable reason is that the elevated temperature of capillary cryofocusing (225°C) is required for 3 minutes to stop any back flush of analytes while injecting in capillary column. Capillary cryofocusing is usually required before GC analysis in order to provide narrow chromatographic bands of the most volatile substances and thus good resolution.



a) Sample transfer to cryo trap from Canister



(b) Trap desorption

Fig. 2. Schematic diagram of sample transfer to gas chromatograph, using Preconcentration steps.

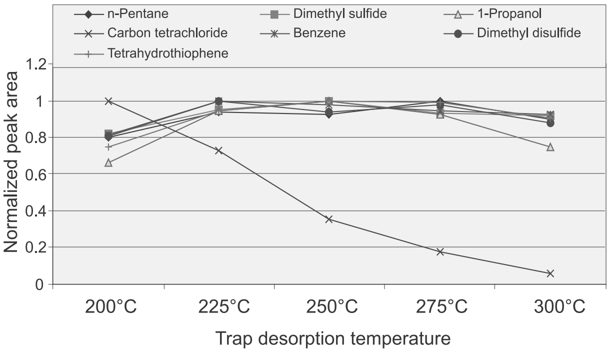


Fig. 3. The dependence of analyte recovery on trap desorption temperature.

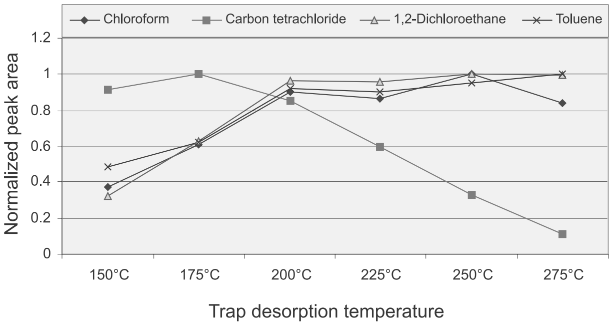


Fig. 4. The dependence of analyte recovery on trap desorption temperature for selected chlorine compounds and toluene.

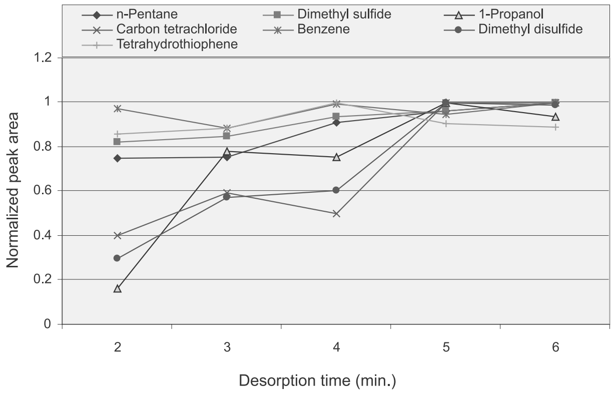


Fig. 5. The dependence of analyte recovery on trap desorption time.

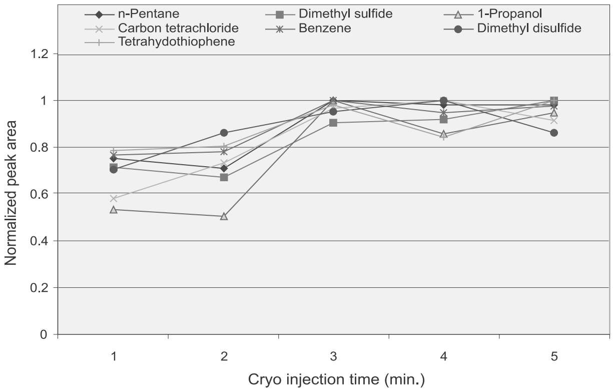


Fig. 6. The dependence of analyte recovery on cryo injection time.

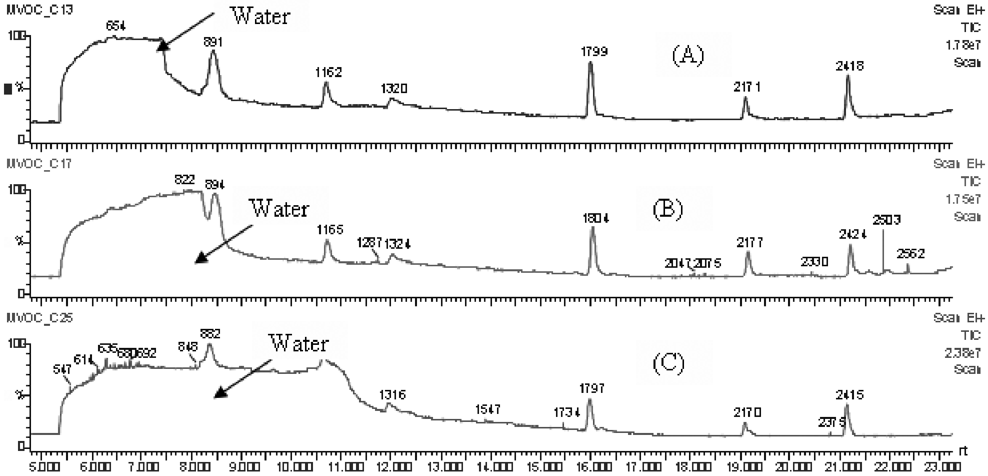


Fig. 7. Chromatogram showing influence of temperature on MCS.

Influence of Temperature on Moisture Control System (MCS)

Influence of temperature on MCS was also evaluated. MCS experiments were carried out at 30°C (ambient temperature) followed by 40°C and 200°C. Chromatograms (A), (B) and (C) shown in Fig. 7 were obtained at 30°C, 40°C and 200°C temperatures, respectively. The impact of moisture was found to be the minimum at 30°C as it appears in chromatogram A. Abundance of moisture increases with the increase in the temperature of MCS. The highest moisture content was observed at the temperature of 200°C of MCS. At this temperature, MCS acts as a simple tube and is not able to condense water. Although 30°C MCS temperature was not able to remove water content completely from the sample, it was found to be optimum.

MCS acts as a cooled zone in the analytical system to condense water from the humid sample. When a humid sample enters the MCS, water condenses on the walls of the ambient temperature tubings [25]. Some moisture is quite essential for sample storage in canister. Storage of VOC in dry air matrix shows decreasing concentration due to lack of water vapor, which is essential to cover the active sites on the interior surface, thus preventing physical adsorption or chemical interaction, while in the case of high moisture content, dissolution of target compounds in condensed water may be a major loss mechanism [20, 23, 26]. High moisture content in the sample can interfere with analyte peaks and may spoil GC column. It is important to remove the moisture from the canister sample prior to injecting in GC for analyses. Nafion dryer (frequently used for moisture removal prior to cryogenic concentration of adsorbent tube or canister sample) or hygroscopic ion exchange membrane is reported to remove water vapour but the nafion dryer is also reported to cause loss of polar compounds and lowers the concentrations of some paraffins, olefins and aromatics [27]. In view of this, MCS may represent a better option to remove at optimum temperature condition.

Conclusions

Some chlorine compounds, especially carbon tetrachloride (CCl_4), show unusual behavior in terms of their thermal desorption conditions compared to other VOCs. Optimum cryo trap desorption temperature for carbon tetrachloride was 200°C or less, whereas the optimum starts at 225°C for all other tested compounds. A possible reason may be the cleavage of its molecule. Unlike with cryotrap desorption temperature, trap desorption time has a positive influence on standards' recovery and it does not influence the recovery of chlorinated compounds in comparison to the others. Our results indicate that MCS can remove moisture up to a certain extent without any major loss of polar compounds, although it is not able to remove moisture completely.

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References

1. YAMAMOTO N., OKAYASU H., MURAYAMA S., MORI S., HUNAHASHI K., SUZUKI K. Measurement of volatile organic compounds in the urban atmosphere of Yokohama, Japan by an automated gas chromatographic system. Atmos. Environ. **34,** 4441, **2000.**
2. DERWENT R.G., JENKIN M.E., SAUNDERS S.M., PILLING M.J., SIMMONDS P.G., PASSANT N.R., DOLLARD G.J., DUMITREAN P., KENT A. Photochemical ozone formation in north west Europe and its control. Atmos. Environ. **37**, 1983, **2003**.
3. KUMAR A., TYAGI S.K. Benzene and toluene profiles in ambient air of Delhi as determined by active sampling and GC analysis. J. Sci. Ind. Res. India. **65**, 252, **2006.**

4. World Health Organization (WHO). Air Quality Guidelines for Europe. WHO Regional Publications, European Series No. 23, Copenhagen. **1987**.
5. HUISMAN M., KOOPMAN E.C., FIDLER V., ALGRA M.H., PAAUW C.G., TUINSTRA L. G. M. TH., KUPERUS N.W., SAUER P.J.J., TOUWEN B.C.L., BOERSMA E.R. Perinatal exposure to polychlorinated biphenyls and dioxins and its effects on neonatal neurological development. Early Hum. Dev. **41**, 111, **1995**.
6. TSAI W.T. A review of environmental hazards and adsorption recovery of cleaning solvent hydro chlorofluorocarbons (HCFCs). J. Loss Prev. Process Ind. **15,** 147, **2002**.
7. BEARD J. DDT and human health. Sci. Total Environ. **355**, 78, **2005**.
8. JIMĖNEZ B., ESTRELLA R.R., MERINO R., GÓMEZ G., RIVERA L., GONZALEZ M.J., ABAD E., RIVERA J. Results and evaluation of the first study of organochlorine contaminants (PCDDs, PCDFs, PCBs and DDTs), heavy metals and metalloids in birds from Baja California, Mexico. Environ. Pollut. **133,** 139, **2005**.
9. KURYLO M.J. The chemistry of stratospheric ozone: its response to natural and anthropogenic influences. Int. J. Refrig. **13,** 62, **1990**.
10. SORKINA R.D.W. Impact of ozone layer depletion II: changes in photo dissociation rates and tropospheric composition. Atmos. Environ. **35**, 1615, **2001.**
11. GUERRA J.C., RODRRIGUEZ S., ARENCIBIA M.T., GARCIA M.D. Study on the formation and transport of ozone in relation to the air quality management and vegetation protection in Tenerif (Canary Islands). Chemosphere. **56**, 1157, **2004**.
12. CHANG S., BULLER E.M., KIMURA Y.K., YARWOOD G., NEECE J., RUSSELL M., TANAKA P., ALLEN D. Sensitivity of urban ozone formation to chlorine emission estimates. Atmos. Environ. 36, 4991, 2002.
13. WALLACE L. A. Volatile organic chemicals. In*:* Samet J, Spengler J (eds) Indoor Air Pollution: A Health Perspective Baltimore, MD: Johns Hopkins Univ. Press, **1991**.
14. WALLACE L.A. Assessing human exposure to volatile organic compounds. In: Spengler JD, Samet JM, McCarthy JF (eds) Indoor air quality handbook. Mcgraw-Hill Publication, USA, pp. 33.1-33.24, **2001.**
15. US Environmental Protection Agency, EPA (Compendium Method TO-14A). Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially prepared Canisters with Subsequent Analysis by Gas Chromatography, EPA 625/R-96/010b, Office of Research and Development, Cincinnati, OH, 45268, **1999.**
16. KELLY T.J., HOLDREN M.W. Applicability of canisters for sample storage in the determination of hazardous air pollutants. Atmos. Environ. **29** (19), 2595, **1995**.
17. ZIELINSKA B., FAUJITA E. Environmental Sampling for Trace Analysis. In: Markert, B. (Eds), Organic Gas Sampling, Federal Republic of Germany, pp. 163-184, **1994.**
18. CAMEL V., CAUDE M. Review: Trace enrichment methods for the determination of organic pollutants in ambient air. J. Chromatogr. A. **710**, 3, **1995**.
19. HEO G.S., LEE J.H., KIM, D.W., LEE, D.W. Comparison of analytical methods for ozone precursors using adsorption tube and canister. Microchem J. **70,** 275, **2001**.
20. COUTANT R.W. Theoretical evaluation of stability of volatile organic chemicals and polar volatile organic chemicals in canisters, Final Report, U.S. EPA, Contract No. 68-DO-0007, Battelle, Columbus, Ohio, **1993.**
21. OCHIAI N., TSUJI A., NAKAMURA N., DAISHIMA S., CARDIN D.B. Stabilities of 58 volatile organic compounds in fused-silica-lined and SUMMA polished canisters under various humidified conditions. J. Environ. Monit. **4**, 879, **2002.**
22. BATTERMAN S.T., ZHANG G.Z., BAUMANN M. Analysis and stability of aldehydes and terpenes in electropolished canisters. Atmos. Environ. **32** (10), 1647, **1998.**
23. PATE B., JAYANTY R.K.M., PETERSON M.R., EVANS G.F. Temporal stability of polar organic compounds in stainless steel canisters. J. Air Waste Manage. Assoc. **42** (4), 460, **1992.**
24. WU C.H., FENG C.T., LO Y.S., LIN T.Y., LO J.G. Determination of volatile organic compounds in workplace air by multisorbent adsorption/thermal desorption-GC/MS. Chemosphere. **56,** 71, **2004.**
25. HARRINGTON D. Introduction to air toxics analyses. Technical Reference, Tekmar Dohrman. **2003**. (http://www.teledynetekmar.com/documents/AIR-004.pdf.)
26. WINSLOW M.G., BOOTH M.B., ROBERTS D.F., HARLOS D.P. GC/MS measurement of 27 polar VOCs in canisters. In: Proceedings, US. EPA/A&WMA International Symposium on the Measurements of Toxic and Related Air Pollutants, Research Triangle Park, North Carolina. **1995**.
27. ZIELINSKA B, SAGEBIEL J.C., HARSHFIELD G., GERTLER A.W., PIERSON W.R. Volatile organic compounds up to C20 emitted from motor vehicles; measurement methods. Atmos Environ. **30** (12), 2269, **1996**.