CHEMICAL ENGINEERING TRANSACTIONS, Volume 15, 2008
Edited by Renato Del Rosso
 ISBN 978-88-95608-09-9

Determination of the breakthrough volume of some volatile organic compounds, produced in municipal solid waste composting facilities, in three different sorbents

A. Narros, A. Caro, M. de la Fuente, M. Piñeiro, M.I. del Peso, E. Rodríguez
Chemical and Environmental Engineering Department, Industrial Engineering School, Technical University of Madrid
José Gutiérrez Abascal, 2; 28006 Madrid , Spain

The aerobic composting process of municipal solid wastes (MSW) produces volatile organic compounds (VOC) that are emitted to the air. Some of these compounds are bad odorous compounds and also precursors of the photochemical smog formation and are normally found in a relatively low concentration in the air. Normally, before the analysis it is necessary to carry out a step of concentration. Active sampling (pumping air) through tubes containing porous polymers, such as Tenax^{TM} TA, Porapak^{TM} N and Chromosorb^{R} 106 as adsorbents is a current practice to concentrate the samples of COV. But the sample volume should be lower than the breakthrough volume (BTV) of all the compounds present in the air in order to assure its quantitative collection.
In this work, the BTV of 14 COV present in the atmosphere of a MSW treatment facility, in the three adsorbents mentioned before, were determined following the method proposed by Bertoni and Tappa in 1997. The BTV were compared, when it was possible, with the BTV data given by the Spanish standard UNE-EN ISO 16017-1, 2001

1. Introduction

The decrease of the amount of municipal solid waste (MSW) to be disposed off is a great deal for governments in developed countries. In order to work on this problem, an acceptable technique is the composting of the biodegradable fraction of the MSW. Moreover, this alternative is especially interesting in countries with extensive land spaces destined to agricultural issues, as compost could be used as soil amendment when its quality is acceptable. However, as a result of the aerobic composting process, volatile organic compounds (VOC) are produced and emitted to the air. Some of these compounds are bad odorous compounds and also precursors of the photochemical smog formation and can produce adverse effects on human health and comfort. Due to the complexity of these emissions, in terms of composition and abundance in the ambient air inside of the facilities, the measurement of VOC is currently done by versatile analytical methods (Ribes el al., 2007).
These undesirable compounds are found in relatively low concentration in the air. Therefore, before the analysis it is necessary to carry out a pre-concentration (Brown and Purnell, 1979). Adsorption is the most widely used method for the collection of trace vapors. Porous polymers, such as Tenax^{TM} TA, Porapak^{TM} N and Chromosorb^{R} 106 have been normally used as adsorbents in adsorption tube samplers, because of their different adsorption capabilities. However, to guarantee the quantitative collection of VOC the breakthrough volume (BTV) has to be determined, especially if results from active and passive sampling are going to be compared. There are many different definitions of breakthrough volume. It is usually defined as the gas volume which

passes through the sampler before a given compound begins to be eluted from the sorbent. This occurs when the concentration ratio of effluent gas to incoming gas reaches a predefined value. In this work, this parameter is defined as the volume sampled when the concentration at the sampler outlet reaches 50% of the inlet concentration (Van der Straeten et al. 1985). In this case, this value is independent from the number of theoretical plates as stated by Senum (1981) and Van der Straeten (1985).
The indirect method proposed by Bertoni and Tappa in 1997 was used for the determination of the BTV. Thermal desorption technique coupled to gas chromatography-mass spectrometry was used. A standard gaseous atmosphere was prepared in 3 L Tedlar bags. These bags had standard concentrations of the most representative VOC found in the indoor air of two composting facilities in Madrid. Sampling tubes containing Tenax, Porapak or Chromosorb as adsorbents were prepared and spiked with a fixed volume of the gaseous mixture. The amounts of analytes added to the sorbents were similar to the amounts collected in actual working conditions. Afterward, the sampler tubes were thermally desorbed at different temperatures, setting a constant flow of carrier gas but different desorption times in the thermal desorber. The tubes where desorbed ensuring that the carrier gas stream flowed in the same direction as in the sampling step. The elution profile of 14 VOC was obtained for a range of temperatures between 25 and 200ºC, and sampling volumes from 50 to 1500 mL, for the three adsorbents.
The main objective was to obtain series of plotted points in a log V_r vs. 1000/T diagram, where V_r is the volume which refers to 50% of the elution value and T is the temperature in Kelvin.
With the knowledge of the BTV for the three sorbents it will be possible to develop quantitative sampling of VOC inside the composting facilities with the purpose of measuring their concentrations in different areas and/or in different steps during the waste biodegradation. And also to obtain the uptake rates of the compounds from the data of simultaneous sampling using active and passive sampling.

2. Experimental

2.1 Chemical and materials

More than 100 VOC has been identified in the atmosphere of two MSW facilities in Madrid; in this study 14 of those were selected on the basis of their high concentration and occurrence. The list of the selected VOC is shown in Table 1.
Liquid mixtures of the VOC were prepared from Aldrich and Fluka pure chemicals, with purity > 98%.
Empty glass desorption tubes (10 cm x 6 mm OD x 3,8 mm ID), fitted with Teflon analytical caps, were purchased from Perkin Elmer.
Solid adsorbents as Tenax TA (60/80 mesh), Chromosorb 106 (60/80 mesh) and Porapak N (50/80 mesh) were obtained from Supelco.
The gaseous standards were prepared in 3 L Tedlar sampling bags obtained from Supelco.
The carrier gas for chromatography was Helium Alphagaz 1 supplied by Air Liquide.

2.2 Gaseous standards

The standard atmospheres were prepared by injection of 25 µL of a liquid mixture of known composition of the 14 VOC into a 3 L Tedlar bag. The liquid mixture was prepared by adding some amount of each component to a vial, weighing it after each addition. The composition of the VOC mixture is shown in Table 1. Gaseous standards

were prepared by fitting a 3 L Tedlar bag to a conventional gas chromatograph packed column sampling port heated to 100ºC. Pure Nitrogen (Alphagaz 1 from Air Liquide) at a rate of 100 mL/min was flowing at the same time through the injector when 25 µL of the standard mixture were injected. The concentrations of VOC in the standard atmosphere were similar to the concentrations founded in the real atmosphere of the MSW facility.

Compound	mass (g)	% Weight	Concentration (mg/µL)
Limonene	5,0644	40,3294	0,3271
Alfa-Pinene	0,2755	2,1939	0,0178
Toluene	0,3768	3,0006	0,0243
3-Hydroxi-2-Butanone	0,9079	7,2299	0,0586
Decane	0,2000	1,5927	0,0129
Octane	0,3022	2,4065	0,0195
Ethylacetate	0,6990	5,5664	0,0451
Methylacetate	0,3741	2,9791	0,0242
2-Butanone	1,0060	8,0111	0,0650
Isobuthanol	1,0933	8,7063	0,0706
3-Methylbutanol	0,4715	3,7547	0,0305
1-Butanol	0,7062	5,6237	0,0456
1-Propanol	0,5176	4,1218	0,0334
Ethyl alcohol	0,5631	4,4841	0,0364

Table 1.- Composition of VOC standard mixture

2.3 Tube preparation

Ten tubes of each sorbent were prepared as follows. One plug of glass wool was placed at one end of each glass tube. Then the tubes were filled with the same amount of each of the three adsorbents until the adsorbent bed length inside the tube was about 6 cm. The final masses inside the tubes were 236,6 ± 1,7 mg when loaded with Tenax TA; 138,3 ± 3,1 mg with Chromosorb 106 and 234,0 ± 4,4 mg with Porapak N. When the tubes were filled another plug of glass wool was placed in the other end of the tube to keep the sorbent inside. Beforehand the tubes were conditioned by thermal treatment heating them to the recommended conditioning temperature for 45 min and flowing helium trough the tubes at 100 mL/min. The conditioning temperature depends on the adsorbent and was 330ºC for Tenax TA; 250ºC for Chromosorb 106 and 180ºC for Porapak N.

2.4 Thermal desorption

Portions of 5 mL of the standard atmosphere were loaded into the tubes using a gas tight syringe. Tubes were desorbed using a Perkin Elmer TurboMatrix 650 automatic thermal desorber (ATD). The ATD was programmed to desorb, in two phases, series of ten tubes that contain the same adsorbent. In the first phase, the tubes were desorbed at the same temperature and at a fixed desorption flow rate of 50 mL/min. The desorption time was varied in each tube in order to obtain different desorption volumes in the range of 50 to 1500 mL. Once the first phase of desorption was completed, the ten tubes were all desorbed in the same conditions at the maximum recommended desorption temperature

for each adsorbent (Tenax TA 300ºC, Chromosorb 106 225ºC and Porapak N 180 ºC) with a helium flow rate of 150 mL/min during 10 min. Consecutive series of ten tubes were prepared and desorbed, varying the desorption temperature in each series in increments of 25ºC, from ambient temperature (about 25ºC) to the maximum desorption temperature of each sorbent. The desorption gas direction is essential and must be from the end of the tube where the VOC mixture was loaded to the other end. The tubes must be clearly marked and correctly positioned in the desorption sampling carrousel of the TurboMatrix. The desorbed VOC from the tubes are trapped in the cooled trap of Tenax (set at -30ºC) inside the TurboMatrix ATD then the trap is desorbed quickly heating at 40ºC/s to 330ºC. The desorbed VOC of the cold trap were analysed by GC/MS as described below. The series was prepared and analysed three times in the same conditions.

2.5 Analysis of the desorbed VOC

Analyses were carried out using a Perkin Elmer Clarus 600 gas chromatograph (GC) coupled to a Perkin Elmer Clarus 600T mass spectrometer. Samples desorbed in the ATD were injected in the GC through a capillary transfer line heated to 200ºC. A Supelco Equity-1 capillary column 60 m x 0,25 mm x 1,0 µm was used to analyse the samples. The oven temperature was initially set at 35ºC for 1 min, then heated at a rate of 15ºC/min to 260ºC and maintained at this temperature for 2 min. The carrier gas flow was set at 1 mL/min. The GC/MS interface was set at 200ºC. The EI mass spectra of the eluted VOC were obtained with an electron energy of 70 eV over a mass range of 30-300 amu. The integrated area of the major characteristic ion in the mass spectra was obtained for each compound. In Figure 1, a total ion chromatogram of the gas standard is shown. The mean retention times and the quantification ion for each compound are shown in Table 2.

Table 2.- Retention time and quantification ion of the VOC standard

Compound	RT (min)	Quantification m/z
Ethyl alcohol	6,63	45
Methyl acetate	7,55	43
1-Propanol	7,96	42
2-Butanone	8,51	43
Ethyl acetate	8,82	43
Isobutanol	9,08	43
1-Butanol	9,67	56
3-Hydroxy-2-Butanone	10,35	45
3-Methyl-1-Butanol	10,94	55
Toluene	11,82	41
Octane	12,35	43
Alfa-Pinene	14,86	93
Decane	15,46	47
Limonene	16,13	68

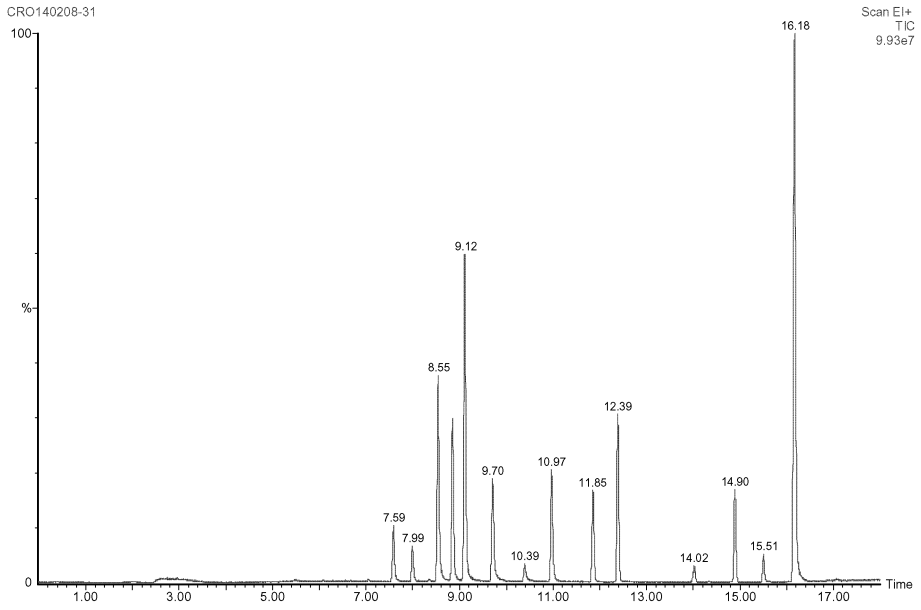

Figure 1.- Total ion chromatogram of the standard mixture

2.6 Determination of BTV

The determination of the breakthrough volume of the VOC in the three adsorbents is based on the method described by Bertoni and Tappa in 1997. In this method the percentages of each VOC eluted in the different conditions of temperature and volume of desorption are calculated as follows:

$$\%E = \frac{100 \cdot a_1}{a_1 + a_2} \qquad (1)$$

Where a_1 is the peak area of one compound eluted at one temperature and one elution volume obtained in the first phase of the elution of each tube; and a_2 is the peak area for the same compound and the same tube obtained in the second phase of the desorption of each tube. The %E data of each VOC, which is the mean of three determinations, at different temperatures are represented versus the elution volume which yields graphs like that of Figure 2.

A plot is obtained for each VOC at least at three different temperatures in every one of the three adsorbents studied. The volume that produces the 50% of the elution at each temperature is the breakthrough volume V_r. This value, according to Bertoni and Tappa 1997, is independent of the number of theoretical plates N (which depend on many parameters like the length of the packing material, carrier gas velocity, temperature, etc.). Then the log V_r is plotted against 1000/T ($^oK^{-1}$), for each compound in the three different sorbents, and a straight line is obtained like the one shown in Figure 3. The BTV at a temperature of 20ºC is obtained extrapolating these lines at 1000/293 $^oK^{-1}$.

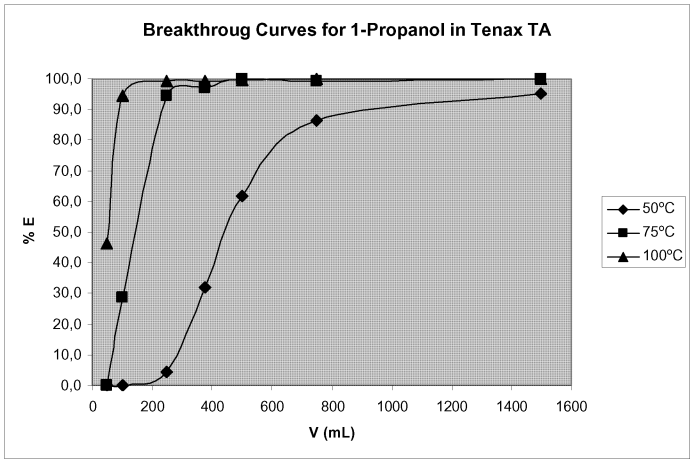

Figure 2.- Example of Breakthrough curves at different temperatures

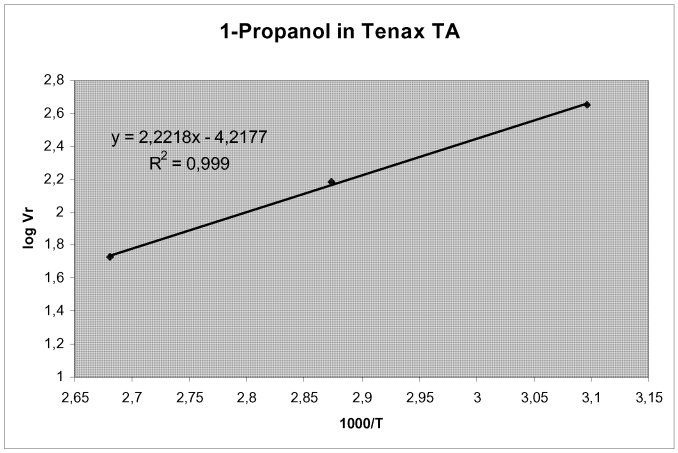

Figure 3.- Plot of log V_r vs. 1000/T for 1-Propanol in Tenax TA

3. Results and discussion

In Table 3, the results of the regression analysis of the plots of log V_r vs. 1000/T for the 14 VOC in the three sorbents are presented. In general, good correlation coefficients are obtained for all the data, only for alfa-pinene the data of the plots log V_r vs. 1000/T are not well aligned. Alfa-pinene shows a different behaviour in Tenax TA than in the other two sorbents. Tenax TA is supposed to be inert respect to sampled compounds but some studies have shown monoterpenes degradation in this adsorbent. Coeur et al., 1997, obtained poor recoveries of the monoterpenes sabinene and alfa-pinene when sampling this type of compounds using glass tubes filled with Tenax TA or Carboxen. Those authors have found that the degradation products are terpenes and aromatics compounds, which suggest rearrangement and dehydrogenation reactions that are observed with higher intensity in previously than on recently prepared Tenax tubes.

Table 3.- Regression analysis of the plots log Vr vs. 1000/T for VOC

	Tenax TA			Chromosorb 106			Porapak N		
Compound	**Slope**	**Intercept**	**R^2**	**Slope**	**Intercept**	**R^2**	**Slope**	**Intercept**	**R^2**
Ethyl alcohol	1,964	-4,229	0,9999	1,964	-3,815	0,9979	2,212	-4,054	0,9999
Methyl acetate	2,256	-4,312	0,9992	2,895	-5,924	0,9890	2,135	-3,552	0,9822
1-Propanol	2,222	-4,218	0,9990	2,849	-5,763	0,9990	1,807	-2,414	0,9916
2-Butanone	2,811	-5,603	0,9970	2,562	-4,562	0,9999	2,263	-3,524	0,9824
Ethyl acetate	2,333	-4,040	0,9993	2,937	-5,321	0,9990	2,319	-3,642	0,9756
Isobutanol	2,650	-5,003	0,9845	2,971	5,567	0,9988	2,431	-3,687	0,9850
1-Butanol	2,582	-4,850	0,9759	3,108	-5,901	0,9999	2,559	-3,894	0,9868
3-Hydroxy-2-Butanone	2,666	-4,633	0,9792	3,411	-6,217	0,9929	2,592	-3,732	0,9647
3-Methyl-1-Butanol	2,828	-5,035	0,9851	3,099	-5,277	0,9999	2,776	-4,144	0,9770
Toluene	2,867	-4,952	0,9894	2,577	-3,875	0,9999	2,432	-3,487	0,9843
Octane	3,316	-6,008	0,9853	2,816	-4,081	0,9998	3,229	-5,122	0,9998
Alfa-Pinene	1,268	-1,319	0,6177	3,219	-4,681	0,9920	3,145	-4,517	0,9999
Decane	4,209	-7,548	0,9792	4,002	-6,138	0,9999	-	-	-
Limonene	3,518	-5,757	0,9585	3,532	-5,133	0,9999	-	-	-

In Table 4, a summary of the results of this study is shown. The extrapolated V_r at 20ºC indicate the volume in litres which are necessary to elute 50% of each compound in the tubes loaded with the indicated quantities of the different sorbents. But the extrapolated V_r values can not be used as a precise sampling limit. This is due to infield variations of the sampling conditions (sampling flow rate, temperature, relative humidity, pressure,…) and also due to effects like deactivation and coadsorption (which depends on the adsorbate/adsorbent ratio). For practical use, a safety factor must be applied in order to obtain a safe sampling volume (SSV) that usually is 50% of the BTV. The SSV is defined (Brown and Purnell, 1979) as the volume of air containing a particular vapour contaminant that may be sampled over a variety of circumstances without significant breakthrough occurring on a sample tube. The SSV data obtained in this work have been calculated per gram of adsorbent in order to compare them with that of the Spanish standard (SSV-UNE) the SSV.

As can be seen in Table 4, the data obtained in this work do not fit precisely with those given in the UNE standard and the differences depend on the compound and the adsorbent considered. It is worth noting that the data of the standard have been obtained by an indirect method by injection in an adsorption tube of one component at a time, while in this work data have been obtained also by an indirect method but injecting a mixture of compounds similar to those found in real atmospheres.

By analysing the figures of Table 4, we can conclude that the data of SSV in Tenax are in better agreement with the SSV-UNE than the data for the other sorbents. In Tenax, all the SSV data are around 30% of the SSV-UNE data, except that for Toluene with a SSV which is 59% greater than the SSV-UNE. For Chromosorb 106, data for eleven of the 14 VOC can be found. The results are worst than that for Tenax TA with variation coefficients (%CV) comparing to the SSV-UNE ranging from 11 to 100%. The worst results are obtained with Porapak N, but for this adsorbent the UNE standard gives only data for sixteen compounds and only five of them are some of the VOC studied in this work. This indicates that Porapak N has been the less studied sorbent of all the three sorbents used in this work.

Table 4.- Breakthrough volumes (V_r) and safe sampling volumes (SSV) at 20ºC

Compound	Tenax TA			Chromosorb 106			Porapak N		
	V_r at 20ºC (L)	SSV (L/g)	SSV-UNE (L/g)*	V_r at 20ºC (L)	SSV (L/g)	SSV-UNE (L/g)*	V_r at 20ºC (L)	SSV (L/g)	SSV-UNE (L/g)*
Ethyl alcohol	0,3	0,6	n.d.**	0,8	2,8	5,3	3,1	6,7	7,5
Methyl acetate	2,5	5,2	n.d.	9,0	32,6	23	5,4	11,6	n.d.
1-Propanol	2,3	4,9	n.d.	9,1	33,0	27	5,7	12,1	40
2-Butanone	9,8	20,7	16	15,1	54,7	35	15,8	33,8	95
Ethyl acetate	11,0	23,2	18	37,2	134,6	67	18,7	40,0	n.d
Isobutanol	9,2	19,4	14	50,8	183,5	100	40,6	86,8	14
1-Butanol	8,4	17,7	25	50,4	182,3	230	69,3	148,2	25
3-Hydroxy-2-Butanone	27,8	58,7	n.d.	266,0	961,8	n.d.	130,5	278,8	n.d.
3-Methyl-1-Butanol	41,4	87,4	n.d.	200,0	723,1	n.d.	214,0	457,2	n.d.
Toluene	68,0	143,6	90	83,1	300,6	270	65,2	139,3	n.d.
Octane	203,9	430,9	390	337,9	1221,8	3300	790,8	1689,8	n.d
Alfa-Pinene	1,0	2,1	n.d.	2019,7	7301,9	11000	1643,8	3512,4	n.d.
Decane	6542,8	13825,6	10000	33280,9	120321,4	100000	-	-	n.d.
Limonene	1777,1	3755,1	n.d.	8359,2	30221,3	n.d.	-	-	n.d.

* Data obtained from the Spanish standard UNE-EN ISO 16017-1

**n.d.: no data in the standard UNE-EN ISO 16017-1

4. Conclusions

In this work the indirect method proposed by Bertoni and Tappa in 1997 has been applied for the determination of the breakthrough volume (BTV) of fourteen volatile organic compounds in three different adsorbents. The method is very simple and can be used to obtain simultaneously the BTV of several compounds of a mixture. This can be the reason of the great differences obseved bettween the measured SSV and the data given in the UNE-EN standard. To be an alternative to the classic methods for the BTV determination more work will have to be done in order to evaluate the factors affecting its accuracy.

Acknowledgment: We would like to thank the company URBASER SA, leader of the OTERSU project, and to the Center for the Development of Industrial Technology (CDTI) for its financial support through the CENIT program without which this work would have not been possible.

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