Background Odors in Tedlar® Bags Used for CAFO Odor Sampling

David B. Parker, Ph.D., P.E., Associate Professor

West Texas A&M University, Canyon, Texas 79016   dparker@mail.wtamu.edu

Marty B. Rhoades, Research Associate

West Texas A&M University, Canyon, Texas 79016   mrhoades@mail.wtamu.edu

Jacek Koziel, Ph.D., Assistant Professor

Texas A&M Research and Ext. Center, Amarillo, TX 79106   ja-koziel@tamu.edu

Jarett Spinhirne, Research Associate

Texas A&M Research and Ext. Center, Amarillo, TX 79106   j-spinhirne@tamu.edu

Abstract*. Tedlar® film is manufactured in a wet solvent process and continues to emit organic compounds after manufacturing. Tedlar® bags are used for odor sampling at concentrated animal feeding operations (CAFOs). Odor regulations for CAFOs vary widely, but maximum detection thresholds (DTs) of 2 to 15 have been proposed downwind of feeding operations. Results at the WTAMU Olfactometry Laboratory have shown that both commercially available Tedlar® bags and homemade Tedlar® bags have a detectable background odor (DTs of 20 to 60 typical) even following standard protocols for purging. Purging the bags before sampling was not effective in reducing DTs to acceptable levels, as verified with SPME analysis. Conditioning the Tedlar® bags by heating for 24 hrs at 100°C, when combined with purging immediately after heating and again prior to odor sampling, reduced background DTs to 10-14. This is an acceptable range for odor sampling at open lot beef cattle feedyards or any other locations where DTs are expected to be greater than this range.*

Keywords. Odor, CAFO, sampling, Tedlar®, feedyard, cattle, SPME

Introduction

Olfactometry is a standard method for assessing odors at concentrated animal feeding operations (CAFOs) (Chen et al., 1997; Clanton et al., 1999; Dravnieks et al., 1978). Odor samples are collected in 'plastic' bags constructed of Teflon®, Tedlar®, or polyethylene. Tedlar® is currently the most widely used sample bag because of its relatively low cost and relative non-reactive qualities. Odor samples are collected using a vacuum chamber so that the odor sample does not come into contact with internal pumps. The odor samples are then presented to a group of human panelists to determine the detection threshold, recognition threshold, intensity, hedonic tone, and any other odor characteristics.

There are many manufacturers and suppliers of Tedlar® bags. Tedlar® polyvinyl fluoride film (PVF) is manufactured by DuPont[TM] (DuPont, 2003a,b). The Tedlar® film is manufactured in a wet solvent process using PVF powder as the raw material. Because it is not possible to simply heat the PVF powder to melt it, the powder is dissolved in a latent solvent at temperatures above 100°C, and the PVF particles coalesce to form a thin film as the solvent evaporates (USCAR, 2003). While there are several latent solvents used to manufacture Tedlar® film, one of the most common is N,N-dimethylacetamide (USCAR, 2003). The film undergoes an elongation process where the film is rolled and stretched as it dries. The film is subjected to temperatures of 100-180°C to enhance the drying process. The DuPont[TM] patent states that the finished film has less than 0.5% solvent by weight, though the exact amount of solvent is typically unknown and unspecified (USCAR, 2003). Because the Tedlar® is manufactured in a wet solvent process, it is logical that it continues to emit organic compounds for some time after drying. Tedlar® gas sampling bags are manufactured by heat-sealing the edges (DuPont, 2003c).

Scientists have recognized for some time that Tedlar® is not the perfect material for gas sampling bags. Though it is relatively inert, there is evidence of adsorption and desorption of some odorous chemical species to the Tedlar® (McGarvey and Shorten, 2000; van Harreveld, 2003). Keener et al. (2002) quantified odorants in Tedlar® bags using sorbent tubes, and concluded that Tedlar® bags emit acetic acid and phenol and greatly adsorb indole and skatole, thereby having the potential to bias olfactometry analyses. However, because a better material for gas and odor sampling has not been proposed, the use of Tedlar® bags will probably continue to be the material of choice for gas sampling bags.

A Tedlar® bag is generally considered odorless if no threshold can be measured, or when the highest DT measured in an odor sample is at least a factor 2^5 (32) lower than the sample to be measured (CEN, 1997). For example, if a Tedlar® bag has a background DT of 64, then this would be acceptable for odor samples with DTs greater than 2048. For odor samples with large DTs (i.e. strong odor), such as might be found within a swine barn or immediately downwind of an anaerobic lagoon, a small background bag odor is acceptable. However, when trying to characterize odor samples with small DTs (i.e. 8 to 64), any detectable bag odor can lead to problems in distinguishing true odor versus bag odor. This is the case for odor characterization at many open-lot beef cattle feedyards, where median downwind DTs of 22 to 45 are typical (Parker et al., 2003).

Research was conducted to evaluate background odor in Tedlar® bags using triangular forced-choice olfactometry and solid phase microextraction (SPME). The objectives of the research were to 1) quantify background odor DTs in typical Tedlar® gas sampling bags, 2) determine how purging and sample storage time affect DTs, and 3) determine if conditioning the bags by heating would reduce background DTs.

Materials and Methods

Commercially available Tedlar® bags manufactured by Environmental Sampling Supply (ESS, Oakland, CA) were obtained from St. Croix Sensory (Lake Elmo, MN). Commercially available bags manufactured by SKC (SKC Gulf Coast, Houston, TX) were also purchased. In addition, homemade bags were constructed using Dupont™ TST20SG4 transparent film. This type of Tedlar®film was recommended by DuPont™ for the construction of gas sampling bags (Dupont, 2003c). The Tedlar® film was ordered directly from DuPont™ in 33 cm wide rolls of length 762 m. The film was cut into lengths of 92 cm for an approximate capacity of 10 L. The film was folded lengthwise, then heat sealed on the three edges using a Vertrod Model 14OB open back heat sealer with 0.63 cm seal width and 51 cm maximum seal length (Therm-O-Seal, Mansfield, TX). A polypropylene valve was installed in one end of the bag prior to making the last seal.

Tedlar® bags were subjected to a variety of treatments. Treatments included the following:

- No heating
- Heating at 100°C for 4 hrs
- Heating at 100°C for 24 hrs
- No purging
- Purge after heating only
- Purge at time of sampling only
- Purge after heating and at time of sampling

Bags were heated in a standard drying oven (VWR Model 1325). No other types of samples were allowed in the oven during the heating process. Whenever purging was required, purge air consisted of bottled ultra pure odor free air (MG Industries, Malvern, PA).

Triangular Forced Choice Olfactometry

Odor samples were analyzed by dynamic triangular forced-choice olfactometry at the West Texas A&M University (WTAMU) odor laboratory following the general guidelines of ASTM (1991). The olfactometer was an AC'SCENT International olfactometer (St. Croix Sensory, Lake Elmo, MN). The olfactometer is basically a dilution meter that precisely mixes the odorous air sample with various dilutions of clean odor-free air. The method consists of presenting a series of dilutions of the odorous sample and odor-free air, starting very dilute (low odor) and gradually increasing the amount of odorous air until the odor could just be detected when compared to two other blanks of odor-free air. The dilutions were halved, resulting in less dilution and stronger odor, until the panelist could just detect that one of the three presentations was different than the other two.

Using this procedure, panelists were presented with three (i.e. triangular) presentations, but only one of them actually had odorous air in the dilution. The other two were blanks of 100% odor-free air. The panelist was required to indicate which of the three samples was different than the other two. If the panelist could not discern a difference, they were required to make a guess (i.e. forced-choice). Dilutions were decreased (concentrations increased) until the panelist had two consecutive correct detections.

A typical panel consisted of 4 to 8 trained odor panelists. Panelists were screened to remove hypernosmic (overly sensitive) or anosmic (non-sensitive) individuals.

GC-MS Method

A GC-MS method was developed for this study on a Varian 3800 GC coupled to a Saturn 2000 ion trap MS (Varian Analytical Instruments, Walnut Creek, CA). The SPME fibers with their extracted compounds were first desorbed for 7 min in the injector (250°C isothermal) and then separated on a 30 m by 0.25 mm by 0.25 µm film ZB-Wax capillary column (Phenomenex, Torrance, CA). An electronic flow controller maintained the 99.9995% pure helium carrier gas (Air Gas, Amarillo, TX) at a constant flow of 1 ml/min throughout the run. The injector was equipped with a 0.8 mm diameter liner and a 11.5 mm LB-2 Thermogreen septum (Supelco, Bellefonte, PA). The initial column oven temperature was 60°C followed by an initial ramp of 60°C/min to 110°C, a second ramp of 10°C/min to 210°C, and finally a third ramp of 60°C/min to 250°C with a final hold time of 6 min.

Compounds were detected between 35 to 200 m/z (ion mass/charge ratio) with a Saturn 2000 MS. The transfer line, manifold, and trap were set at 200, 40, and 150°C respectively. The electron multiplier voltage was set to 1340 eV. The electron ionisation emission current was 10 µA. Analytes were initially identified with the National Institute of Standards and Technology (NIST) MS spectral library. Compounds in field samples were identified with a Saturn user library created with the spectra of pure compounds collected by 'sniffing' their vapours with SPME. These samples were generated by exposing SPME fibers to the headspace of pure compounds for approximately 0.5 s followed by analysis with the same GC-MS program.

SPME Sampling and Analysis

Four Tedlar® bags (10L) were purchased (SKC Gulf Coast, Houston, TX) and were used in 4 treatment groups. Bag 1 was filled with UHP nitrogen to 75% of its volume and was held for 10 min before sampling with SPME. Bag 2 was filled with UHP nitrogen to 75% of its volume and was held for 24 h before sampling with SPME. Bag 3 was filled to 75% of its volume, purged, filled again, and held for 10 min before sampling with SPME. Bag 4 was filled to 75% of its volume, purged, filled again, and held for 24 h before sampling with SPME.

A DVB/Carboxen/PDMS 50/30 µm SPME fiber was inserted into the Tedlar® bags through the sampling septum in the valve of the bag for a sampling time of 30 min. Contaminants inside the Tedlar® bags readily concentrated on the SPME fiber coating and then were introduced, via the injector, into the GC-MS for separation and analysis. Compounds were compared with the in-house Saturn user library and were reported only if they had matches 700 or above on a scale of 1-1000. A fifth SPME extraction was taken from the UHP nitrogen source to verify the purity of the gas.

Data Analysis

Panel detection thresholds were calculated following guidelines in ASTM (1991). Individual panelist detection thresholds (IDT) were calculated as the geometric mean of the concentration at which the last incorrect guess occurred and the next higher concentration which was correctly detected. The panel detection threshold (PDT) was calculated as the geometric mean of the IDTs.

Results and Discussion

Precision and Bias

Because odor DTs are a function of individual panelist sensitivities, *odor panel session results cannot be interpreted statistically in the usual way* (ASTM, 1991). There are several reasons for this, but the most obvious have to do with large variability and limited replications. Day to day variation in odor panel results can be divided into individual panelist variation and whole panelist variation. Individual panelist variation relates to how panelist sensitivity varies from day to day. We have noted that many panelists are especially sensitive to rapid changes in outside climatic conditions, and their sensitivity usually drops for a few days whenever the weather changes. Whole panelist variation is a function of individual panelist variation and varies day to day because the members of the panel can change from day to day. Replications are a serious consideration when working with odor panel data. Only six to eight samples can be analyzed during a single odor session, which usually lasts for 3-4 hours. When multiple quality assurance samples (blank and n-butanol) are included, the number of samples that can be analyzed is reduced further. Panelist sensitivity drops noticeably after 3-4 hours, therefore analysis of several replications of more than 2 or 3 treatments within a single odor session is not possible. To reduce variability and improve confidence in any conclusions, comparisons made on the same day and with the same odor panelists are of greater quality than comparisons made on different days. For this reason, in this paper the results for each odor session are considered individual experiments and interday comparisons for treatment effects are avoided.

Typical Background Odors in Tedlar® Bags

Background DTs in Tedlar® bags varied from day to day. DTs increased as the holding time increased, evidently because more solvent was released into the air sample within the bag. Background DTs in nonheated bags, purged at the time of sampling, with 24 hr holding times typically ranged from about 20 to 60 (Tables 1-3). DTs with holding times on the order of 10 minutes were typically less than 16 (Table 1).

Effect of Heating on Release of Solvent

To evaluate how heating affects the release of the solvent in the Tedlar®, two bags were filled with 5 L of odorless air and placed in the oven at 100°C. One bag was heated for 4 hrs, the other for 24 hrs, and the bags were presented to the panel without any purging. The samples were analyzed on different days. The bag heated for 4 hrs had a panel detection threshold (PDT) of 200, while the bag heated for 24 hrs had a PDT of 152 (Table 4). Though there was relatively little difference between the 4 and 24 hr heating times for these two samples, it was obvious that heating of the bags increased the concentration of volatiles in the bag and aided in releasing the solvent.

Effect of Purging and Holding Time

Purging of nonheated bags decreased DTs by about 2 times (Table 1). Purging reduced the DTs in heated bags by 5 to 7 times (Tables 2, 5). Purging the bags was more important on bags that had been heated, as the heat released the solvent and trapped it within the bag.

Increasing the holding time from 10 minutes to 24 hours increased the DT by 3 to 10 times (Table 1). Increasing the holding time from 8 to 72 hours only increased the DT by 1.3 to 1.7 times (Table 5), while increasing the holding time from 24 to 72 hours was negligible (Table 6).

Effect of Heating on Reduction of Background Odor

Heating for 4 hrs when combined with purging resulted in minimal difference in the DT (Tables 2, 3). DTs of 16 to 34 were still observed even after heating for 4 hrs. Heating for 24 hrs combined with purging at the time of sampling produced DTs of less than 19 (Tables 3, 5). When bags were heated for 24 hrs, purged immediately after heating and again at sampling time, DTs of less than 14 were observed (Table 6).

Heating the Tedlar® bags for 24 hrs, combined with purging after heating and again prior to odor sampling, reduced background DTs to less than 14. This is an acceptable range for odor sampling at open lot beef cattle feedyards.

SPME Results

Volatile organic compounds have been detected in air using SPME (Koziel and Pawliszyn, 2001; Koziel et al., 2001; Spinhirne et al., 2002). Many (15) VOCs, many odorous, were detected in new Tedlar® bags. Bags purged once had fewer detected number of contaminants than their non-purged counterparts, supporting the idea that purging the bags before filling them with sample will dispose of interferences. However, acetic acid and phenol were persistent and were easily extracted in quantities that eclipsed that of other contaminants even when purging was used (Figures 1&2). The number of contaminants and their corresponding area counts (related to mass extracted) increased in samples held for 24 hrs, a reasonable time interval before samples are analyzed by olfactometry or other methods for the measurement of odors (Tables 7 and 8). Mass loading over time may negatively affect the usable shelf-life of samples stored in Tedlar® bags.

Sampling with SPME was a very good qualitative measure of the effectiveness of the common practice of purging Tedlar® bags before collecting odor samples. Purging of bags did lower the amount of contamination for samples stored for only a short time. However, acetic acid and phenol extracted on SPME were not affected by purging. A long sampling time of 30 min may allow competitive adsorption of acetic acid and phenol on the SPME fiber. A short sampling time or alternative preconcentration method i.e. desorption tubes, could be used to avoid competitive adsorption and are currently being tested in our laboratory.

Conclusions

The following conclusions were drawn from this research:

1. Background odors in Tedlar® bags, as measured by detection threshold (DT) using triangular forced-choice olfactometry, have a typical range of about 20 to 60.

2. DTs increased by 3 to 10 times during the first 24 hrs of holding time, as did many VOCs as verified by SPME. Increases after the first 24 hrs were minimal. Purging of nonheated bags decreased the DT by about 2 times, however, acetic acid and phenol extracted by SPME were not affected by purging. Purging of heated bags decreased the DT by 5 to 7 times. Purging was more important in heated bags, as heating released the solvent and trapped it within the bag.

3. Heating the Tedlar® bags for 24 hrs, when combined with purging immediately after heating and again prior to odor sampling, reduced background DTs to 10-14. This is an acceptable range for odor sampling at open lot beef cattle feedyards or any other locations where DTs are expected to be greater than this range.

Table 1. Panel detection thresholds for homemade bags at 0.2 and 24 hr holding times. Bags were subjected to no heating. These samples were analyzed on the same day by the same panelists.

Heat Time (hrs)	0	0	0	0
No. of Purges after Heating	0	0	0	0
No. of Purges at Sampling Time	0	0	1	1
Holding time (hrs)	0.2	24	0.2	24
Panel DT	7	76	16	38

Table 2. Panel detection thresholds for homemade bags subjected to 0 and 4 hr heating, with and without purging. These samples were analyzed on the same day by the same panelists.

Heat Time (hrs)	0	4	0	4
No. of Purges after Heating	0	0	0	0
No. of Purges at Sampling Time	0	0	1	1
Holding time (hrs)	24	24	24	24
Panel DT	61	244	21	34

Table 3. Panel detection thresholds for ESS bags subjected to different heat times. All samples were analyzed on the same day by the same panelists except for the nonheated bags.

Heat Time (hrs)	0	0	4	4	8	24	30
No. of Purges after Heating	0	0	0	0	0	0	0
No. of Purges at Sampling Time	1	1	1	1	1	1	1
Holding time (hrs)	0.2	24	24	24	24	24	24
Panel DT	11*	52**	16	20	8	13	6
* Median of 35 bags analyzed over a 5-month period. **Median of 20 bags analyzed over a 5-month period.							

Table 4. Panel detection thresholds for homemade bags. Bags were filled with 5 L odorless air and heated full of air with no purging after heating. These samples were analyzed on different days.

Heat time (hrs)	4	24
No. of Purges after Heating	0	0
No. of Purges at Sampling Time	0	0
Holding time (hrs)	4	24
Panel DT	200	152

Table 5. Panel detection thresholds for homemade bags. Bags were filled with small amount of odorless air (0.5 L) prior to heating. These samples were analyzed on the same day by the same panelists.

Heat Time (hrs)	24	24	24	24
No. of Purges after Heating	**	**	**	**
No. of Purges at Sampling Time	0	0	1	1
Holding time (hrs)	8	72	8	72
Panel DT	67	90	11	19
** Bags were not filled and purged completely as would normally be done, instead the 0.5 L of air that was in the bags was pressed out by collapsing the bag by force.				

Table 6. Panel detection thresholds for homemade bags subjected to 24 hr heating time. Bags were filled with small amount of odorless air (0.5 L) prior to heating. These samples were analyzed on the same day by the same panelists.

Heat time (hrs)	24	24	24
No. of Purges after Heating	1	1	1
No. of Purges at Sampling Time	1	1	1
Holding time (hrs)	24	48	72
Panel DT	10	14	10

Table 7. List of VOCs and corresponding area counts found in 30 min SPME samples from UHP nitrogen held in new Tedlar® bags for 10 min. Bag 3 was purged once prior to filling with nitrogen, while bag 1 was not.

Peak Number*	VOC	Retention Time (minutes)	Area Counts (No Purge, Bag 1)	Area Counts (Purged, Bag 3)
1	Acetone	1.632	13,322	nd
2	Acetic acid	3.768	14,223,779	14,553,165
3	Phenol	8.862	3,799,824	4,505,181
* Numbers correspond with peak number in figure 1.				

Table 8. List of VOCs and corresponding area counts found in 30 min SPME samples from UHP nitrogen held in new Tedlar® bags for 24 hrs. Bag 4 was purged once prior to filling with nitrogen, while bag 2 was not.

| Peak Number*	VOC	Retention Time (min)	Area Counts (No Purge, Bag 2)	Area Counts (Purged, Bag 4)
1	Acetone	1.627	22,713	13,988
2	Acetaldehyde	1.742	6,484	nd
3	Decane	1.891	11,365	nd
4	Octane	1.965	10,915	nd
5	Toluene	2.045	9,777	nd
6	2,3-Butadione	2.144	15,481	nd
7	Ethylbenzene	2.368	14,905	nd
8	Nonane	2.486	6,822	nd
9	Isoprene	2.566	3,471	nd
10	Tridecane	2.888	10,129	nd
11	Dodecane	2.922	4,223	nd
12	Tetradecane	3.473	8,021	nd
13	Acetic acid	3.755	23,777,408	23,094,724
14	Pentadecane	4.155	8,709	nd
15	Phenol	8.851	6,010,021	5,997,447
* Numbers correspond with peak number in figure 2.				
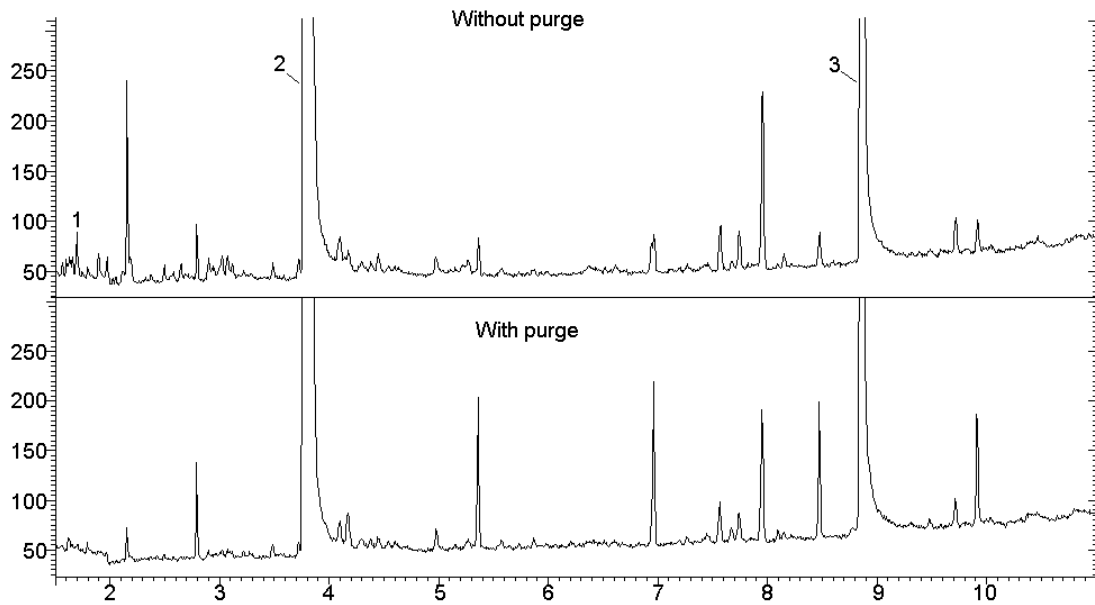
Figure 1. Chromatogram of SPME samples from UHP nitrogen held in Tedlar® bags for 10 min. Numbers correspond with peak number in Table 7.
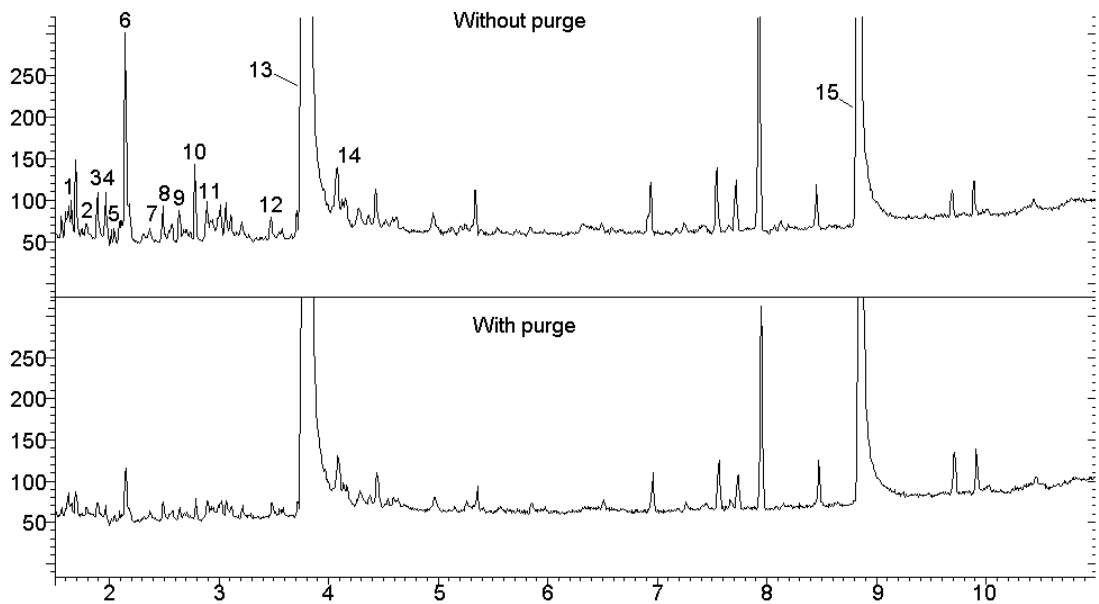

Figure 2. Chromatogram of SPME samples from UHP nitrogen held in Tedlar® bags for 24 hr. Numbers correspond with peak number in Table 8.

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