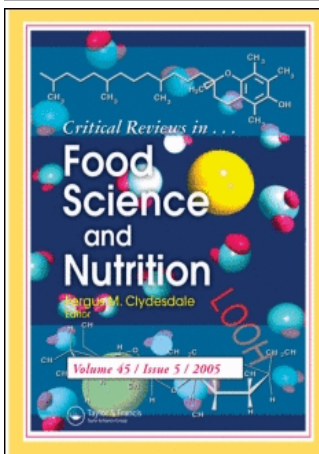


On: 8 November 2007  
Access Details: Free Access  
Publisher: Taylor & Francis  
Informa Ltd Registered in England and Wales Registered Number: 1072954  
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Critical Reviews in Food Science and Nutrition

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title-content=t713606380>

### Emissions from Cooking Microwave Popcorn

Jacky A. Rosati<sup>a</sup>; Kenneth A. Krebs<sup>a</sup>; Xiaoyu Liu<sup>ab</sup>

<sup>a</sup> U.S. Environmental Protection Agency, National Risk Management Research Laboratory, RTP, NC

<sup>b</sup> Arcadis G & M, RTP, NC

Online Publication Date: 01 November 2007

To cite this Article: Rosati, Jacky A., Krebs, Kenneth A. and Liu, Xiaoyu (2007) 'Emissions from Cooking Microwave Popcorn', *Critical Reviews in Food Science and Nutrition*, 47:8, 701 - 709

To link to this article: DOI: 10.1080/10408390701638951

URL: <http://dx.doi.org/10.1080/10408390701638951>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article maybe used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Emissions from Cooking Microwave Popcorn

JACKY A. ROSATI and KENNETH A. KREBS

U.S. Environmental Protection Agency, National Risk Management Research Laboratory, RTP, NC 27711

XIAOYU LIU

U.S. Environmental Protection Agency, National Risk Management Research Laboratory, RTP, NC 27711; Arcadis G & M, RTP, NC 27711

*This study characterized chemicals released into a chamber in the process of cooking microwave popcorn. Seventeen types of microwave popcorn from eight different brands were studied. The work proceeded in two phases: phase one investigated chemicals emitted during popping and opening, phase two investigated chemicals emitted at discrete intervals from 0–40 minutes post-pop opening. The research was performed using a microwave oven enclosed in a chamber with ports for air sampling of particulate matter (PM) and volatile organic compounds (VOCs). VOCs in the air samples were identified and quantified using gas chromatography/mass spectrometry (GC/MS). PM was characterized using both an aerodynamic particle sizer (APS) and a scanning mobility particle sizer (SMPS) to cover a full range of emitted sizes. The compounds measured during popping and opening included butter flavoring components such as diacetyl, butyric acid, acetoin, propylene glycol, 2-nonanone, and triacetin and bag components such as p-xylene and perfluorinated alcohol 8:2 telomer. The greatest chemical quantity is emitted when the bag is opened post-popping; more than 80% of the total chemical emissions occur at this time.*

**Keywords** air sampling, diacetyl, perfluorinated compounds, volatiles

## INTRODUCTION

This study identified and quantified chemical emissions released in the process of popping and opening a bag of microwave popcorn. Microwave popcorn, a product that is used extensively worldwide and in a large number of households and businesses in America, is thought to have a detrimental effect on lung health in the manufacturing industry (Kreiss et al., 2002; Kullman et al., 2005). This research was initiated in response to an occupational incident in 2000 in which eight workers at a microwave popcorn production plant in Missouri were diagnosed with the severe lung disease, bronchiolitis obliterans (Kreiss et al., 2002; Kullman et al., 2005). These plant workers were exposed to not only the raw corn and salt used in microwave popcorn production, but the oil, flavorings, and the microwaveable packagings (Kreiss et al., 2002; Kullman et al., 2005). The National Institute for Occupational Safety and Health (NIOSH) identified more than 100 volatile organic compounds inside of the Missouri plant

(Kullman et al., 2005). Quality control (QC) personnel, who pop corn and open bags, had a high incidence of respiratory and dermal symptoms (Kanwal et al., 2006; Kreiss et al., 2002). NIOSH scientists confirm that workers in the QC areas have shown an increased risk of lung disease (Kanwal et al., 2006). This prompted EPA's interest in what is released into the immediate environment when microwaving popcorn, and its potential to impact indoor air quality.

Seventeen types of microwave popcorn from eight different brands were studied. Data on volatile chemicals produced from microwave popcorn packaging during cooking were documented previously in 1993 (McNeal and Hollifield, 1993; Risch, 1993), but some manufacturers have changed their bag formulations. Limited data were available on the indoor concentrations of particulate matter less than 10 microns in diameter (PM<sub>10</sub>) and particulate matter less than 2.5 microns in diameter (PM<sub>2.5</sub>) released during the popping of a single type of microwave popcorn (Fortmann et al., 2001). No data on particulate matter (PM), characterization, flavoring, or corn emissions during the cooking of microwave popcorn, was found in the literature. Thus, this is the first study to take a comprehensive look at chemicals released while microwaving an entire conventional microwave popcorn product.

This article not subject to United States copyright law.

Address correspondence to Jacky A. Rosati, Ph.D., U.S. Environmental Protection Agency, E343-06, 109 TW Alexander Drive, RTP, NC 27711. Tel: (919)541-9429; Fax: (919)541-0496; E-mail: rosati.jacky@epa.gov

## EXPERIMENTAL METHODS

### Popcorn Selection

Microwave popcorn used in this study was selected based on market share information from manufacturer's websites and availability in local retail outlets. Preference was given to those brands with a larger market share (General Mills, 2003; MarketResearch.com, 2001) but allowances were made to get a diversity of popular styles and flavorings. Tested popcorn was obtained from multiple batches. Batches were distinguished by comparing codes available on the boxes. Popcorn flavors tested included butter, light butter, and kettle corn (butter, salty and sweet), with numerous other "specialty flavors" falling into one of these three categories. Seventeen types of microwave popcorn from eight different brands were tested, with at least three batches of each type used to ensure consistency within a popcorn type. In addition, one brand of air popped corn from two different batches was tested to compare to the microwave popcorn. As this air popped corn contained no flavorings, salt, or additives, it was used as a control for microwave popcorn chemical emissions. The only possible contaminant for this corn would be its plastic packaging. Chemical emissions from the air popper itself would have been noted in background samples.

### Project Design

This work proceeded in two phases. Phase I involved the sampling, the identification, and the rough quantification of all compounds emitted while popping and opening popcorn. Seventy-seven experiments including 12 re-tests were conducted during phase I. Phase II involved the sampling, the identification, and the quantification of specific compounds (listed in bold italics in Table 1) at background, popping, and the opening of the popcorn, as well as at 10, 20, 30, and 40 minutes post-bag opening. Twenty-nine experiments including one re-test were conducted during phase II. Popcorns were assigned a number and a random number generator was used to determine the order in which the corns were tested. This random approach was used to avoid potential bias due to testing order.

### Phase I Air Sampling

A microwave oven (Magic Chef, Model DM15K-7S, 1100W) or hot air popper (West Bend Poppery II) was placed in the center of a stainless steel chamber (515 L). This chamber had a plexiglass glove box entry to ensure a sealed system and allowed the monitoring and/or control of the air flow (rate, temperature, humidity) during the popping process (Fig. 1). Once the chamber was sealed, the glove entry was used for all popcorn manipulations i.e. starting the microwave, opening the microwave, and opening the bag. Nitrile gloves were worn to ensure minimal VOC emissions into the chamber. Any VOC emissions from

these gloves were determined by background air samples. The inlet air flow was dried and filtered with charcoal to remove outside contaminants and mass flow controllers (Dwyer; Michigan City, IN) provided 2.3 clean air exchanges per hour (20 Lpm). A small fan mounted at the center of the chamber ceiling ensured even mixing in the chamber. A glass multi-sampling port was placed on the side of the chamber opposite the entering chamber flow. Air samples were taken from this port during the popping and the opening of microwave popcorn and during the popping of air popped corn. Specifically, a vacuum pump (GAST, Model DAA-V175-EB, Benton Harbor, MI) was used to draw chamber air through Perkin-Elmer stainless steel tubes packed with 200 mg Tenax TA 60–80 mesh at a flow of 150 cc/min, as regulated by mass flow controllers.

Five-minute background samples, drawn at 150 cc/min were taken from the sampling port. Once the background samples were complete, the popcorn bag was weighed and placed inside the microwave. The microwave and the chamber doors were closed and sealed. The popcorn was popped on high for 135 to 150 seconds, with sampling occurring for 120 seconds of the popping time. The popping time varied to ensure a sufficient amount of the corn popped. If the popped volume and the number of kernels popped were insufficient to meet QC standards, a longer popping time was used for the replacement run. Two minutes after the completion of the sampling during popping, the microwave door was opened. Using the glove box feature of the chamber, the bag was removed from the oven and opened inside the sealed chamber. Once the bag was opened, sampling began again for 120 seconds. Once this sampling was complete, the bag was removed from the chamber and was re-weighed, along with the outer package. The unpopped kernels were also counted and weighed to ensure sufficient popping. No more than three runs were performed each day since dry, filtered house air was used to purge the chamber at 20 Lpm for at least two hours prior to conducting additional testing.

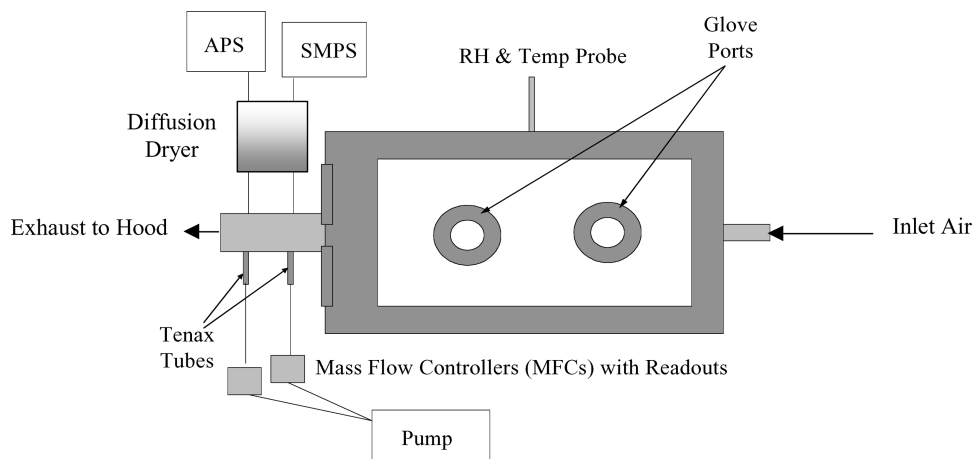
For hot air popping, sufficient kernel popcorn was used to achieve a pop volume equivalent to the microwave popcorn products tested (approximately 1.8–2.0 liters volume). This amount was determined empirically to be ~50 grams. The kernels were placed in the hot air popper and popped until all kernels were out of the popper, with the sampling (as described above) occurring during popping. The air popped corn was removed from the chamber post-pop. Again, dry, filtered air was used to purge the chamber at 20 Lpm for at least two hours prior to conducting additional testing.

Air from the test chamber was sampled using the EPA Method TO-17 (EPA, 1999). Preliminary tests indicated Tenax to be an acceptable sorbent for the types of emitted VOCs; the suitability of Tenax to collect the perfluorinated alcohol telomers was inferred from its suitability to collect the analogous n-alkyl alcohols (Manura, 1999). Calibrated mass flow controllers ensured that a constant flow was drawn through the Tenax tubes. Replicates were taken for every tenth sample. Once the sampling was complete, the tubes were capped and marked with the date, the time, the flow, the sampling time, and the sample

**Table 1** Emitted volatile organic compounds grouped by average concentration across all microwave popcorns during popping and opening—measured while flow was exiting chamber. The GC/MS was calibrated for the ten compounds in *bold italics*

Compound & average concentration in chamber	Other names	CAS number	Concentration range in chamber ng/cc	Min detection limit for GC/MS ng/cc
<b>&gt;1.0 (ng/cc)</b>				
<i>butyric acid</i>	butanoic acid	107-92-6	0.1–8.6	0.027
<b>0.5–1.0 (ng/cc)</b>				
<i>diacetyl</i>	2,3-butanedione	431-03-8	0.02–5.8	0.023
acetoin	3-hydroxy-2-butanone	513-86-0	0.01–4.2	
<b>0.20 – 0.49 (ng/cc)</b>				
propylene glycol	1,2-propanediol	57-55-6	0.005–1.3	
2-nonanone*	methyl heptyl ketone	821-55-6	0.005–1.4	
<i>triacetin</i>	glycerol triacetate	102-76-1	0.01–1.2	0.0073
<b>0.1–0.19 (ng/cc)</b>				
acetic acid		64-19-7	0.005–0.5	
2-butoxy-1-methyl-2-oxoethyl ester	butyl butyryl lactate	7492-70-8	0.005–0.7	
butanoic acid*				
<b>&lt;0.1 (ng/cc)</b>				
<i>p-xylene</i>	1,4-dimethylbenzene	106-42-3	0.01–0.4	0.011
pentanal	n-valeric aldehyde	110-62-3	0.01–0.02	
toluene	methyl benzene	108-88-3	0.01–0.04	
hexanal	caproaldehyde	66-25-1	0.01–0.05	
2-methyl propanoic acid*	methacrylic acid	79-41-4	0.01–0.27	
<i>2-octanone</i>	n-hexyl methyl ketone	111-13-7	0.01–1.28	0.013
heptanal*	enanthal	111-71-7	0.01–0.02	
benzaldehyde	benzoic aldehyde	100-52-7	0.01–0.02	
2-(2-hydroxypropoxy) 1-propanol	dipropylene glycol	106-62-7	0.01–0.5	
acetophenone	methyl phenyl ketone	98-86-2	0.015–0.01	
3-isopropyl-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethyl)tetrasiloxane*		General Group of Siloxanes	0.01–0.03	
2-tridecanone*	methyl undecylketone	593-08-8	0.01–0.16	
3-methyl butanal*	isovaleraldehyde	590-86-3	0.01–0.01	
2-methyl butanal	methyl butyraldehyde	96-17-3	0.01–0.03	
<i>furfural</i>	2-furaldehyde	98-01-1	0.01–0.37	0.011
4-methyl-3-penten-2-one	mesityl oxide	141-79-7	0.01–1.20	
2-pentyl furan	2-amylfuran	3777-69-3	0.01–0.01	
2-(2-ethoxyethoxy) ethanol	diethylene glycol monoethyl ether (DGEE)	111-90-0	0.01–0.3	
2-ethyl 1-hexanol	2-ethylhexyl alcohol	104-76-7	0.01–0.06	
3-hexanone	ethyl propyl ketone	589-38-8	0.01–0.17	
ethyl ester butanoic acid	ethyl butyrate	105-54-4	0.01–0.05	
butyl ester 2-propenoic acid*	butyl acrylate	141-32-2	0.01–0.04	
<i>2,3 butanedioldiacetate*</i>		1114-92-7	0.01–0.33	0.010
cyclotetrasiloxane		556-67-2	0.01–0.09	
decamethyl cyclopentasiloxane*		541-02-6	0.01–0.02	
octanoic acid*	caprylic acid	124-07-2	0.01–0.16	
dodecamethyl cyclohexasiloxane	cyclomethicone	540-97-630	0.01–0.05	
dodecamethyl pentasiloxane*		141-63-9	0.01–0.03	
dihydro-5-pentyl-2(3H)-furanone*	gamma-nonanolactone	104-61-0	0.01–0.08	
octanal*	octyl aldehyde	124-13-0	0.015–0.01	
styrene*		100-42-5	0.01–0.02	
1-ethoxy-2-methyl propane*	ethyl isobutyl ether	627-02-1	0.01–0.02	
methyl ester octanoic acid*	methyl caprylate	111-11-5	0.01–0.01	
ethyl ester octanoic acid*	ethyl octanoate	106-32-1	0.01–0.05	
tridecane*		629-50-5	0.01–0.05	
<i>2-(perfluorohexyl)ethanol 6:2-telomer*</i>	perfluorinated alcohol telomers	678–39-7	Below Detection Limit	0.001
<i>2-(perfluorooctyl)ethanol 8:2-telomer</i>	perfluorinated alcohol telomers	647–42-7	0.0005–0.009	0.0005
<i>2-(perfluorodecyl)ethanol 10:2-telomer*</i>	perfluorinated alcohol telomers	865–86-1	Below Detection Limit	0.002

\* Indicates that the chemical is present in less than 75% of all popcorn types, where type is defined by brand and flavor.



**Figure 1** Experimental set-up with chamber and sampling equipment used during popping and opening.

type. The sample tubes were then stored in a freezer below zero degrees Celsius until analysis, and analyzed within seven days (168 hours) of collection. As Tenax was not suitable for all carbonyl compounds, Sep-Pak dinitrophenylhydrazine (DNPH) silica gel cartridges (Waters Corporation, Milford, MA) were also used. An Agilent Technologies (Palo Alto, CA) 1100 high performance liquid chromatograph (HPLC) with photodiode array detector (EPA method IP-6A) was used for analysis. DNPH samples were collected by pulling air from sampling ports in the chamber exhaust, and were collected at a sampling rate of 0.3 Lpm for 10 minutes.

Particulate matter (PM) was sampled using an Aerodynamic Particle Sizer (APS Model 3321, TSI, Inc., St. Paul, MN) and a Scanning Mobility Particle Sizer (SMPS Model 3934, TSI, Inc., St. Paul, MN) during popping and opening only, as well as during hot air popping. The Aerodynamic Particle Sizer (APS) has an aerodynamic particle size range of 0.5–20  $\mu\text{m}$  and the Scanning Mobility Particle Sizer (SMPS) has a mobility equivalent diameter size range of 0.02–0.5  $\mu\text{m}$ . Both instruments were calibrated prior to the study commencement. Due to the high moisture levels associated with popping corn, the sampled air was dehumidified with a diffusion dryer prior to entering the particle sampling instruments. The background samples were taken through the diffusion dryer to ensure no contamination of the sample stream from the dryer or the dessicant. The particle sizing instrument operation coincided with the Tenax tube sampling.

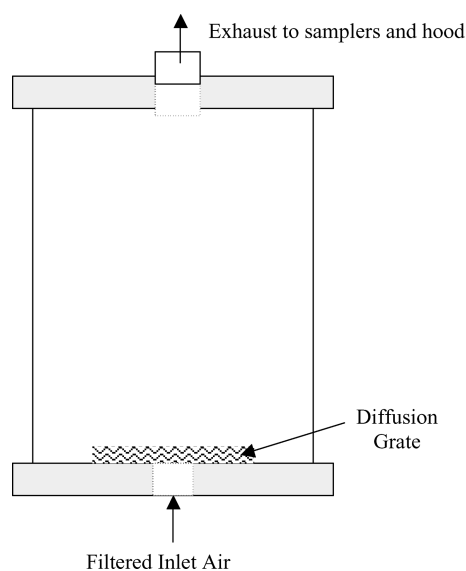
### Phase I Sample Analysis

The analysis of the Tenax tube samples was by an automated thermal desorber (Perkin-Elmer ATD 400) interfaced with a gas chromatograph (HP 6890) equipped with a mass selective detector (HP 5973). A Supelco DB-WaxEtr GC column (30 m  $\times$  0.25 mm id; 0.25 film thickness) (Bellefonte, PA) was used. The temperature program consisted of 45°C for 4 min, to 130°C at

6°C/min, to 220°C at 35°C/min. Calibration with diacetyl and p-xylene was performed. Both the compounds were found to be emitted during the prior scoping experiments. A lower analytical quantification limit of 8.8 ng was used; this is the lowest level standard. This translates to a lower concentration quantification limit of 0.033 ng/cc for the typical sample volume of 300 cc. The detection limit was calculated as three times the standard deviation for seven replicate analysis of the lowest level standard, 0.011 ng/cc for p-xylene, and 0.023 ng/cc for diacetyl. The semi-quantification for other compounds was made using the response factor of p-xylene and the peak area of the total ion chromatogram. These other compounds were identified with a 95% or greater match to the mass spectra in the NIST library as determined by AMDIS search routines (Stein, 1999). The analyst then confirmed the identification by reviewing the spectra data including retention time. APS and SMPS data were analyzed to calculate the concentration of PM as well to determine the average size distribution and standard deviation.

### Phase II Air Sampling

In Phase II, air sampling followed the same procedures as at Phase I but once the post-bag opening sample was collected, the microwave popcorn was immediately removed from the chamber in Fig. 1 and placed in the chamber shown in Fig. 2. This process took less than 60 seconds. The glass, plug (laminar) flow chamber in Fig. 2 was then closed and sealed. This 46 L chamber had a flow of 40 L per minute and thus accomplished approximately one air exchange every minute ensuring that the emitted chemicals sampled were not a result of previous release or decay products but were being emitted by the popcorn or the bag at the time of the sample. Five minute VOC samples were taken from the plug flow chamber at 10 minute intervals, up to 40 minutes post-bag opening. PM samples were not collected during this 10–40 minute period, and air popping was not performed in Phase II.



**Figure 2** Experimental plug flow chamber used 10 to 40 minutes post-popping.

### Phase II Sample Analysis

In addition to diacetyl and *p*-xylene, this phase included the calibration of the GC/MS for five additional compounds determined to be present in Phase I, as well as three perfluorinated alcohol telomers that were present in some microwaveable bags (Begley et al., 2005). These compounds are distinguished by bold italics in Table 1. The non-fluorinated calibration compounds were purchased from Chem Service, Inc. (West Chester, PA) or Aldrich (St. Louis, MO). The standard perfluorinated alcohol telomers (2-(perfluorohexyl)ethanol – 6:2-telomer), (2-(perfluorooctyl)ethanol – 8:2-telomer) and (2-(perfluorodecyl)ethanol – 10:2-telomer) were purchased from Oakwood Products, Inc. (West Columbia, SC). Non-fluorinated calibration compounds were chosen because of aggregate concentrations present in the Phase I samples and/or a uniquely high level present in individual popcorns. Many compounds identified in Phase I were not available in a form suitable for calibration purposes. A surrogate for these compounds was used when a suitable surrogate of the same compound class could be found. In cases where standards were not used, the response factor for *p*-xylene was again used. As in Phase I, a lower analytical quantification limit of 8.8 ng was used (17.3 ng for butyric acid, 5.8 ng 6:2 telomer, 1.6 ng 8:2-telomer, 1.5 ng 10:2-telomer). This translates to a lower concentration quantification limit of 0.029 ng/cc for the typical sample volume of 800 cc (0.01 ng/cc for 6:2-telomer and 0.003 ng/cc for the 8:2 and 10:2-telomers). The detection limits were calculated as three times the standard deviation for seven replicate analysis of the lowest level standard. These detection limits are listed in Table 1.

The GC/MS calibration was conducted using either an extracted ion quantification technique or a selected ion monitoring quantification. In the extracted ion quantification tech-

nique, the full mass spectrum was collected and specific ions indicative of the compound of interest were extracted to quantify the amount present in the sample. The VOCs, for which standards were used, that were quantified by the extracted ion technique were butyric acid, diacetyl, *p*-xylene, triacetin, 2-octanone, furfural, and 2,3 butanedioldiacetate (Table 1, bold italics). In the selected ion monitoring technique, only specific ions indicative of the compound are collected, increasing sensitivity and the detection limit for those compounds. The perfluorinated alcohol telomers ((2-(perfluorohexyl)ethanol – 6:2-telomer), (2-(perfluorooctyl)ethanol – 8:2-telomer) and (2-(perfluorodecyl)ethanol – 10:2-telomer) were quantified using selected ion monitoring. Because two different quantification techniques were used, two separate Tenax samples were collected at the same time. For the calibrations, three series of standards were prepared in methanol. Butyric acid was prepared in water due to its methanol reactivity. Five calibration levels of each series were analyzed in triplicate to determine the GC/MS response to these standards. Standard concentrations were such that the sorbent tubes were spiked with two microliters of standard at each level. A gas phase internal standard, deuterated toluene, was spiked on the sample tubes prior to GC analysis. Again, the quantification for other compounds was made using the response factor of *p*-xylene and the peak area of the total ion chromatogram. These other compounds were matched (match factor of 95 or greater) to the mass spectra in the NIST library as determined by AMDIS search routines (Stein, 1999) and confirmed by analyst review of the retention times.

APS and SMPS data were analyzed to determine the average size distribution and standard deviation, as well as the percent of respirable PM. An Electrical Low Pressure Impactor (ELPI; Dekati, Finland) was used to collect particles on aluminum substrates for the characterization by optical microscopy (Bristolscope 800175, Bristoline, Japan) but was not used for additional particle characterization. Clean popcorn bag samples (4 cm in diameter) were adhered to inert backing pellets and a Philips PW2404 X-ray fluorescence (XRF) spectrometer with SuperQ data collection software and UniQuant data evaluation software was used to determine the presence of fluorine in these microwave popcorn bags.

### Quality Assurance/ Quality Control

The sorbent collection efficiencies were evaluated using a permeation oven and generating test atmospheres with deuterated xylene. The variation in the concentration of deuterated xylene across all samples was 10%, compared to a 5% variation in the deuterated toluene response used as an internal standard for quantification.

To ensure adequate corn popping during a run, the volume of the popped corn was determined using a beaker. Additionally, the mass of the unpopped kernels was determined. If the popcorn volume was found to be greater than 1.5 liters, and the mass of the unpopped kernels was less than 20% of the

total product mass, the run was considered usable. If the run did not meet these specifications, an additional run was performed and the first run was not used. If the popped volume was insufficient, and there were a large number of still unpopped kernels, a longer popping time was used. This longer popping time ensured that at least 1.5 liters of popcorn was "popped." As the popping level varied by brand, the preliminary data deemed these practices reasonable for determining an adequately popped bag.

Field blanks were carried for each day of sampling, and were analyzed in the same manner as other Tenax samples. The background samples were included in every run. The backgrounds were used to ensure that the chamber was sufficiently purged prior to additional testing, and that there were no other sources of contamination present. Field blank and background values were subtracted from the sample concentrations. Duplicates were taken for every tenth sample.

Flow calibrations for the mass flow controllers and aerosol sampling instruments were performed prior to each day's sampling. Precision standards were laid forth in the QA plan prior to the commencement of the study. A leak check on the sampling system was performed weekly. The system was held at  $-80\text{kPa}$  for two minutes, and vacuum maintenance over this time period indicated that no leaks were present. Additionally, a microwave oven calibration following ASTM Method F 1317-90 (ASTM, 1990) was performed weekly to ensure consistent operation. No decrease in microwave power was noted over the duration of the study.

Daily calibration checks (DCCs) were performed on the analytical systems. These DCCs used calibration compounds at levels near the mid-calibration range. These DCCs were generated by spiking a liquid solution onto a sorbent tube and analyzing in the same manner as the sample sorbent tubes.

Background samples were drawn during each microwave calibration to ensure no residual contamination of the microwave oven occurred. The chamber and the microwave oven were cleaned and thoroughly rinsed between each type of popcorn tested.

## RESULTS AND DISCUSSION

### *Quality Assurance/Quality Control*

For daily calibration checks performed on the analytical system, recoveries were within the 15% guidelines specified in the laboratory's operating procedures and quality assurance project plan.

VOCs on the blank sorbent tubes collected during each day of testing were below the analytical detection limits except for the following cases. During Phase I, butyric acid slightly exceeded the detection limit three times. In each of these instances, the amounts measured in the samples were two to three orders of magnitude higher than the blanks and may have represented cross-contamination from sample handling procedures. In three

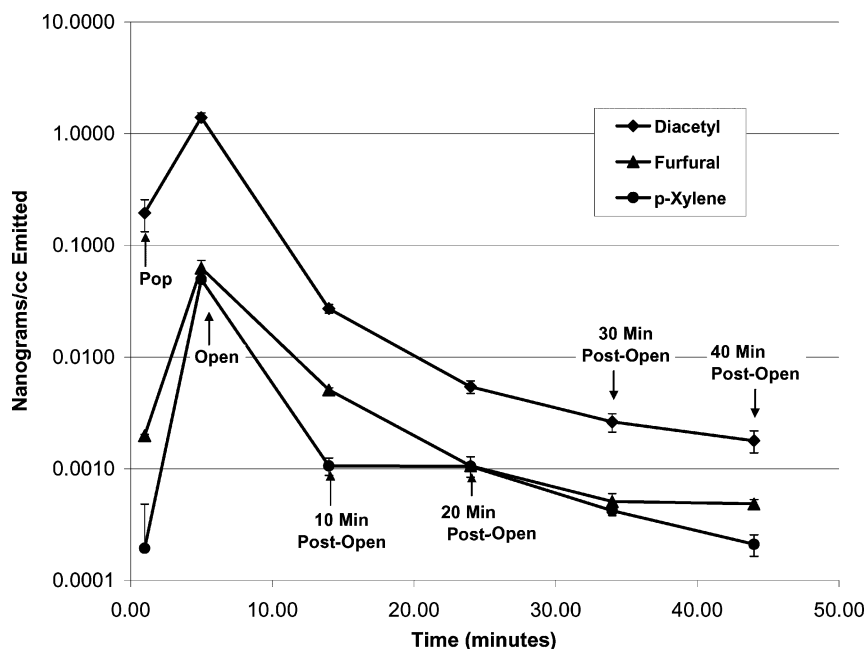
other samples, toluene and hexanal were slightly above the analytical detection limit, but the samples contained levels significantly above these amounts. Duplicate samples were all within the 15% data quality objectives for precision specified in the quality assurance project plan.

### *Test Chamber VOC Concentrations Used to Calculate Chemical Emissions*

Numerous chemicals were measurable in air exiting the chamber during microwave popcorn popping and opening. The predominant emitted chemicals agreed with those chemicals sampled by NIOSH inside microwave popcorn manufacturing plants (Kullman et al., 2005) with the exception of methyl ethyl ketone (MEK). MEK was not emitted while popping or opening microwave popcorn and thus, was likely the result of another plant process. The volatile organic compounds (VOCs) emitted during popping and opening, and measured leaving the test chamber, are presented by average concentration sampled for all microwave popcorns in Table 1. Chemicals that are not present in at least 75% of popcorn types are noted with a star. The level of chemicals varied with the popcorn type, thus, the concentration ranges are provided. It should be noted that in general, the sampling of VOCs in the presence of particles lends itself to the possibility of VOC partitioning and hence, a lower gas phase VOC concentration. No information on partitioning in this environment for the measured compounds is available in the literature. No evidence of contamination by popcorn-related compounds was determined on any field blank during the course of the study. One compound, 4-cyanocyclohexene (tetrahydrobenzoxazole), was found in all background samples and was determined to be a byproduct of the nitrile gloves used in the chamber. Chemicals emitted during hot air popping were extremely low, with all chemical concentrations well below  $0.1\text{ ng/cc}$ , thus, the hot air popped corn provided a reasonable control for microwave popcorn.

As shown in Fig. 3, chemicals continue to be released from microwave popcorn after bag opening. This includes chemicals originating from the inks or glues on the bag (*p*-xylene) (IPCS, 2006) and the chemicals originating from the popcorn flavorings (diacetyl and furfural) (FEMA, 2004; NIOSH, 2003a, 2003b, 2004a, 2004b, 2006). The greatest quantities of these chemicals are released during popping and opening, with extremely low levels seen 40 minutes post-bag opening. This figure averages multiple popcorn types, so standard error bars are provided on the figure to show the variability between the popcorn types.

Perfluorinated alcohol telomers were determined to be emitted at low levels by some bags of popcorn. While individual results varied, the averages for the 6:2 and 10:2 telomers were below the analytical detection limits of  $0.001$  and  $0.002\text{ ng/cc}$  respectively (Table 1). The average emitted concentration for the 8:2-telomer was two orders of magnitude higher than its detection limit of  $0.0005\text{ ng/cc}$ , but still very low. These alcohol telomers are a product of the perfluorinated coatings on

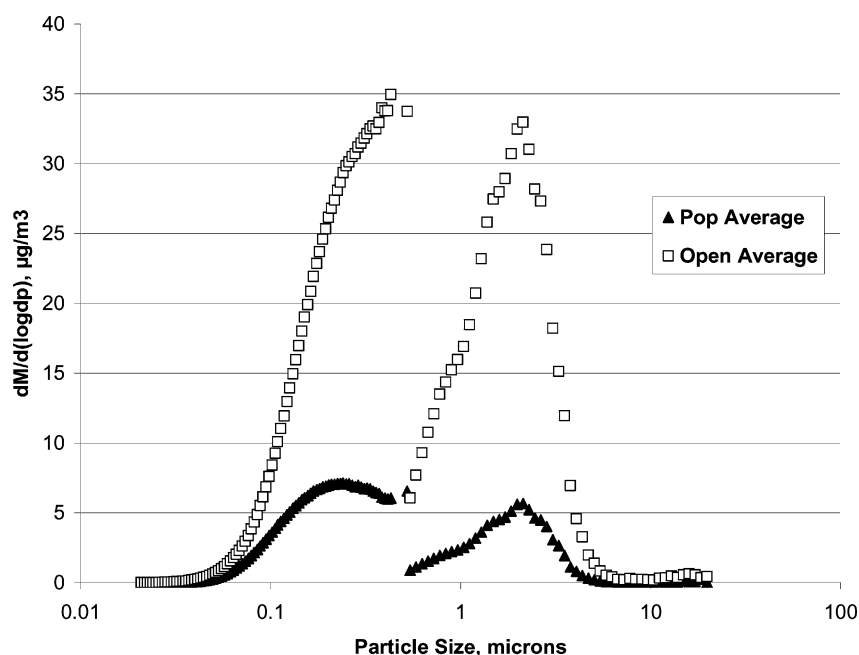


**Figure 3** Average diacetyl, furfural, and *p*-xylene emissions for all popcorns: Popping through 40-minutes post-pop.

microwave popcorn bags that are used to keep oils from seeping through the paper (Begley et al., 2005). XRF analysis determined the presence of fluorine in several brands of bags. Fluorine was found to be one of the top three elements present by weight percent in bags. It should be noted that not all microwave popcorn bags are coated with perfluorinated compounds.

The average concentration of PM emitted during popping and opening in the 515 Liter chamber across all popcorns was

$1900 \mu\text{g}/\text{m}^3$ , with a range from  $0.76 \mu\text{g}/\text{m}^3$  to  $3100 \mu\text{g}/\text{m}^3$ . Ninety-nine percent of this PM emitted was in the respirable range ( $<4$  microns). Figure 4 shows the average concentration of PM by particle size during popcorn popping and bag opening, with particles less than 0.5 microns sampled by the SMPS and particles greater than 0.5 microns sampled by the APS. The size distribution appears bimodal, with the fine component having a mass median aerodynamic diameter (MMAD) and geometric



**Figure 4** Particle concentration as a function of particle size during popping and opening of a bag of microwave popcorn.

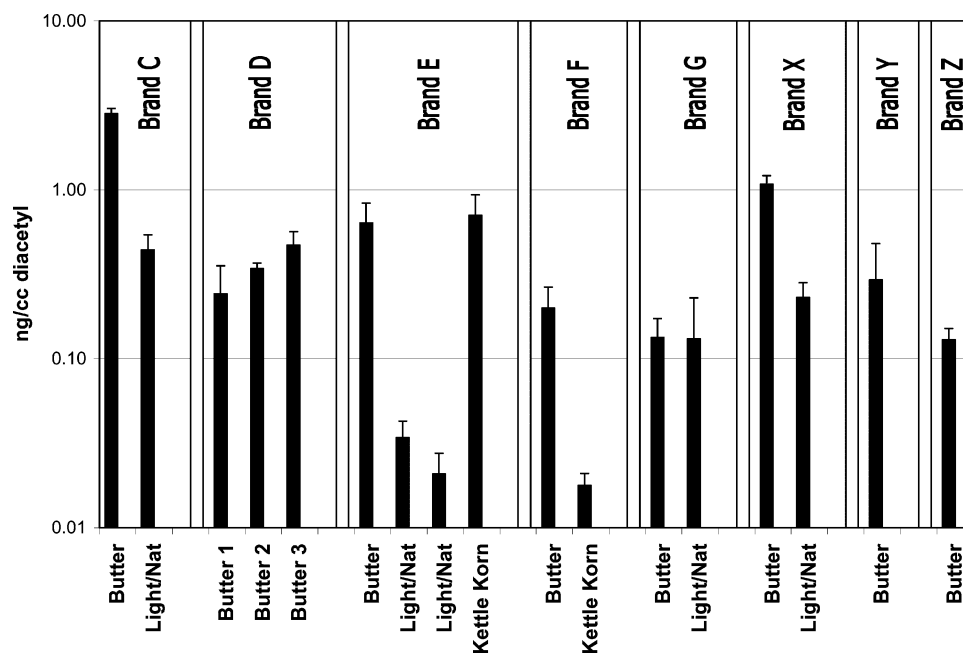


Figure 5 Diacetyl concentration by popcorn flavoring/type, sorted by popcorn brand.

standard deviation (GSD) of 0.23 and 1.7, respectively, while the coarse component has a MMAD and GSD of 1.72 and 1.7, respectively.<sup>1</sup> While following the same trend, the emissions of PM during bag opening are greater than the emissions of PM during the popping of the microwave popcorn. Particles, when analyzed using optical microscopy, appeared to be oil-based liquid droplets. Thus, a density of 0.91 g/cc was used in the mass concentration calculations.

### Concentration and Popcorn Type

The concentration of emitted chemicals correlated with the level of the popcorn flavoring (popcorn type). Lower levels of diacetyl were associated with a “light” popcorn as opposed to a “butter” popcorn (Fig. 5). The difference was statistically significant in three of the four brands where both butter and light were tested (Brand C,  $p = 0.00004$ ; Brand E,  $p = 0.009$ ; Brand X,  $p = 0.08$ ). Note that in the two cases where kettle corn (salty and sweet) was tested, one brand had levels of diacetyl in their kettle corn similar to that of butter flavoring (Brand E,  $p = 0.6$ ), and the other had significantly lower levels of diacetyl in their kettle corn (Brand F,  $p = 0.01$ ). The P values were determined by a two-tailed student’s t-test using  $\alpha = 0.05$ . The diacetyl was not emitted by air popped corn, and thus air popped corn was not

included in Fig. 5. The variability in the diacetyl concentration by brand is representative of the concentration variability of the other chemical emissions.

### Average Chemical Emissions per Bag of Popcorn

As all compounds were measured while the flow was exiting the chamber, the numbers presented above are representative of chamber concentrations. To determine the mass of chemicals emitted per bag of popcorn, ASTM D5116 (ASTM, 1997) was utilized. The total chemical emissions from the popcorn were assumed to be the mass leaving the chamber plus the mass remaining in the chamber. As shown in Fig. 3, the emissions of the three compounds, diacetyl, p-xylene, and furfural, were calculated per bag of popcorn using Equation 1. The samples 0–6 are background, popping, opening, 10, 20, and 30 minute samples, respectively. The samples 0, 1, and 2 were taken in the 500 L stainless steel chamber and the samples 3–6 were taken in the 45 L glass plug flow chamber.

$$\frac{\text{Emissions}}{\text{Bag of popcorn}} = \left\{ \sum_0^1 \left[ Q \left( \frac{C_i + C_{i+1}}{2} \right) \Delta t \right] + C_a V_a \right\} + \left\{ \sum_3^5 \left[ Q \left( \frac{C_i + C_{i+1}}{2} \right) \Delta t \right] + C_b V_b \right\} \quad (1)$$

Where:

- $Q$  is the flow rate through the respective chamber
- $C_i$  is the chamber concentration for sample  $i$

<sup>1</sup>The aerodynamic diameter is an equivalent diameter that standardizes for particle shape and density. For a particular particle, the aerodynamic diameter is defined as the diameter of a spherical particle with a density of 1 g/cm<sup>3</sup> that has the same settling velocity as the particle (Hinds, 1999). The mass median aerodynamic diameter (MMAD) is the calculated aerodynamic diameter where, by weight, 50% of the particles will be larger than the MMAD and 50% of the particles will be smaller than the MMAD (U.S. Environmental Protection Agency, 2006).

**Table 2** Average emissions per bag of popcorn

Compound	$\mu\text{g}$ emitted/bag of popcorn
diacetyl	$778.9 \pm 135$
<i>p</i> -xylene	$27.2 \pm 3.1$
furfural	$36.5 \pm 2.6$

- $\Delta t$  is the change in time between sample  $i$  and sample  $i + 1$
- $C_a$  is the concentration of the chemical left in the 500 L stainless steel chamber;  $C_b$  is the concentration of the chemical left in the 45 L glass chamber (not exhausted from the chamber)
- $V_a$  is the volume of the stainless steel chamber;  $V_b$  is the volume of the glass chamber

Table 2 shows the average chemical emissions per bag of popcorn for the three compounds displayed in Fig. 3.

Based on the information determined during this study, the greatest amount of chemicals are emitted when the bag is opened post-popping; more than 80% of the total chemical emissions occur at this time. With the exception of the particulate matter, the emissions of chemicals from a single bag of microwave popcorn appear to be low, often within an order of magnitude of the detection limit of the GC/MS. This was a source characterization study and the potential exposure to the compounds measured and any associated potential risks were not estimated.

## ACKNOWLEDGEMENTS

The authors would like to thank Shirley Wasson, Scott Moore, Betsy Howard, and John Holland of the U.S. EPA for their support of this project. This project was funded by a U.S. EPA National Risk Management Laboratory internal grant.

## DISCLAIMER

The U.S. Environmental Protection Agency through its Office of Research and Development funded the research described here. It has been subjected to the Agency's review and has been approved for publication as an EPA document.

## REFERENCES

- ASTM. (1990). Standard Test Method for Calibration of Microwave Ovens, Designation F-1317-90.
- ASTM. (1997). Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products, Designation D-5116-97, 1997.
- Begley, T. H., White, K., Honigfort, P., Twaroski, M. L., Neches, R., and Walker, R. A. (2005). Perfluorochemicals: Potential sources of and migration from food packaging. *Food Additives and Contaminants*, **22**:1023-1031.
- EPA, U. S. (1999). *U.S. EPA. Compendium Method TO-17, Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes.*
- FEMA. (2004). *The Flavor and Extract Manufacturer's Association of the United States, Respiratory Health and Safety in the Flavor Manufacturing Marketplace*, Accessed 3/5/2007 from <http://www.femaflavor.org/html/public/RespiratoryRpt.pdf>.
- Fortmann, R., Kariher, P., and Clayton, R. (2001). *Indoor Air Quality: Residential Cooking Exposures. State of California Air Resources Board 97-330.*
- General Mills (2003). *2003 Annual Report*, Accessed 3/5/2007 from [http://media.corporate-ir.net/media\\_files/irol/74/74271/reports/2003\\_AR.pdf](http://media.corporate-ir.net/media_files/irol/74/74271/reports/2003_AR.pdf)
- Hinds, W. (1999). *Aerosol Technology, Properties, Behavior and Measurement of Airborne Particles*. John Wiley & Sons, Inc., New York.
- IPCS. (2006, 1990). *Poison Information Monographs (PIM 565)*. Accessed 6/7/2006, from <http://www.inchem.org/documents/pims/chemical/xylene.htm>.
- Kanwal, R. M., Kullman, G. P., Piacitelli, C. M., Boylstein, R. M., Sahakian, N. M., and Martin, S. M. (2006). Evaluation of flavorings-related lung disease risk at six microwave popcorn plants. *Journal of Occupational & Environmental Medicine*, **48**:149-157.
- Kreiss, K., Gomaa, A., Kullman, G., Fedan, K., Simoes, E. J., and Enright, P. L. (2002). Clinical bronchiolitis obliterans in workers at a microwave-popcorn plant. *N Engl J Med.*, **347**: 330-338.
- Kullman, G., Boylstein, R., Jones, W., Piacitelli, C., Pendergrass, S., and Kreiss, K. (2005). Characterization of respiratory exposures at a microwave popcorn plant with cases of bronchiolitis obliterans. *Journal of Occupational and Environmental Hygiene*, **2**:169-178.
- Manura, J. J. (1999). *Application Note 32a: Selection and Use of Adsorbent Resins for Purge and Trap Thermal Desorption Applications. Thermal Desorption & Cryo-Trap Notes*. Accessed 6/7/2006, from <http://sisweb.com/referenc/applnote/app-32-a.htm>.
- MarketResearch.com (2001). Popcorn—US, Accessed 3/5/2007 from <http://www.marketresearch.com/product/display.asp?productid=717669&SID=45062997-377897891-338286838&curr=USD&kw=popcorn%09MR%2D4618&view=toc>.
- McNeal, T., and Hollifield, H. (1993). Determination of volatile chemicals released from microwave-heat-susceptor food packaging. *J. AOAC Int.*, **76**:1268-1275.
- NIOSH. (2003a). *Health Hazard Evaluation Report No. 2002-0408-2915, Agrilink Foods Popcorn Plant, Ridgway, IL, October 2003*. Accessed 6/7/2006 from <http://www.cdc.gov/niosh/hhe/reports/pdfs/2002-0408-2915.pdf>.
- NIOSH. (2003b). *Preventing Lung Disease in Workers Who Use or Make Flavorings Publication NO. 2004-110 December 2003*. Accessed 6/7/2006, from <http://www.cdc.gov/niosh/docs/2004-110/>
- NIOSH. (2004a). *Health Hazard Evaluation Report No. 2001-0474-2943, American Pop Corn Company, Sioux City, Iowa, July 2004*. Accessed 6/7/2006, from <http://www.cdc.gov/niosh/hhe/reports/pdfs/2001-0474-2943.pdf>.
- NIOSH. (2004b). *Health Hazard Evaluation Report No. 2003-0112-2949, ConAgra Snack Foods, Marion, Ohio*. Accessed 6/7/2006, from <http://www.cdc.gov/niosh/hhe/reports/pdfs/2003-0112-2949.pdf>.
- NIOSH. (2006). *Health Hazard Evaluation Report No. 2000-0401-2991, Gilster-Mary Lee Corporation, Jasper, MO, January 2006*. Accessed 6/7/2006, from <http://www.cdc.gov/niosh/hhe/reports/pdfs/2000-0401-2991.pdf>.
- Risch, S. (1993). Safety assessment of microwave susceptors and other high temperature packaging materials. *Food Addit Contam.*, **10**:655-661.
- Stein, S. E. (1999). An integrated method for spectrum extraction and compound identification from gas chromatography/mass spectrometry data. *Journal of the American Society for Mass Spectrometry*, **10**:770-781.
- U.S. Environmental Protection Agency. (2006). *Terminology Reference System—Mass Median Aerodynamic Diameter*. Accessed 7/3/07 from [http://iaspub.epa.gov/trs/trs\\_proc.qry.navigate\\_term?p\\_term\\_id=28116&p\\_term\\_cd=TERM](http://iaspub.epa.gov/trs/trs_proc.qry.navigate_term?p_term_id=28116&p_term_cd=TERM).