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Potential Hazards Not Communicated in Safety Data Sheets of Flavoring Formulations, Including Diacetyl and 2,3-Pentanedione

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Abstract

Objectives: Workers using flavoring formulations containing diacetyl and 2,3-pentanedione may be at risk of inhalational exposure, as these volatile hazardous chemicals are emitted from the bulk material, especially at elevated temperatures. However, flavoring formulations that contain diacetyl and 2,3-pentanedione might not list these ingredients because they are generally recognized as safe to ingest, may be part of a proprietary mixture deemed a trade secret, or may not be required to be listed if they are present at <1% composition. The objective of this study was to investigate whether potential inhalational hazards present in flavoring samples were reported as chemical ingredients on their corresponding safety data sheets (SDSs).

Methods: A convenience sample of 26 bulk liquid flavorings obtained from two coffee roasting and packaging facilities in the USA was analyzed for 20 volatile organic chemicals present in the headspaces of vials containing flavoring liquids using gas chromatography-mass spectrometry. Flavoring samples were included in the study if headspace analysis results and SDSs were available. Flavoring samples included hazelnut, French vanilla, amaretto, chocolate, and caramel as well as some flavoring mixtures containing added fruit flavors such as cherry and raspberry. The presence of a chemical in the flavoring formulation was then compared to the ingredient list on the SDSs.

Results: All the flavoring SDSs contained trade secret designations. None of the SDSs listed diacetyl or 2,3-pentanedione. Headspace analyte concentrations revealed that diacetyl was present in 21 of 26 samples (81%) with a maximum concentration of 5.84×10^4 μg m^{-3} in flavor 18 (caramel). 2,3-Pentanedione was present in 15 flavors (58%) with a maximum concentration of 3.79×10^5 μg m^{-3} in flavor 24 (oatmeal cookies).

Conclusions: A majority of the flavorings tested had diacetyl, 2,3-pentanedione, or both as volatile constituents in the headspace. These chemicals were not listed on the SDSs, but inclusion

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of diacetyl and 2,3-pentanedione on SDSs would serve to protect downstream users from unrecognized exposure and potential respiratory disease. The headspace technique presented here is a viable tool to rapidly screen for volatile hazardous chemicals that may be present in flavoring formulations. Facilities that use flavorings should be aware that constituents in flavorings may present a potential inhalational hazard even if not identified as such by the SDS. A precautionary approach is warranted when working with flavorings, including exposure monitoring and effective exposure control strategies such as containment and local exhaust ventilation.

Keywords

acetyl propionyl; 2,3-butanedione; diacetyl; headspace; 2,3-pentanedione; safety data sheets; volatile organic compounds

Introduction

The US Occupational Safety and Health Administration (OSHA) first introduced the Hazard Communication Standard §1910.1200 in 1983 (Kolp *et al.*, 1993). The Hazard Communication Standard was created to inform employees about (i) the hazards of the chemicals that they may encounter in their workplace and (ii) precautions that they can take to minimize risk from exposure to hazardous chemicals (OSHA, 2012). The standard dictates that the chemical manufacturer, distributor, or importer systematically categorize hazards present in chemical mixtures, identify hazardous properties and routes of exposure for each chemical constituent, and share these hazards in a safety data sheet (SDS).

One limitation in relying on SDSs for hazard information is that for acute toxicity and specific target organ toxicity with repeated or prolonged exposure, the ‘relevant ingredients’ of a mixture are defined as those present in concentrations of ≥1% by weight (0.1% by weight for compounds that are carcinogenic or toxic to the reproductive system). Under these specifications, disclosure in an SDS of a chemical ingredient present in a mixture in a concentration <1% by weight depends on whether that ingredient affects the hazard classification (OSHA, 2012). Thus, an ingredient present at <1% may not be listed on an SDS unless the person interpreting the standard considers that the ingredient will affect hazard classification. A second limitation is that a mixture may be designated by the manufacturer as trade secret, in which case the chemical constituents may not be listed regardless of chemical constituents’ percent concentration by weight. A trade secret is defined in the OSHA Hazard Communication Standard as ‘any confidential formula, pattern, process, device, information or compilation of information that is used in an employer’s business, and that gives the employer an opportunity to obtain an advantage over competitors who do not use it’ (OSHA, 2012). Hazard classification and trade secret limitations have also been expressed by other researchers (Bernstein, 2002; Nicol *et al.*, 2008). Trade secret information about chemicals that may be present in a mixture can be disclosed by the manufacturer upon request from a treating physician or nurse responding to a medical emergency. In nonemergencies, health professionals such as physicians, industrial hygienists, toxicologists, epidemiologists, or occupational health nurses may request the specific chemical identities or percentage composition from the manufacturer in writing when the need for such information has been established. Information such as chemical

identity and percent composition may be needed by a health or occupational hygiene professional to conduct an assessment of chemical hazards present, prepare for chemical exposure sampling, advise selection of personal protective equipment, and/or conduct studies to assess health effects of exposure.

The butter flavorings diacetyl and 2,3-pentanedione are examples of hazardous chemicals that may be present in chemical mixtures but not disclosed on an SDS (Day *et al.*, 2011; Duling *et al.*, 2016; NIOSH, 2016). These two α-diketones can be added to flavoring formulations because they have a US Food and Drug Administration (FDA) designation of generally recognized as safe (GRAS) for flavorings' intended purpose, ingestion by consumers. However, the GRAS designation does not consider the likelihood of emissions from bulk flavorings in work settings or the potential for respiratory toxicity in exposed workers. Inhalational exposure to diacetyl has been associated with a debilitating lung disease called obliterative bronchiolitis (NIOSH, 2016), and its common substitute, 2,3-pentanedione, has been found to have similar respiratory toxicity in animal studies (Hubbs *et al.*, 2012). The National Institute for Occupational Safety and Health (NIOSH) has recommended exposure limits of 17.6 μg m^{-3} [5 parts per billion (ppb)] for diacetyl and 38.1 μg m^{-3} (9.3 ppb) for 2,3-pentanedione. Additionally, the vapor pressure for pure diacetyl is relatively high at 52.5 mm Hg at 20°C with a saturation concentration in air of 243 000 mg m^{-3} at 20°C. Because of their volatility, low exposure limits, and associations with respiratory toxicity, diacetyl and 2,3-pentanedione are examples of chemicals that warrant consideration when classifying the hazard for an SDS whenever present in mixtures, even at low concentrations by weight in liquid flavoring formulations.

The objective of the study was to investigate the associations between the presence of inhalational hazards in flavorings samples and any reported chemical ingredients on their respective SDS. Bulk samples of liquid flavorings were collected at two workplaces where employers requested a Health Hazard Evaluation and listed concerns about occupational exposure to flavoring chemicals and possible risks for respiratory impairment. A facility representative reported to NIOSH that the manufacturer told them there was no added diacetyl or 2,3-pentanedione. The manufacturer later clarified to the facility that diacetyl may be present as a natural by-product of acetoin, which is added to almost all coffee flavors used by that facility. The bulk samples of liquid flavorings were analyzed using a static headspace sampling technique to identify the presence and emission potential of volatile organic compounds with an emphasis on diacetyl and 2,3-pentanedione.

Methods

A convenience sample of 26 bulk liquid flavorings and their SDSs were obtained from two coffee roasting and packaging facilities in the USA. Most of the samples (24 of 26: 92%) were from a single flavoring manufacturer. The flavorings were compound mixtures of flavoring chemicals with commonly observed flavors for coffee products such as hazelnut, French vanilla, amaretto, chocolate, and caramel as well as some flavoring mixtures containing added fruit flavors such as cherry and raspberry. SDSs were reviewed for each of the flavoring mixtures to ascertain the components listed.

The headspaces above the liquid flavoring samples were analyzed for 20 different volatile organic compounds (VOCs) quantified as part of a typical suite targeted for canister analysis in the Field Studies Branch Organics Laboratory, Morgantown, WV, USA. Headspace analysis was performed once for each sample by placing ~1 g of liquid flavoring in a preweighed 40 ml amber volatile organic analysis vial (actual volume ~42 ml). The vial plus sample was weighed again to determine mass of liquid flavoring. The sample was allowed to equilibrate for 24 h at room temperature (23°C). Then 2 ml of headspace gas was transferred using a 2.5-ml gastight syringe to a 450-ml fused-silica-lined evacuated canister. The canister was pressurized with ultrahigh-purity nitrogen to ~1.5 times atmospheric pressure equating to a dilution factor of 338. Typical minimum detectable concentrations in the vial headspace ranged from 320 μg m^{-3} for acetaldehyde to 1600 μg m^{-3} for D-limonene. A nominal 250-ml gas aliquot was analyzed using a 7200/7032 preconcentrator/autosampler (Entech Instruments, Simi Valley, CA, USA) attached to a 7890/5977 gas chromatograph/mass spectrometer (Agilent Technologies, Santa Clara, CA, USA) (LeBouf *et al.*, 2012). Lower injection volumes or pressure dilutions with ultrahigh-purity nitrogen were used to capture high concentrations of ethanol. These dilutions increased detection limits for analytes in some samples. The internal standards were a mixture of bromochloromethane (132.3 μg m^{-3}), 1,4-difluorobenzene (116.7 μg m^{-3}), and chlorobenzene-d5 (120.2 μg m^{-3}) with 50 mL added to the preconcentrator trap prior to sample transfer.

The majority of quantified analytes were not expected in the samples: eight analytes (acetone, acetonitrile, benzene, isopropyl alcohol, toluene, α-pinene, *m,p*-xylene, and *o*-xylene) had a low frequency of detection; and six analytes (methyl methacrylate, methylene chloride, styrene, hexane, ethylbenzene, and chloroform) had no detectable concentrations. Acetoin cannot be measured using this headspace analysis technique. The reported compounds are as follows: diacetyl (2,3-butanedione)†, 2,3-pentanedione†, 2,3-hexanedione†, acetaldehyde†, ethanol‡, and D-limonene. Analytes denoted with a dagger (†) are high-priority substances and analytes denoted with a double dagger (‡) are low-priority substances on the Flavor and Extract Manufacturers Association of the United States (FEMA) list of substances that 'may pose potential respiratory hazards when improperly handled' (FEMA, 2012). Acetaldehyde is possibly carcinogenic to humans [International Agency for Research on Cancer (IARC) Group 2B] (IARC, 1999). D-limonene is GRAS to ingest but inhalation may cause irritation and bronchoconstriction (NCBI, 2018a).

Results

Headspace analyte concentrations indicated that diacetyl was present in 22 of 26 samples (85%) with a maximum concentration of 5.84×10^4 μg m^{-3} in flavor 18, which is a caramel flavor (Table 1). 2,3-Pentanedione was observed in 15 flavors (58%) with a maximum concentration of 3.79×10^5 μg m^{-3} in flavor 24, which is a blended flavor designed to imitate oatmeal cookies. Flavors 21 and 22 are blended flavors designed to have notes of caramel and vanilla. These two flavors were produced by two different manufacturers and showed a large difference in 2,3-pentanedione concentrations (9.90×10^4 μg m^{-3} versus $<4.83 \times 10^2$ μg m^{-3}). For 2,3-hexanedione, only flavor 4 (caramel) had a measurable headspace concentration of 9.80×10^2 μg m^{-3}.

Acetaldehyde, ethanol, and D-limonene were also quantified by headspace analysis. Acetaldehyde was observed in 20 flavors (77%) with a maximum headspace concentration of 1.57×10^5 μg m^{-3} in flavor 1. Flavor 1 is a blended flavor with notes of whiskey, caramel, and vanilla. Ethanol was observed in all samples, even in those samples where ethanol was not noted in SDSs, with a maximum headspace concentration of 1.29×10^8 μg m^{-3} in flavor 19, which is a blended caffeine flavor. D-limonene was observed in 14 flavors (54%) with a maximum headspace concentration of 5.08×10^5 μg m^{-3} in flavor 14, which is a chocolate cherry flavor. Ethanol may be added as a dilution agent for the flavoring chemicals or may be present as a residual solvent from extraction of plant material (Liu, 2008) or preparation of plant extracts.

Discussion

Headspace analysis can rapidly reveal the presence of hazardous chemicals in a mixture, even when present in small quantities or when not listed in the SDSs. A benefit of the headspace technique used here is the rapid identification of volatile chemical constituents present in bulk samples of liquid flavorings. Propylene glycol, the main vehicle for flavoring formulations, has a low vapor pressure (0.08 mm Hg at 20°C) (NCBI, 2018b) and will not readily evaporate into the headspace without heat. The proposed headspace analysis technique identifies the volatile fraction of the mixture at room temperature, which is more representative of field conditions than elevated temperatures used in traditional headspace techniques. The method allows diacetyl to be detected at headspace concentrations at or above 320 μg m^{-3} at 23°C, which is equivalent to 13.1 ng diacetyl in the headspace gas of the vial. Because the vapor pressure for diacetyl is relatively high and there is little interaction assumed between diacetyl and propylene glycol, the main solvent, diacetyl would be predominantly present in the gas phase as opposed to the liquid phase. Diacetyl content as percentage by weight of the bulk material can be estimated using a theoretical gas–liquid partition coefficient of 4.58×10^{-9}, derived from chemical properties assuming propylene glycol as the flavoring base instead of a propylene glycol/vegetable glycerin base used elsewhere (LeBouf *et al.*, 2018). Using this partition coefficient, headspace air concentrations of 320 μg m^{-3} diacetyl equate to very low percentages by weight (~0.00017%) in solution.

Diacetyl can be formed from the spontaneous decarboxylation of 2-hydroxy-2-methyl-3-oxobutanoic acid, an acetoin precursor, and can also be reduced to acetoin by reductase (Xiao and Lu, 2014). Diacetyl and 2,3-pentanedione can be present in starter distillates used to enhance the aroma of food products such as cottage cheese, margarine, vegetable oil spreads, processed cheese, and sour cream (Rincon-Delgadillo *et al.*, 2012). Starter distillates have a GRAS designation and are defined in 21 CFR §184.1848 as a steam distillate of a number of bacterial species grown on a medium of skim milk usually fortified with 0.1% citric acid (FDA, 2008). Water accounts for >98% of the starter distillate with the remainder being a mixture of flavor compounds of which diacetyl may be 80–90% (FDA, 2008). Diacetyl is a product of citrate metabolism from some bacteria including *Lactococcus lactis* ssp. *diacetylactis* and *Leuconostoc citrovorum;* diacetyl has been found in the headspace above starter distillates at concentrations ranging from 1.2 to 22 000 μg diacetyl per gram starter distillate (Rincon-Delgadillo *et al.*, 2012).

None of the SDSs listed diacetyl, 2,3-pentanedione, or acetoin. Acetaldehyde, 2,3-hexanedione, and D-limonene were also not listed on the SDS. Ethanol was listed on 16 of the 26 SDSs (62%). Propylene glycol is a common vehicle for flavoring formulations and was listed on 20 of 26 SDSs (77%). All of the SDSs used a 'trade secret' designation as justification for not providing constituent identity.

Flavor description may be a good indicator of the potential for the flavoring formulation to contain diacetyl or 2,3-pentanedione, either as added ingredients or from the addition of other ingredients that may contain them such as acetoin or starter distillate. OSHA has proposed a list of flavorings that may contain diacetyl and highlights categories such as (i) Dairy (e.g. butter, cheese, or starter distillate), (ii) Hybrid Dairy (e.g. butter pecan or vanilla crème), (iii) Brown (e.g. caramel, vanilla, or chocolate), (iv) Alcohol (e.g. brandy or rum), (v) Other (e.g. nutmeg or honey), and (vi) Fruit (e.g. strawberry or cider) (OSHA, 2010). Most of the tested flavorings fit into one or more of these categories and contain diacetyl, 2,3-pentanedione, or both (Table 1). Flavors 17 (vanilla, sugar) and 20 (chocolate) in Table 1 fit into these categories but did not contain diacetyl or 2,3-pentanedione. Flavor 26 (peppermint) does not fit into these categories but had a low headspace concentration of diacetyl (5.72×10^2 μg m^{-3}) just above the detection limit.

A limitation of the headspace technique is that the levels of VOCs detected in headspaces within enclosed, unventilated vials containing flavoring liquids are much higher than those that would be expected to be present in workplaces where the flavorings are used. Many factors might affect workplace levels, including engineering controls, general ventilation, and administrative controls. However, the headspace technique may be useful for identifying flavoring liquids with the potential to generate hazardous exposures. A limitation of the study is that most of the flavoring samples came from a single manufacturer. However, other researchers have reported the presence of diacetyl and 2,3-pentanedione in the headspace above flavoring samples with no-added diacetyl known to be supplied by a different manufacturer from the two presented in the current study (Duling *et al.*, 2016). They found diacetyl, 2,3-pentanedione, and 2,3-hexanedione in the headspace above flavorings used to flavor coffee at concentrations comparable to those seen here (Duling *et al.*, 2016). In another study, Day *et al.* (2011) found the presence of acetoin, diacetyl, 2,3-pentanedione, and other α-diketones in the headspace of a substitute liquid buttermilk flavoring that only listed acetoin as a hazardous ingredient on the SDS.

Although diacetyl and 2,3-pentanedione may not have been added to some of the flavorings tested here, they were identified using the headspace technique. Their presence may be due to the addition of acetoin or another ingredient that contained diacetyl and/or 2,3-pentanedione as an impurity. They may also be components of the trade secret formulation or of the mixture in a concentration <1% by weight. It is crucial that manufacturers recognize sources of diacetyl that may be found in flavoring formulations and identify its presence in SDSs so that workers who may be exposed to fugitive emissions during manufacturing or use of flavorings can be protected. Equipped with this information, the employer can make informed decisions about appropriate occupational exposure protection strategies such as engineering controls, administrative controls, or personal protective

equipment. A precautionary approach to worker safety is advisable when working with any flavorings as the inhalational hazards may not be readily known without testing.

Conclusion

Identification of diacetyl and 2,3-pentanedione in flavoring formulations is important, as these chemicals could pose an inhalational hazard to workers. A majority of the 26 flavorings tested had diacetyl, 2,3-pentanedione, or both as volatile constituents in the headspace, but these chemicals were not listed on the SDSs. Inclusion of diacetyl and 2,3-pentanedione on SDSs would serve to inform downstream users so they could take steps to reduce exposure and potential respiratory disease. The headspace technique presented here is a sensitive tool to rapidly screen for volatile hazardous chemicals in flavoring formulations. This technique can also identify volatile components such as ethanol in the vehicle or contaminants from the source ingredients such as acetaldehyde. Facilities that use flavorings should be aware that constituents in flavorings may present a potential inhalational hazard even if not identified as such by the SDS. A precautionary approach is warranted when working with flavorings, including exposure monitoring and effective exposure control strategies such as containment and local exhaust ventilation.

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Table 1.

Headspace analyte concentrations (μg m^{-3}) for 26 liquid flavorings.

Flavor	Flavor description	Diacetyl concentration (μg m^{-3})	2,3-Pentanedione concentration (μg m^{-3})	2,3-Hexanedione concentration (μg m^{-3})	Acetaldehyde concentration (μg m^{-3})	Ethanol concentration (μg m^{-3})	D-limonene concentration (μg m^{-3})
1	Whiskey, caramel, vanilla	3.95×10^4	4.99×10^4	<LOD	1.57×10^5	2.90×10^6	<LOD
2	Butter rum	3.78×10^4	3.43×10^3	<LOD	1.69×10^4	6.79×10^5	2.08×10^3
3	Chocolate, caramel	3.58×10^4	4.93×10^3	<LOD	3.81×10^4	1.38×10^6	<LOD
4	Caramel	2.73×10^4	2.67×10^4	1.06×10^3	4.74×10^4	2.30×10^7	<LOD
5	Vanilla nut	1.46×10^4	9.98×10^3	<LOD	2.55×10^4	1.93×10^6	2.37×10^3
6	Caramel	1.36×10^4	2.32×10^4	<LOD	2.52×10^4	1.20×10^6	<LOD
7	Nut	1.31×10^4	4.50×10^3	<LOD	4.22×10^4	7.95×10^5	<LOD
8	Vanilla, nut	1.18×10^4	1.20×10^4	<LOD	1.40×10^4	1.23×10^6	4.06×10^3
9	Vanilla, nut	1.13×10^4	7.14×10^3	<LOD	1.19×10^4	1.37×10^6	<LOD
10	Hazelnut	1.07×10^4	1.67×10^4	<LOD	2.67×10^3	2.18×10^4	<LOD
11	Hazelnut	1.07×10^4	<LOD	<LOD	2.05×10^4	9.34×10^5	1.35×10^4
12	Hazelnut, vanilla	1.05×10^4	1.35×10^4	<LOD	2.96×10^4	1.04×10^6	<LOD
13	Almond, cherry	7.59×10^3	4.13×10^3	<LOD	1.54×10^4	1.45×10^6	<LOD
14	Chocolate, cherry	2.97×10^3	<LOD	<LOD	1.95×10^3	1.08×10^6	5.08×10^5
15	Chocolate, raspberry	1.30×10^3	1.67×10^3	<LOD	9.66×10^2	2.13×10^6	7.69×10^4
16	Almond, cherry	8.28×10^3	<LOD	<LOD	1.26×10^4	7.57×10^6	2.09×10^3
17	Vanilla, sugar	<LOD	<LOD	<LOD	<LOD[a]	1.23×10^8	<LOD
18	Caramel	5.84×10^4	<LOD	<LOD	1.02×10^5	6.87×10^6	1.99×10^3
19	Caffeine	<LOD	<LOD	<LOD	5.03×10^3	1.29×10^8	<LOD
20	Chocolate	<LOD	<LOD	<LOD	1.01×10^4	6.03×10^6	1.76×10^3
21	Caramel, vanilla	<LOD	9.90×10^4	<LOD	<LOD[a]	3.07×10^6	1.09×10^4
22	Caramel, vanilla	1.04×10^3	<LOD	<LOD	<LOD[a]	4.13×10^6	1.36×10^4
23	Hazelnut	5.17×10^3	<LOD	<LOD	9.49×10^4	8.98×10^4	1.84×10^3
24	Oatmeal cookie	1.07×10^4	3.79×10^5	<LOD	3.55×10^3	2.23×10^6	1.86×10^3

Flavor	Flavor description	Diacetyl concentration (μg m^{-3})	2,3-Pentanedione concentration (μg m^{-3})	2,3-Hexanedione concentration (μg m^{-3})	Acetaldehyde concentration (μg m^{-3})	Ethanol concentration (μg m^{-3})	D-limonene concentration (μg m^{-3})
25	Nut	6.37×10^3	<LOD	<LOD	3.24×10^4	3.44×10^6	1.98×10^3
26	Peppermint	5.72×10^2	<LOD	<LOD	2.16×10^3	2.31×10^4	<LOD

<LOD = below the detection limit (all in μg m^{-3}) of 3.2×10^2 for diacetyl, 4.8×10^2 for 2,3-pentanedione, 9.8×10^2 for 2,3-hexanedione, and 1.6×10^3 for D-limonene.

[a]<LOD = below the detection limit of 3.2×10^3 μg m^{-3} for acetaldehyde, which is 10 times higher than typical detection limit of 3.2×10^2 because of lower injection volume used for high ethanol headspace concentration of sample.