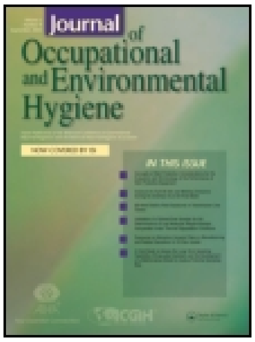

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Analytical Performance Criteria

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Analytical Performance Criteria
Field Evaluation of Diacetyl Sampling and Analytical Methods

INTRODUCTION

Diacetyl and acetoin are ketones that are used extensively in the flavoring and food production industries. Both compounds are monitored in the workplace to assess exposures, to aid in the selection of respirators, and to evaluate the effectiveness of ventilation and other control procedures. Researchers from the National Institute for Occupational Safety and Health (NIOSH) published methods to sample and analyze airborne concentrations of diacetyl and acetoin in workplaces.(1) Recent laboratory investigations indicate that the diacetyl method is affected by humidity, resulting in an underestimation of true diacetyl concentration.(2)

The effects of humidity on the collection and subsequent desorption of organic compounds on solid sorbent media has been investigated previously. McCammon and Woebkenberg(3) describe the effects of humidity on both silica gel and carbon molecular sieve. The polar nature of silica gel causes it to both adsorb water vapor and show a decrease in breakthrough capacity for non-water-soluble substances with increasing humidity. Carbon molecular sieves retain adsorbed species according to molecular size, and small organic compounds with molecular size similar to water must compete for sorption sites in an equilibrium at least partially based on concentration, which favors adsorption of water. In a study more specific to this effect, Karbiwnyk et al.(4) found that water vapor can interfere significantly in the measurement of volatile organic compounds using solid sorbents of varying hydrophobic characteristics. That interference is attributed to a reduction in retention of analyte during sampling.

A compound-specific change in minimum detectable level of analyte with increase in humidity was seen using an Environmental Protection Agency Carbotrap/Carboxen 1000 method,(5) although this change produced both increased as well as decreased detection levels. Similarly, a study of dual phase (vapor/particulate) pesticide sampling(6) concluded that a competitive mechanism seems to exist "between water molecules in gas phase and pesticides to adsorb on the receiving sites of the particles." The effect of humidity on the collection of volatile polar organic compounds using carbon molecular sieve tubes may have a threshold below which humidity is not an issue, although that threshold seems to vary with sorbent material and possibly with analyte.(7)

To aid in the evaluation of sampling and analytical methods for diacetyl, a field comparison between new and existing sampling collection methods was conducted. Side-by-side field samples were collected and analyzed according to NIOSH method 2557, OSHA method PV 2118, and a modified version of the Occupational Safety and Health Administration (OSHA) method. Because many of these samples were analyzed for acetoin as well as diacetyl, data are presented for both measurements in this report.

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TABLE I. Sites 1 and 2 Diacetyl and Acetoin Data

Sample Location	Diacetyl Analytical Results (ppm) NIOSH	Diacetyl Analytical Results (ppm) Modified OSHA	Acetoin Analytical Results (ppm)^A NIOSH
A	0.04	0.11	0.01
B	0.02	0.04	0.03
B	0.07	0.08	0.04
B	0.04	0.12	0.02
C	0	0.08	0.03
C	0.1	0.15	0.05
C	0.01	0.04	0.01
D	0.42	0.54	0.02
D	0.08	0.16	0.01
D	0	0.04	0.01
E	0	0	0.04
E	0.02	0.16	0.04
E	0	0	0.05
F	0.17	0.35	0.10
F	0.02	0.07	0
G	0.26	0	0.08
G	0.39	0.48	0.10
G	0	0.52	0.05
H	0.01	0	0.09
H	1.05	1	0.26
H	0.05	0.37	0.03
I	0.02	0.04	0.12
I	0.01	0	0.01
I	0.04	0	0.08

NIOSH: Samples analyzed according to NIOSH method 2557.
Modified OSHA: Samples analyzed according to modified OSHA method PV2118.
^{A}During Surveys 1 and 2, acetoin samples were analyzed only by the NIOSH method.

This evaluation was conducted as part of an investigation of occupational exposures to diacetyl and other food flavorings at two flavoring manufacturing facilities. The primary objective of these surveys was to characterize potential occupational exposures and identify common work tasks, plant processes, and procedures within the flavoring industry. These surveys also provided an opportunity to compare sampling methods, analytical methods, and field procedures. The lessons learned have provided the basis for refined methods that are employed in our current research program.

SAMPLING AND ANALYTICAL METHODS

This evaluation, conducted using the protocol described below, was a field comparison of three sampling and analytical methods for diacetyl in workplace air. These methods were the NIOSH method 2557/2558, an existing OSHA method PV 2118, and a modified version of the OSHA method PV2118. Details of each are available in their respective references, and a summary of each is presented here for comparison. NIOSH method 2557 for diacetyl$^{(8)}$ and NIOSH method 2558$^{(8)}$ for acetoin are published as separate methods but use the same sampling procedures and analytical techniques but for two separate analytes. There is a difference in desorption solution employed, with diacetyl (2557) acetoin (2558) methods using acetone/methanol at ratios of 99:1 and 95:5, respectively. One set of samples was collected for simultaneous analysis for both compounds following desorption with 99:1 acetone/methanol. For the purposes of this column, the analytical method is referred to as NIOSH method 2557.

NIOSH method 2557 calls for the collection of sample on 150/75 mg Anasorb carbon molecular sieve solid sorbent tube (cat. no. 226-121, SKC Inc., Eighty Four, Pa.) at a calibrated flow rate between 10 and 200 mL/min for a sample volume between 1 and 10 L. Samples were shipped cold (5°C), stored in the dark and analyzed within 7 days of collection. The individual sections of each tube were placed in separate vials and desorbed with 1 mL of a 1% methanol/ acetone solution (method 2558 calls for 5% methanol solution). Analysis was by GC/FID using a 60M Stabilwax 1.0 μm film thickness column.

OSHA method PV2118$^{(9)}$ uses two 150/75 mg silica gel tubes in series (cat. no. 226-10, SKC) at a recommended flow rate of 50 mL/min for 1 hr. Each section of these tubes is placed in separate vials for desorption with 1 mL of a 95% ethanol/5% water solution. Analysis was by GC/FID using a 60M DB-5 1.5 μm film thickness column.

The third technique evaluated, a "modified OSHA" method, differs from OSHA PV2118 only in that the sample is collected on larger silica gel sorbent tubes (400/200 mg silica gel tubes, cat. no. 226-10-03, SKC), which require 2 mL of desorbing solution. The expectation is that the larger silica gel beds will enable longer duration samples without resulting in breakthrough.

Test Procedure

Three site visits were made at two facilities that mix and formulate food flavorings. A total of 54 area air samples for diacetyl and 30 area air samples for acetoin were collected in work areas such as liquid production, powder production, warehouse storage, quality assurance, and spray drying operations. Relative humidity and temperature data were collected using HOBO Pro Model H08-032-08 temperature and humidity dataloggers (Onset Computer Corp., Bourne, Mass.) for Site 3. All sampling pumps were calibrated in accordance with the sampling methods using a Bios Drycal DC-LITE, model DCL-M primary flow standard (BIOS, Butler, N.J.).

During the first two site visits, 24 time-weighted average (TWA) air samples of 8 hr each were collected over 3 consecutive days using battery-powered model 210-1002 personal sampling pumps (SKC). Samples were collected for 8 hr at a flow rate of approximately 0.1 L/min onto the carbon molecular sieve and silica gel media described above. During the third site visit, 30 TWA air samples of 2 hr each were collected throughout 2 consecutive days using battery-powered model

TABLE II. Site 3 Diacetyl and Acetoin Data

	Diacetyl (ppm)			Acetoin (ppm)					
Area	NIOSH	OSHA	Modified OSHA	NIOSH	OSHA	Modified OSHA	Temp°F	Relative Humidity (%)	Absolute Humidity
J	0.05	0.65	0.63	0	0.29	0.24	75	54	76
J	0	0.25	0.21	0	0	0	76	49	74
J	0	0.09	0.10	0	0	0	79	45	72
J	0	0.26	0.28	0.07	0	0.26	73	57	72
J	0	0.06	0.10	0	0	0.20	78	52	86
J	0.57	1.43	1.58	0.08	0	0.13	83	40	70
K	0	0.89	0.67	0.06	0	0	75	53	70
K	0	1.16	1.04	0	0	0	76	47	65
K	0	0.28	0.26	0	0	0	80	43	70
K	0	0.58	0.56	0	0	0	75	57	75
K	0	0.36	0.34	0.06	0	0	79	50	78
K	0	0.30	0.30	0	0	0	81	47	75
L	0	0.40	0.38	0	0	0.13	NC	NC	—
L	0	0.19	0.16	0	0	0	77	45	67
L	0	0.08	0	0	0	0	80	41	64
L	0	0.37	0	0	0	0	74	53	72
L	0	0.24	0	0	0	0	77	51	78
L	0.04	0.20	0	0	0	0	81	44	76
M	0	0	0	0	0	0	75	46	63
M	0	0	0	0	0	0	80	40	63
M	0	0	0	0	0	0	83	40	70
M	0	0	0	0	0	0	75	57	78
M	0	0.06	0.06	0	0	0	NC	NC	—
M	0.08	0.10	0.14	0	0	0	NC	NC	—
N	0.53	4.82	6.33	0.17	0.41	0.30	NC	NC	—
N	0	0	0	0.09	0	0.37	82	43	75
N	0.06	0	0	0.12	0	0	84	37	76
N	0	0	0.04	0.09	0	0.18	77	50	72
N	0.03	0	0.03	0.09	0	0.19	83	42	82
N	0.04	0	0	0.07	0	0	88	34	68

NIOSH: Samples analyzed according to NIOSH method 2557.
Modified OSHA: Samples analyzed according to a modified OSHA method PV2118.
OSHA: Samples analyzed according to OSHA method PV2118.
NC: Information not collected.

210-1002 personal sampling pumps (SKC). Because selected results from site visit 2 exhibited breakthrough of the front tube due to extended sampling volumes, the sample volumes were reduced for site visit 3. Samples were collected for 2 hr at a flow rate of approximately 0.05 L/min onto the carbon molecular sieve, 150/75 mg silica gel media, and 400/200 mg silica gel media described above. Area samples were collected near employee workstations to maximize similarity in sample composition.

Laboratory reports provided sample results in micrograms (μg) of analyte per sample. Analytical results were converted to an airborne concentration by dividing by the air volume associated with the sample (mg/m^3), then converting to parts per million (ppm) by volume using the gram molecular weight of the analyte at standard temperature and pressure. All calculations to determine airborne concentrations were conducted using SAS (9.1.3, SAS Institute).

Because each analytical method had a different limit of detection (LOD), sampling results that were below the LOD for the sampling methods used were assigned a value of zero for statistical analysis. An adjustment was further complicated as the OSHA methods used two media tubes, whereas the NIOSH method used one. It was deemed inappropriate to adjust by dividing by 2 or the square root of 2, as the different LOD and tube numbers would unfairly affect the method comparison.

TABLE III. Descriptive Statistics

Analyte	Method	No. Samples	% Non-Detect	Mean	SD	Min	Max
			Site Visits 1 and 2				
Acetoin	NIOSH	24	66	NR	NR	0	0.259
	Modified OSHA	0					
Diacetyl	NIOSH	24	21	0.117	0.231	0	1.05
	Modified OSHA	24	25	0.181	0.246	0	1.00
			Site Visit 3				
Acetoin	NIOSH	30	67	NR	NR	0	0.173
	OSHA	30	93	NR	NR	0	0.408
	Modified OSHA	30	70	NR	NR	0	0.365
Diacetyl	NIOSH	30	73	0.046	0.139	0	0.574
	OSHA	30	30	0.426	0.902	0	4.82
	Modified OSHA	30	37	0.440	1.169	0	6.33

Note: NR, Given the high censoring rate for acetoin, the mean and standard deviation are not reported. Analytical results (last four columns) in units of parts per million (ppm).

Differences between the three sampling methods were determined using the sign rank test.

RESULTS

Table I shows measurement results for diacetyl and acetoin from the initial two survey sites. Table II shows results for these compounds from the third site as well as temperature, relative humidity, and absolute humidity measurements. For tabulated data, the analytical techniques are referred to as NIOSH (NIOSH method 2557), OSHA (OSHA method PV 2118), and modified OSHA (the modified version of OSHA method PV2118).

Table III shows the descriptive statistics and non-detection rates, respectively, for the site visits. The differences in the means of measurements made by each technique can be seen in these tables. It is noted that 31% of the samples collected on silica gel tubes (modified OSHA method) were below the LOD for the diacetyl analytical technique, whereas 50% for the samples collected on carbon molecular sieve (the NIOSH method) were below the LOD.

TABLE IV. Signed Rank Median Difference Diacetyl Analytical Methods

Methods Compared	Diacetyl P-value[A]
OSHA and NIOSH	<0.0001
Modified OSHA and NIOSH	<0.0001
OSHA and Modified OSHA	0.297

OSHA: Samples analyzed according to OSHA method PV2118.
NIOSH: Samples analyzed according to NIOSH method 2557.
Modified OSHA: Samples analyzed according to a modified OSHA method PV2118, including larger silica gel media (400 mg/200 mg).
[A] P-values were calculated according to Signed Rank test comparing median difference between method results.

Because the data were not normally distributed, nonparametric tests were used in the analyses. Table IV shows the comparison of each method to the others. Statistically significant differences were observed between NIOSH method 2557 and the OSHA and modified OSHA techniques for diacetyl. The latter two methods were not significantly different from one another, and both indicated significantly higher diacetyl concentrations in the field as compared with NIOSH method 2557 within ranges of humidity 31–65%. NIOSH method 2557 also yielded a large non-detect rate compared with the other methods (Table III).

For the acetoin comparisons, the number of detectable samples was low for all of the methods ($n = 2$, OSHA method; $n = 9$ modified OSHA; $n = 10$ NIOSH method). The small number of samples precludes a valid method comparison. Further method validation for acetoin should be conducted both in the laboratory and in field settings.

Spearman correlation coefficient analyses were used to compare the diacetyl analytical techniques under investigation with the effects of temperature, relative humidity and absolute humidity (mass of water per volume of air) analyzed independently (Table V). As relative humidity increases, the difference between the OSHA and NIOSH methods also increases (p-value = 0.010), as does the difference between the modified OSHA method and the NIOSH method (p-value = 0.055). As temperatures decreased, the mean difference between the OSHA and NIOSH methods increases (p-value = 0.019), as does the mean difference between the modified OSHA method and the NIOSH method (p-value = 0.013). Absolute humidity was not significantly associated with differences between the methods.

DISCUSSION

Although this data set is relatively small, it highlights many important issues for diacetyl sampling. Importantly, the field comparison data presented concur with laboratory

TABLE V. Spearman Correlations for Diacetyl Samples

	Humidity		Temperature	
Difference Between Methods	Correlation Coefficient	P-value[A]	Correlation Coefficient	P-value[A]
OSHA and NIOSH	0.61	0.001	−0.58	0.002
Modified OSHA and NIOSH	0.53	0.005	−0.48	0.013
OSHA and Modified OSHA	0.210	0.304	−0.307	0.126

OSHA: Diacetyl samples analyzed according to OSHA method PV2118.
NIOSH: Diacetyl samples analyzed according to NIOSH method 2557.
Modified OSHA: Diacetyl samples analyzed according to a modified OSHA method PV2118, including larger silica gel media (400mg/200mg).
[A] P-values were calculated according to Spearman correlation.

recovery studies for NIOSH method 2557 for diacetyl. Both demonstrate that NIOSH method 2557 underestimates true diacetyl concentrations as relative humidity increases. What is equally troubling is that the non-detection rate for the NIOSH method is higher than the OSHA or modified OSHA method. Above 43% relative humidity, the NIOSH method non-detection rate was 85%, whereas the OSHA method was 15% and the modified OSHA method was 25%. At moderate relative humidity, NIOSH method 2557 shows no detectable diacetyl when significant concentrations are present using the OSHA or modified OSHA methods. It is of concern that measurable concentrations were observed using the OSHA or modified OSHA methods while the corresponding NIOSH measured values were below the detection limit.

These data also illustrate that both temperature and relative humidity are significantly correlated with a greater difference (i.e., greater underestimation by the NIOSH method) between the diacetyl methods. In contrast, the data suggest that absolute humidity is not related. These data suggest that both the temperature and relative humidity at the time of collection, and not moisture content alone, are important to this phenomenon. Although temperature and relative humidity are independent variables, we could not separate their effect in our analysis (correlation coefficient: $r = -0.89$). As it turned out, our lowest relative humidity measurements were observed on days with the highest temperatures, while the highest relative humidity measurements were observed during time periods with the lowest temperatures. Because the majority of laboratory evaluations have been completed at ambient temperature, temperature differentials should also be investigated in efforts to create a correction factor for the NIOSH method.

CONCLUSIONS

Recent laboratory investigations indicated that the NIOSH method for diacetyl is affected by relative humidity, resulting in an underestimation of true concentrations. A NIOSH laboratory-based study and a chamber study with generated atmospheres are also under way to investigate the potential development of a correction factor for previously collected data with the NIOSH method. The results of the field work presented here confirm the tendency of the NIOSH method to underestimate the true concentration of diacetyl. These data indicate that an increased relative humidity produces decreased sampling efficiency for diacetyl using the NIOSH method discussed here. However, no mathematical correlation was found in this data set that would produce an adjustment factor to allow for correction of results to compensate for that decrease in efficiency.

Although data presented here do not provide validation of the OSHA or modified OSHA techniques, there was no evidence that either of these sampling and analytical methods had a tendency to underestimate diacetyl concentration under the conditions encountered. It is recommended that NIOSH method 2557 not be used to determine the concentration of airborne diacetyl. Until a new method is developed, NIOSH investigators currently use the modified OSHA method with 400/200 mg media and collect measurement for both temperature and relative humidity during investigations or research studies.

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