Backup Data Report for Revised Vinyl Acetate Analytical Method, NMAM 1453

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RATIONALE: Revision of this method became necessary due to changes in supplies of sorbent tubes provided by manufacturers. It was necessary to reevaluate the method using currently commercially available sorbent tubes, which replaced those used in previous method evaluations, ORBO-90.

Carbon molecular sieve sampling tubes (ORBO-92 adsorbent tube, 160/80 mg., Supelco) were loaded with known amounts of vinyl acetate. These tubes were desorbed with 1 mL of methylene chloride/methanol (95:5 v/v) for 30 minutes and analyzed by gas chromatography (GC) with flame ionization detection (FID). The GC analytical parameters were as follows:

Gas Chromatograph:	Hewlett-Packard Model 5890A equipped with a flame ionization detector
Injector Temperature:	210 °C
Detector Temperature:	260 °C
Column:	30 m x 0.32 mm fused silica capillary column coated internally with 1.00 µm (5% - Phenyl)-methylpolysiloxane
Oven Condition:	35 °C hold 5 minutes; 5 °C/minute to 50 °C, hold one minute
Carrier Gas:	Nitrogen, split flow 21.0 mL/min

Experiments and statistical computations were carried out in accordance with E. R. Kennedy et al., *Guidelines for Air Sampling and Analytical Development and Evaluation*, CDC/NIOSH: Cincinnati (1995); DHHS (NIOSH) Publ. No. 95-117. A summary of the calculations performed and the data obtained follows.

A. Precision, Bias, & Accuracy Study

Two sets of data: spikes and generated samples

Data were collected using spiked sample tubes as well as samples collected using generated test atmospheres.

1. Analysis of spiked samples was used to calculate CV1 based on mean % recovery
2. Sampling and analysis data from generated test atmospheres was used to (a) calculate CV2 based on pooled mean values, and (b) calculate mean bias and method accuracy.

User check procedures

The User Check study was carried out in accordance with CEMB SOP 504.

Bias Precision and Accuracy Estimation

For details on procedures used for data evaluation, refer to NMAM Chapter P & Documentation of the NIOSH Validation Tests (77-185):

$$bias = (c - C) / C$$

$$TRSD = \sigma / C$$

$$A = 1.960 \times \sqrt{bias^2 + TRSD^2}, \ if \ |bias| < TRSD / 1.645;$$

$$A = |bias| + 1.645 \times TRSD, \ otherwise.$$

CV1: CV based on spiked samples - Experimental error due to analysis

CV2: CV based on generated data - Experimental error due to sampling and analysis

(CVp)**2=(0.05)**2=0.0025 - Uncertainty component due to sampling pump error

CVT: CV total

(CVT)**2=(CV2)**2+(CVp)**2

CV_ADE=Square root[(n+1/n)]*CV1

Tables summarizing the performance data hereby follow:

Vinyl Acetate
Analytical – Desorption Efficiencies (D.E.) – Data summary

Obs	sequence	LOD	LOQ	sample	found	level	Taken	% Recovery
1	10898-CA	0.5	1.6	5	45.2	1	46.7	96.788
2	10898-CA	0.5	1.6	6	43.4	1	46.7	92.9336
3	10898-CA	0.5	1.6	13	40.6	1	46.7	86.9379
4	10898-CA	0.5	1.6	18	43.3	1	46.7	92.7195
5	10898-CA	0.5	1.6	20	45.4	1	46.7	97.2163
6	10898-CA	0.5	1.6	21	46	1	46.7	98.5011
7	10898-CA	0.5	1.6	2	88.2	2	93.4	94.4325
8	10898-CA	0.5	1.6	4	90.6	2	93.4	97.0021
9	10898-CA	0.5	1.6	8	87.5	2	93.4	93.6831
10	10898-CA	0.5	1.6	12	86.4	2	93.4	92.5054
11	10898-CA	0.5	1.6	17	86.5	2	93.4	92.6124
12	10898-CA	0.5	1.6	19	88.6	2	93.4	94.8608
13	10898-CA	0.5	1.6	3	189	3	205.5	91.9708
14	10898-CA	0.5	1.6	9	201	3	205.5	97.8102
15	10898-CA	0.5	1.6	11	195	3	205.5	94.8905
16	10898-CA	0.5	1.6	14	183	3	205.5	89.0511
17	10898-CA	0.5	1.6	15	191	3	205.5	92.944
18	10898-CA	0.5	1.6	16	201	3	205.5	97.8102

Mean % recovery, Grubb test, 95% CI of mean % recovery

Level	Taken	mean	m_found	std	n	cv	outlier	LL	UL
1	46.7	94.1827	43.983	4.26208	6	0.045253	no	90.3913	97.9742
2	93.4	94.1827	87.967	1.67334	6	0.017767	no	92.6942	95.6713
3	205.5	94.0795	193.333	3.45007	6	0.036672	no	91.0104	97.1486

Bias RSD, and RSD (CV)

n	k	% Recovery	est_bias	est_rsd (CV_1)	(CV_1)**2	CV_ADE
3	1	94.16	-0.05852	0.020299	0.001236	0.023439

Sampling and Analysis – Data summary

Obs	Level	sample	Humidity	Front	Back	Found	Taken	flow_rate	% Recovery
1	1	1	L	85.2	0	85.2	89	98.4	95.8
2	1	2	L	91.3	0	91.3	89	105	103
3	1	3	L	89.9	0	89.9	89	96.3	101
4	1	4	L	90.2	0	90.2	89	94	101
5	1	1	H	81.5	0	81.5	89	98.1	91.6
6	1	2	H	85.3	0	85.3	89	102	95.9
7	1	3	H	79.3	0	79.3	89	99	89.2
8	1	4	H	82.3	0	82.3	89	99	92.5
9	2	1	L	199	0	199	200	102	99.5
10	2	2	L	196	0	196	200	101	98
11	2	3	L	205	0	205	200	93.9	103
12	2	4	L	202	0	202	200	106	101
13	2	1	H	175	0	175	200	103	87.5
14	2	2	H	188	0	188	200	96.9	94
15	2	3	H	201	0	201	200	106	101
16	2	4	H	174	0	174	200	91.7	87
17	3	1	L	530	0	530	623	103	85.1
18	3	2	L	561	0	561	623	104	90
19	3	3	L	573	0	573	623	106	92
20	3	4	L	576	0	576	623	95.8	92.5
21	3	1	H	626	0	626	623	92.5	100
22	3	2	H	620	0	620	623	102	99.5
23	3	3	H	614	0	614	623	108	98.6
24	3	4	H	632	0	632	623	99.7	101
25	4	1	L	1050	0	1050	1110	106	94.6
26	4	2	L	1000	0	1000	1110	100	90.1
27	4	3	L	1090	0	1090	1110	101	98.2
28	4	4	L	1110	0	1110	1110	100	100
29	4	1	H	1040	0	1040	1110	96.8	93.7
30	4	2	H	1130	0	1130	1110	97.6	102
31	4	3	H	1040	0	1040	1110	101	93.7
32	4	4	H	1110	0	1110	1110	98.3	100

Mean % recovery, Grubb test, 95% CI of mean % recovery

Humidity	level	Taken	m_found	m_recovery	n	CV_found	outlier	LL	UL
H	1	89	82.1	92.3	4	0.030	no	89.28	95.32
H	2	200	184.5	92.375	4	0.069	no	85.21	99.54
H	3	623	623	99.775	4	0.012	no	98.68	100.87
H	4	1110	1080	97.35	4	0.043	no	92.67	102.03
L	1	89	89.15	100.2	4	0.03	no	96.84	103.56
L	2	200	200.5	100.375	4	0.019	no	98.05	102.70
L	3	623	560	89.9	4	0.038	no	86.22	93.58
L	4	1110	1062.5	95.725	4	0.046	no	90.96	100.49

Bias, RSD, Accuracy Estimates and 95 % CI Estimates

%rRecovery	n	(CV2)**2	CV2	CVT
96	8	0.00156	0.0395	0.063731

n	K	est_bias	est_rsd	Accuracy	Acc_U95
8	2	-0.04022	0.039518	0.10523	0.14127

Conclusion: Based on the bias, precision, and accuracy results, this method meets the NIOSH criteria for method accuracy (Kennedy et al., 1995).

B. Sample Storage Stability Study

Spiked samples of vinyl acetate were stored at two temperatures: room temperature and 4 °C, and at two concentration levels: 'Low' (187 micrograms) and 'High' (747 micrograms). For the room temperature, data were collected at days 1 and 7. For the cold temperature, data were collected for days 1,7,14, and 30.

Analysis of Variance (ANOVA) procedures followed by Tukey's multiple comparison technique was used to test for difference in recovery among the storage days (1, 7, 14, 30). The test was performed at the 5% significance level.

Statistically significant differences were found:

1. 4 °C and high concentration, the recovery of day 30 is higher than those of days 1, 7, 14.
2. 4 °C and low concentration, the recovery of days 30 and 14 are higher than those of the days 1, 7.

When day 30 was excluded, the ANOVA shows no statistically significant difference in % recovery among days 1, 7, and 14 except for one case: cold temperature and low concentration, the recovery of days 14 remains higher than those of the days 1, 7.

However, the individual % recovery of day 30 results are mostly with the acceptable ranges of the 90%-110% with two exceptions (112%* and 111%* at the 4 °C -High loading). In any case, the mean percent recoveries are all in the acceptable ranges of the 90%-110% **. This leads to a conclusion of acceptable recovery for up to 1 month storage

Vinyl Acetate – User check Storage Data

Obs	temp	Level	day	Samp	Result µg	Spiked µg	Recovery	pt_bias
1	C	H	1	‘1-1	760	747	101.74	1.7403
2	C	H	1	‘1-2	681	747	91.165	-8.8353
3	C	H	1	‘1-3	703	747	94.11	-5.8902
4	C	H	1	‘1-4	691	747	92.503	-7.4967
5	C	H	1	‘1-5	696	747	93.173	-6.8273
6	C	H	7	‘2-1	748	747	100.134	0.1339
7	C	H	7	‘2-2	711	747	95.181	-4.8193
8	C	H	7	‘2-3	727	747	97.323	-2.6774
9	C	H	7	‘2-4	770	747	103.079	3.079
10	C	H	7	‘2-5	727	747	97.323	-2.6774
11	C	H	14	‘3-1	632	747	84.605	-15.3949
12	C	H	14	‘3-2	674	747	90.228	-9.7724
13	C	H	14	‘3-3	680	747	91.031	-8.9692
14	C	H	14	‘3-4	696	747	93.173	-6.8273
15	C	H	14	‘3-5	769	747	102.945	2.9451
16	C	H	30	‘4-1	837	747	112.048*	12.0482
17	C	H	30	‘4-2	753	747	100.803	0.8032
18	C	H	30	‘4-3	807	747	108.032	8.0321
19	C	H	30	‘4-4	786	747	105.221	5.2209
20	C	H	30	‘4-5	833	747	111.513*	11.5127
21	C	L	1	‘1-1	171	187	91.444	-8.5561
22	C	L	1	‘1-2	176	187	94.118	-5.8824
23	C	L	1	‘1-3	173	187	92.513	-7.4866
24	C	L	1	‘1-4	167	187	89.305	-10.6952
25	C	L	1	‘1-5	171	187	91.444	-8.5561
26	C	L	7	‘2-1	173	187	92.513	-7.4866
27	C	L	7	‘2-2	173	187	92.513	-7.4866
28	C	L	7	‘2-3	171	187	91.444	-8.5561
29	C	L	7	‘2-4	174	187	93.048	-6.9519

30	C	L	7	‘2-5	173	187	92.513	-7.4866
31	C	L	14	‘3-1	184	187	98.396	-1.6043
32	C	L	14	‘3-2	185	187	98.93	-1.0695
33	C	L	14	‘3-3	193	187	103.209	3.2086
34	C	L	14	‘3-4	184	187	98.396	-1.6043
35	C	L	14	‘3-5	190	187	101.604	1.6043
36	C	L	30	‘4-1	189	187	101.07	1.0695
37	C	L	30	‘4-2	195	187	104.278	4.2781
38	C	L	30	‘4-3	190	187	101.604	1.6043
39	C	L	30	‘4-4	188	187	100.535	0.5348
40	C	L	30	‘4-5	202	187	108.021	8.0214
41	R	H	1	‘1-1	690	747	92.369	-7.6305
42	R	H	1	‘1-2	684	747	91.566	-8.4337
43	R	H	1	‘1-3	712	747	95.315	-4.6854
44	R	H	1	‘1-4	705	747	94.378	-5.6225
45	R	H	1	‘1-5	701	747	93.842	-6.158
46	R	H	7	‘2-1	661	747	88.487	-11.5127
47	R	H	7	‘2-2	739	747	98.929	-1.071
48	R	H	7	‘2-3	688	747	92.102	-7.8983
49	R	H	7	‘2-4	782	747	104.685	4.6854
50	R	H	7	‘2-5	684	747	91.566	-8.4337
51	R	L	1	‘1-1	181	187	96.791	-3.2086
52	R	L	1	‘1-2	173	187	92.513	-7.4866
53	R	L	1	‘1-3	165	187	88.235	-11.7647
54	R	L	1	‘1-4	171	187	91.444	-8.5561
55	R	L	1	‘1-5	193	187	103.209	3.2086
56	R	L	7	‘2-1	183	187	97.861	-2.139
57	R	L	7	‘2-2	186	187	99.465	-0.5348
58	R	L	7	‘2-3	186	187	99.465	-0.5348
59	R	L	7	‘2-4	189	187	101.07	1.0695
60	R	L	7	‘2-5	190	187	101.604	1.6043

Summary Statistics of percent recovery

temp	level	day	Mean % Recovery	Min	max	N	Std
C	H	1	94.538	91.165	101.74	5	4.166
C	H	7	98.608	95.181	103.079	5	3.056
C	H	14	92.396	84.605	102.945	5	6.692
C	H	30	107.523**	100.803	112.048	5	4.667
C	L	1	91.765	89.305	94.118	5	1.757
C	L	7	92.406	91.444	93.048	5	0.586
C	L	14	100.107**	98.396	103.209	5	2.185
C	L	30	103.102**	100.535	108.021	5	3.104

R	H	1	93.494	91.566	95.315	5	1.517
R	H	7	95.154	88.487	104.685	5	6.552
R	L	1	94.438	88.235	103.209	5	5.78
R	L	7	99.893	97.861	101.604	5	1.484

C. Review of User Check for NMAM Method 1453-3, Vinyl Acetate

User check samples were prepared by the Quality Assurance group of the NIOSH/DART contract laboratory in order to evaluate the update of NIOSH Method 1453 (Vinyl Acetate). A total of twenty-one ORBO 92 sample tubes were spiked with vinyl acetate on January 13, 2009. The NIOSH contract industrial hygiene laboratory (Bureau Veritas) analyzed the samples on February 5, 2009. The procedure followed by the laboratory was as given in the method.

The limit of detection (LOD) was 0.5 µg/sample and the limit of quantitation (LOQ) was 1.6 µg/sample for vinyl acetate. The laboratory method blanks were none detected for vinyl acetate. The recoveries for the laboratory control samples were acceptable for vinyl acetate at 99.5%. The blind spikes were within the default limits of 80%-120% for vinyl acetate. Replicate analyses were within the 20% acceptable limit.

The table below summarizes the data from the independent laboratory report for vinyl acetate:

Sample ID	Spiked Amt	Amt found	Recovery	Ave Recovery	RSD
VA NMAM - 1	0 µg	ND	N/A		
VA NMAM - 7	0 µg	ND	N/A		
VA NMAM - 10	0 µg	ND	N/A		
VA NMAM - 5	46.7 µg	45.2 µg	96.8%		
VA NMAM - 6	46.7 µg	43.4 µg	92.9%		
VA NMAM - 13	46.7 µg	40.6 µg	86.9%		
VA NMAM - 18	46.7 µg	43.3 µg	92.7%		
VA NMAM - 20	46.7 µg	45.4 µg	97.2%		
VA NMAM - 21	46.7 µg	46.0 µg	98.5%	94.2%	4.5%
VA NMAM - 2	93.4 µg	88.2 µg	94.4%		
VA NMAM - 4	93.4 µg	90.6 µg	97.0%		
VA NMAM - 8	93.4 µg	87.5 µg	93.7%		
VA NMAM - 12	93.4 µg	86.4 µg	92.5%		
VA NMAM - 17	93.4 µg	96.5 µg	103.3%		
VA NMAM - 19	93.4 µg	88.6 µg	94.9%	96.0%	4.1%
VA NMAM - 3	205.5 µg	189 µg	92.0%		
VA NMAM - 9	205.5 µg	201 µg	97.8%		
VA NMAM - 11	205.5 µg	195 µg	94.9%		
VA NMAM - 14	205.5 µg	183 µg	89.1%		
VA NMAM - 15	205.5 µg	191 µg	92.9%		
VA NMAM - 16	205.5 µg	201 µg	97.8%	94.1%	3.7%

Overall this user check to update NMAM 1453 showed excellent performance, and the user check has been passed and is acceptable. It is recommended that the draft 3rd issue of method 1453 be accepted and placed into NMAM for publication.

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