BACKUP DATA REPORT FOR NIOSH 0501/5100

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Background

The previous issues of NIOSH Methods for gravimetric analysis, NIOSH 0500 and 5000, specified the use of polyvinyl chloride (PVC) filters housed in closed-face filter cassettes (CFCs) for collection of airborne particles for subsequent gravimetric analysis.[1] As described in these earlier versions of the NIOSH methods, the PVC filter is weighed before and after sample collection, with the reported weight of sampled particulate matter being the difference between pre- and post-weighing. However, airborne particles collected using CFCs can deposit elsewhere than on the PVC filter, and thus would not be included in gravimetric analysis of the filter alone.[2] An alternative technique for ensuring that internal non-filter deposits are included in the analysis is to collect airborne particles within an internal capsule, housed within the CFC, which is weighed in its entirety before and after sample collection. PVC capsules for gravimetric analysis of airborne particulate matter have been commercially available for several years. The filter capsules are designed to be inserted into 37-mm plastic CFC samplers on top of cellulose support pads, as illustrated in Figure 1. The evaluation described in this report was undertaken in order to provide necessary performance data for validation of the new NIOSH 0501 & 5100 methods, which is based on the use of PVC internal capsules. The validation protocol followed here is analogous to that which was carried out to validate the previous filters-only procedures for 0500 and 5000.[1]

Procedure

Polyvinyl chloride (PVC) Accu-caps® with 5-µm pore size PVC filters (Lot #11136-7DBPASK-104, SKC, Eighty-Four, PA) were allowed to equilibrate to room temperature and humidity in the laboratory under a dust cover box for at least two hours (most were equilibrated for 24 hours). Once equilibrated, the Accu-caps were weighed on a Mettler Toledo high-precision analytical balance (Model XP205DR, Greifensee, Switzerland) before spiking with certified reference material (CRM) dust; balance calibration was checked before each use with ASTM Class 1 weights. A ^{210}Po static control device (NRD, Grand Island, NY, USA) was used to eliminate electrostatic effects during weighing. The pre-spiked weight of each PVC Accu-cap was recorded to the nearest 0.1 mg. The Accu-caps were then were placed into two-piece SKC plastic cassettes (Lot #2039-7D6PASK-010) and were then sealed in the cassettes. For spiking with CRM, each cassette was connected to a personal sampling pump (Aircheck Sampler, Model #224-PCXR7, SKC) set to a calibrated flow rate of 2.5 ± 0.1 L/min.

The certified reference materials (CRMs) used were Standard Reference Material (SRM) 1648, Urban Particulate Matter (National Institute of Standards and Technology, Gaithersburg, MD) and Arizona Road Dust – Air Cleaner Test Dust (General Motors AC Spark Plug Division, Flint, MI). On glycine weighing paper, five different levels of CRM (4 mg, 2 mg, 1 mg, 0.5 mg, 0.1 mg), with 3 samples (minimum) at each level, were weighed to the nearest 0.1 mg. The test materials were loaded into separate Accu-caps via 23-mm plastic micro funnels (Poly Micro Funnel, The Science Company, Denver, CO), which were inserted into the inlets of the cassettes housing the Accu-caps. Once the weighed test material was poured into the funnel, the sampling pump was activated so that the particulate material was drawn completely out of the funnel and into the PVC Accu-cap housed within the cassette. The pump was

1 NIOSH Manual of Analytical Methods, 4th ed. NIOSH: Cincinnati, OH (2003).

2 Ashley K, Harper M, "Closed-face filter cassette (CFC) sampling – Guidance on procedures for inclusion of material adhering to internal sampler surfaces," J. Occup. Environ. Hyg. 10: D29-D33 (2013).

used to pull air through the system for approximately one minute, which enabled complete transfer of CRM from the funnel into the Accu-caps.

The cassettes were removed from the pump and then the PVC Accu-caps were removed from the cassettes using a cassette opener and were then weighed individually. The mass of the spiked Accu-caps for all replicate levels were weighed using the same balance and were recorded as mass for Day 1. Collection efficiency was calculated by dividing the collected mass of the test material by the total material weight before transfer to the Accu-cap. For each of the sets of CRM samples (i.e., SRM 1648 and Arizona Road Dust – Air Cleaner Test Dust), 6 lab blanks were weighed and sealed, recording their Day 1 masses as well.

Once the Day 1 masses were recorded for all replicate samples and lab blanks, the PVC Accu-caps (sealed in their labeled testing cassettes) were stored in cardboard boxes (organized by sample set) for a 4-week storage study. On 7-day intervals, the Accu-caps were weighed and the results recorded for comparison to their Day 1 mass. Percent change in mass was calculated by subtracting the Day1 mass from the Day 7 (and then Day 14, 21, and 28) masses, dividing by the Day 1 mass and multiplying by 100%.

Pressure drop experiments[3] were carried out (by Dr. T. Lee, NIOSH/HELD) in order to further characterize the PVC Accu-caps. Five different Accu-caps were placed in 37-mm plastic cassettes and the absence of leakage was verified before measurement. The pressure drop from a 5-µm pore PVC filter was measured for comparison.

Results

Storage stability

Storage stability data are presented in Tables 1 and 2 (for NIST SRM 1648 and Arizona Road Dust sample sets, respectively). In each table, sample mass (i.e., mass of internal capsule plus mass of added dust) is indicated by descending order for each spiking level (4 mg; 2 mg; 1 mg; etc.). Laboratory blank data are also included and are indicated in the tables. Percent changes in weights were generally less than 5 percent for SRM 1648 (Table 1) at the 1, 2, and 4mg sample loadings but are quite a bit higher at the 0.5 and 0.1 mg levels. SRM 1648 seemed to have greater variability especially at the levels near the LOD/LOQ. For the Arizona Road Dust SRM samples the percent changes were lower at the 0.5, 1, 2, and 4 levels. The percent changes for the 4, 2 and 1mg sample was ≈1. The 0.5 mg level was higher at ≈8 percent for Arizona Road Dust (Table 2) for time periods up to 28 days.

Limits of detection and quantitation

The estimated method detection limit (MDL) and limit of quantitation (LOQ) of the gravimetric procedure was obtained from PVC Accu-cap blank data based on Day 1 to 7 weight changes (n=12). The overall mean weight change was -0.000013 g and the standard deviation was 0.000016. Thus the estimated MDL is obtained by three times this value or 0.000048 g, ≈0.05 mg (50 µg). The estimated LOQ is ten times the standard deviation of blank results, i.e., ≈0.16 mg (160 µg).

Analytical recovery

Measured recoveries of spiked Accu-caps are shown in Table 3 for capsules spiked with ≈1 mg, ≈2 mg and ≈4 mg of SRM 1648 and Arizona Road Dust. Recoveries were computed as the ratio of the amount of material weighed after spiking to the amount of material weighed prior to spiking. (These gravimetric measurements attempted to account for CRM losses onto weighing paper during spiking; recovery calculations of course subtracted the weights of Accu-caps obtained before spiking was carried out.) Measured recoveries for these spiked PVC Accu-caps ranged from ≈92% to ≈102%. (See Table 3)

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3 Breuer, D., "Flow resistance of samplers for personal monitoring in work areas and requirements for sampling pump performance," J. Occup. Environ. Hyg. 9: D25-D32 (2012).

Pressure drop tests

At sampling pump flow rates of 2 and 4 L/min, the average pressure drop values for PVC Accu-caps were 0.134 (±0.008) and 0.270 (±0.026) psi, respectively. For the PVC filter, these values were 0.154 and 0.302 psi for flow rates of 2 and 4 L/min, respectively.

Observations

Sample stability and analytical range

The data presented in Tables 1 and 2 illustrate the long-term weight stability of blank and spiked PVC Accu-caps for up to at least 28 days. For loadings of ≈1mg and greater, measured weights are all within 100% ± 5% for NIST SRM 1648 and Arizona Road Dust (Air Cleaner Test Dust). Arizona Road Dust is observed to be more weight stable than NIST SRM 1648 (Tables 1-2), and this is attributed to trace moisture loss / off-gassing from the latter material, especially during the first week of storage. Despite this, the excellent weight stability of the PVC internal capsule material is clearly seen. The weight stability demonstrated by the PVC capsules is greatly superior to that of plastic cassettes, which have been shown to adsorb or desorb significant amounts of moisture (as much as 1-2 mg over a several-day period), depending on humidity conditions[9]

Analytical Range

At loading (spiking) levels of ≈1 mg and greater, recoveries of SRM 1648 and Arizona Road Dust from PVC Accu-caps (spiked as described above) were >90% (Table 3). However, for spiking levels of ≈0.5 mg and below, the measured recoveries were inconsistent, varying from <40% to >500% (data not shown). To investigate whether there was any appreciable background dust being collected during spiking, air was drawn through a completely separate set of blank Accu-caps. But these experiments did not show any statistically significant differences between the blank capsules, indicating that there was no measureable dust collected. It should also be noted that the MDL for all sample loadings was above the expected level for the gravimetric method using the Accu-cap samplers. Causes of high imprecision at spiking levels of ≈0.5 mg are ascribed to inherent difficulties in accurately weighing and transferring masses of CRMs below 1 mg.

Pressure drop tests

Measured pressure drops for PVC Accu-caps and the PVC filter were comparable. No collapse or other physical failures of the Accu-caps were observed when using sampling pump flow rates of up to 5 L/min. At sampling pump flow rates of 2 and 4 L/min, the average pressure drop values for PVC Accu-caps were 0.924 (±0.055) kPa and 1.86 (±0.18) kPa, respectively. For PVC filters, these values were 1.06 kPa and 2.08 kPa for flow rates of 2 and 4 L/min, respectively. (Similar pressure drop results for PVC filters have been reported elsewhere.[3])

Special precautions

Because of the generally delicate nature of the PVC Accu-caps, there should be as little pressure on the plastic top as possible (even little pressure created a sizable indentation on the top of the Accu-caps). Deformation of the Accu-caps could lead to a misalignment of the collection holes of the Accu-cap with the cassette inlet ports, which in turn could result in incomplete aerosol collection and poor collection rates. Accu-caps having misaligned inlet holes were not used in this evaluation. During sample preparation, when removing the PVC Accu-caps from the cassettes in which they were housed, the Accu-caps tended to adhere to the top-half section of the cassette. In the method, it is suggested that the filters be removed by using a scalpel blade or something similar, but for the Accu-caps, this is not always effective. When the Accu-caps did become stuck, they required more than a little applied pressure to remove them from the cassettes. To remove them, it was often necessary to use a forceps and, with gloved fingers, physically grab the outer plastic edge of the Accu-cap and pull as hard as practicable. Because of the effort that was required to remove the Accu-caps from the cassettes, misplacement or slippage of the forceps can occur, often resulting in tears of the filters of the Accu-caps. Accu-caps that were damaged during removal from cassettes were not used in this evaluation.

It was observed that some Accu-caps were prone to sticking inside the cassettes, and this was ascribed to their non-uniformity in manufacture. From batch to batch, or even Accu-cap to Accu-cap, the appearance and construction of the different Accu-cap capsule inserts can vary significantly. For example, the fringe plastic on one Accu-cap can be noticeably wider than that of a different Accu-cap. The top shell of one Accu-cap can also be considerably different from that of another capsule (in terms of thickness of the capsule dome and/or position of the inlet hole). About one in twenty capsules was found to have fabrication deficiencies. It is apparent that these problems are due to the manufacturing technique used to make the capsules, thus the manner in which these imperfections are avoided during fabrication should be addressed and corrective action taken. Damaged Accu-caps should not be analyzed.

It is strongly recommended to use long insert plugs that will ensure complete sealing of the PVC internal capsules after sample collection. This will help to prevent collected particulate matter from being lost through the inlet hole of each capsule during transport and handling. The use of short inlet plugs that have historically been used with cassette sampling should be avoided.

Independent results

Laboratory data

In order to test the internal capsule weighing procedure in an independent laboratory, PVC Accu-cap gravimetric measurements were carried out at the NIOSH contract lab, Bureau Veritas North America (BVNA, Novi, MI). Analysts at BVNA carried out LOD/LOQ and stability studies (NIOSH Project Seq. No. 11481-CA & -CB). From seven Accu-cap blanks, the standard deviation was 0.0000189 g, which yielded estimated values for the LOD and LOQ of 0.057 mg (≈60 µg) and 189 mg (≈190 µg), respectively. For seven Accu-cap blanks that were stored for six months, the average deviation of the individual blank measurement from the average blank was 0.02 mg, with a maximum deviation of 0.05 mg. The absolute value of the average percent deviation over this time period was less than 0.01%. These figures of merit are comparable to those obtained independently in the NIOSH/DART laboratory.

A subsequent "User Check" study was done wherein the PVC Accu-cap of Tables 1 and 2 (SRM 1648 and Arizona Road Dust spikes as well as media blanks) were sent to BVNA for weighing by an independent laboratory. The results from BVNA are listed vs. the final weights obtained at the NIOSH laboratory in Table 4. With the exception of one statistical outlier, all independently reported results are within 10% of the weights obtained by NIOSH.

*Field dat*a

To test the gravimetric method using internal capsules in the field, results from PVC Accu-caps and Institute of Occupational Health (IOM) samplers were compared in air samples obtained at metal foundries in France. Side-by-side static (area) samples for gravimetric analysis were obtained using the Institut de recherché Robert-Sauvé en santé et en sécurité du travail (IRSST) Method 48-1,[4] which specifies PVC Accu-caps, and the Health and Safety Executive (HSE) MDHS Method 14/3,[5] which relies on IOM samplers. The purpose of the field experiments was to evaluate the use of internal capsules housed within CFCs against the established 'reference' sampler for inhalable aerosols, the IOM sampler.[6] The IRSST method specifies a flow rate of 1.5 L/min and a minimum sample volume of 180 L, while the

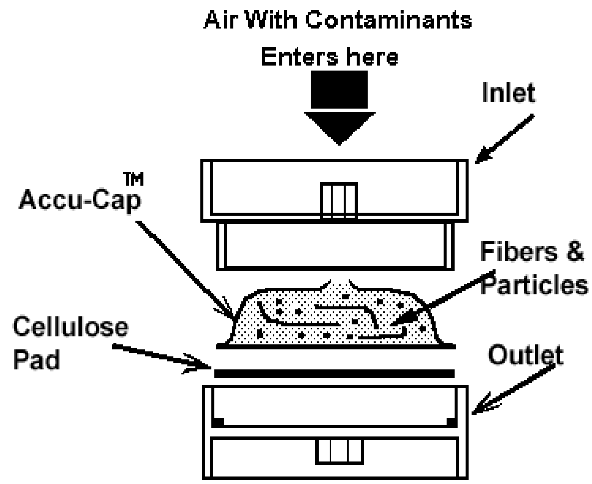
4 IRSST. "Poussière totale," Méthode 48-1; in Méthodes analytiques. IRSST: Montréal, Canada (1998).

5 HSE, "General methods for sampling and gravimetric analysis of respirable and inhalable dust," MDHS Method 14/3. HSE Books: Sudbury, UK (2000).

6 Woebkenberg, M.L., Bartley, D.L., "Inhalable aerosol samplers," Appl. Occup. Environ. Hyg. 13: 274-278 (1998).

HSE method specifies a flow rate of 3.5 L/min and a minimum sampling time of 4 h. Results from these experiments are presented in Table 5, and demonstrate the comparability of the Accu-cap gravimetric method and the IOM sampling method.

Figure 1. (a) Photograph of a 37-mm diameter plastic close-face cassette sampler (left) and an internal filter capsule (right); (b) Schematic of the CFC sampler showing placement of the filter capsule (shaded portion) and cellulose back-up pad within the cassette.



(b)

Accuracy

The results of Table 2, for spiking levels of 1 to 4 mg/sample, were used to estimate overall method accuracy, in accordance with NIOSH guidelines.[7] From these data an overall pooled recovery of 94.3% is obtained, thereby yielding a bias estimate of -0.057. The CV_{Total} was calculated to be 0.059. Also, a pooled estimate of precision (as overall relative standard deviation) of 0.031 was obtained from these results. Using the nomogram relating accuracy to precision and bias,[7,8] an accuracy estimate of ±15.4% is obtained. Given that the NIOSH accuracy criterion is ±25%, these analytical figures of merit demonstrate that the performance criteria for accuracy for acceptance as a NIOSH method are satisfied for gravimetric measurement using PVC capsule inserts. The statistical calculations are shown in Appendix 1.

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7 Kennedy, E.R., Fischbach, T.J., Song, R., Eller, P.M., Shulman, S.A., "Guidelines for Air Sampling and Analytical Method Development and Evaluation." CDC/NIOSH, Cincinnati, OH, 1995; DHHS (NIOSH) Publ. No. 95-117.

8 Kennedy, E.R., Fischbach, T.J., Song, R., Eller, P.M., Shulman, S.A., "Development and Evaluation of Methods", Chap. E., in NIOSH Manual of Analytical Methods, 4th ed. CDC/NIOSH, Cincinnati, 1994.

9 Smith, J. P.; Bartley, D. L.; Kennedy, E. R.: Laboratory investigation of the mass stability of sampling cassettes from inhalable aerosol samplers. Am. Ind. Hyg. Assoc. J. (1998) 59, 582-585.

Table 1. Storage stability data for polyvinyl chloride (PVC) Accu-caps spiked with National Institute of Standards and Technology Standard Reference Material (NIST SRM) 1648, Urban Particulate Matter; percent change (%Δ) values are with respect to Day 0 masses (in grams). The sample weights are corrected for capsule weight and error in mean blank tare weight.

SRM 1648 ≈4 mg	Day 0 wt. (g)	Day 7 wt. (g)	% Δ	Day 14 wt. (g)	% Δ	Day 21 wt. (g)	% Δ	Day 28 wt. (g)	% Δ
Sample 1	0.00386	0.00378	-2.07	0.00375	-2.85	0.00376	-2.59	0.00376	-2.59
Sample 1	0.00386	0.00378	-2.07	0.00375	-2.85	0.00376	-2.59	0.00376	-2.59
Sample 2	0.00383	0.00376	-1.83	0.00375	-2.09	0.00371	-3.13	0.00374	-2.34
Sample 3	0.00385	0.00379	-1.56	0.00378	-1.82	0.00379	-1.56	0.00377	-2.08
%Δ mean			-1.82 ± 0.26	-2.25 ± 0.54			-2.43 ± 0.80		-2.34 ± 0.26
≈ 2 mg									
Sample 1	0.00169	0.00166	-1.78	0.00165	-2.37	0.00166	-1.78	0.00165	-2.37
Sample 2	0.00130	0.00126	-3.08	0.00125	-3.84	0.00124	-4.62	0.00124	-4.62
Sample 3	0.00170	0.00165	-2.94	0.00165	-2.94	0.00167	-1.76	0.00165	-2.94
%Δ mean			-2.60±		-3.05±		-2.72 ±		-3.31 ±
≈ 1 mg									
Sample 1	0.00090	0.00088	-2.2	0.00088	-2.2	0.00088	-2.2	0.00088	-2.2
Sample 2	0.00110	0.00111	+0.91	0.00110	-0-	0.00111	+0.91	0.00111	+0.91
Sample 3	0.00117	0.00114	-2.56	0.00113	-3.42	0.00115	-1.71	0.00113	-3.42
%Δ mean			-1.28 ±		-1.87 ±		-1.00 ±		-1.57 ±
≈0.5 mg									
Sample 1	0.00035	0.00020	-43	0.00017	-51	0.00020	-43	0.00020	-43
Sample 2	0.00035	0.00031	-11	0.00023	-34	0.00023	-34	0.00024	-31
Sample 3	0.00049	0.00040	-18	0.00039	-20	0.00039	-20	0.00040	-18
Sample 4	0.00045	0.00029	-36	0.00026	-42	0.00025	-44	0.00026	-42
%Δ mean			-27± 15		-37± 13		-35± 11		-34± 12
≈0.1 mg									
Sample 1	0.00005	-0.00006	-220	-0.00008	-250	-0.00006	-220	-0.00006	-220
Sample 2	0.00016	0.00018	+13	0.00017	+6.3	0.00017	+6.3	0.00017	+6.5
Sample 3	0.00024	0.00024	-0-	0.00022	-8.3	0.00024	-0-	0.00024	-0-
Sample 4	0.00018	0.00019	+5.6	0.00019	+5.6	0.00019	+5.6	0.00020	+11
%Δ mean			-50± 110		-64± 130		-52± 110		-51±
Media									
Sample 1	0.28025	0.28021	-0.0143	0.28023	-0.0071	0.28021	-0.0143	0.28019	-0.0214
Sample 2	0.29180	0.29179	-0.0034	0.29177	-0.0103	0.29177	-0.0103	0.29177	-0.0103
Sample 3	0.28421	0.28421	-0-	0.28419	-0.0070	0.28419	-0.0070	0.28419	-0.0070
Sample 4	0.30742	0.30744	+0.0065	0.30744	+0.0065	0.30744	+0.0065	0.30745	+0.0098
Sample 5	0.31681	0.31676	-0.0158	0.31677	-0.0126	0.31676	-0.0158	0.31677	-0.0126
Sample 6	0.32797	0.32791	-0.0183	0.32791	-0.0183	0.32792	-0.0152	0.32792	-0.0152
%Δ mean		-0.0092 ±		-0.0081±		-0.0094±		-0.0095±	

Table 2. Storage stability data for PVC Accu-caps spiked with Arizona Road Dust – Air Cleaner Test Dust; percent change (%Δ) values are with respect to Day 0 masses (in grams). The sample weights are corrected for capsule weight and error in mean blank tare weight.

AZ Rd. dust ≈4 mg	Day 0 wt. (g)	Day 7 wt. (g)	%Δ	Day 14 wt. (g)	%Δ	Day 21 wt. (g)	%Δ	Day 28 wt. (g)	%Δ
Sample 1	0,00418	0,00421	+0,72	0,00420	+0,48	0,00420	+0,48	0,00420	+0,48
Sample 2	0,00394	0,00396	+0,51	0,00397	+0,76	0,00397	+0,76	0,00396	+0,51
Sample 3	0,00374	0,00373	-0,27	0,00373	-0,27	0,00373	-0,27	0,00375	+0,27
%Δ mean ± std. dev.			+0,32 ± 0,52		+0,32 ± 0,53		+0,32 ± 0,53		+0,42 ± 0,13
≈2 mg									
Sample 1	0,00221	0,00219	-0,90	0,00220	-0,45	0,00219	-0,90	0,00219	-0,90
Sample 2	0,00185	0,00186	+0,54	0,00186	+0,54	0,00186	+0,54	0,00186	+0,54
Sample 3	0,00185	0,00189	+2,16	0,00189	+2,16	0,00190	+2,70	0,00190	+2,70
Sample 4	0,00187	0,00190	+1,60	0,00186	-0,53	0,00188	+0,53	0,00188	+0,53
%Δ mean ± std. dev.			+0,85 ± 1,34		+0,43 ± 1,25		+0,72 ± 1,49		+0,72 ± 1,49
≈1 mg									
Sample 1	0,00100	0,00103	+3,0	0,00103	+3,0	0,00103	+3,0	0,00103	+3,0
Sample 2	0,00114	0,00116	+1,8	0,00118	+3,5	0,00117	+2,6	0,00117	+2,6
Sample 3	0,00098	0,00099	+1,0	0,00098	-0-	0,00100	+2,0	0,00099	+1,0
Sample 4	0,00097	0,00096	-1,0	0,00095	-2,1	0,00097	-0-	0,00097	-0-
%Δ mean ± std. dev.			+1,2 ± 1,7		+1,1 ± 2,6		+1,9 ± 1,3		+1,7 ± 1,4
≈0,5 mg									
Sample 1	0,00036	0,00037	+2,8	0,00037	+2,8	0,00037	+2,8	0,00039	+8,3
Sample 2	0,00041	0,00044	+7,3	0,00044	+7,3	0,00044	+7,3	0,00044	+7,3
Sample 3	0,00044	0,00047	+6,8	0,00046	+4,5	0,00048	+9,1	0,00048	+9,1
Sample 4	0,00051	0,00054	+5,9	0,00053	+3,9	0,00055	+7,8	0,00055	+7,8
%Δ mean ± std. dev.			+5,7± 2,0		+4,6 ± 1,9		+6,8 ± 2,8		+8,1 ± 0,8
≈0,1 mg									
Sample 1	0,00032	0,00033	+3,1	0,00034	+6,3	0,00019	-41	0,00019	-41
Sample 2	0,00008	0,00013	+63	0,00014	+75	0,00014	+75	0,00014	+75
Sample 3	0,00010	0,00011	+10	0,00012	+20	0,00012	+20	0,00014	+40
Sample 4	0,00008	0,00012	+50	0,00010	+25	0,00011	+38	0,00011	+38
%Δ mean ± std. dev.			+32 ± 29		+32 ± 30		+23 ± 48		+28 ± 49
media blank									
Sample 1	0,32999	0,33000	+0,0030	0,33002	+0,0091	0,33000	+0,0030	0,33002	+0,0091
Sample 2	0,23152	0,23150	-0,0086	0,23153	+0,0043	0,23150	-0,0086	0,23151	-0,0043
Sample 3	0,26775	0,26772	-0,0112	0,26775	-0-	0,26774	-0,0037	0,26775	-0-
Sample 4	0,30638	0,30637	-0,0033	0,30639	+0,0033	0,30638	-0-	0,30639	+0,0033
Sample 5	0,32830	0,32830	-0-	0,32834	+0,0122	0,32831	+0,0030	0,32832	+0,0061
Sample 6	0,32176	0,32172	-0,0124	0,32177	+0,0031	0,32176	-0-	0,32177	+0,0031

AZ Rd. dust ≈4 mg	Day 0 wt. (g)	Day 7 wt. (g)	%Δ	Day 14 wt. (g)	%Δ	Day 21 wt. (g)	%Δ	Day 28 wt. (g)	%Δ
%Δ mean ± std. dev.			-0,0054 ± 0,0063		+0,0053 ± 0,0045		-0,0011 ± 0,0045		+0,0029 ± 0,0048

Table 3. Computed recoveries from spiked PVC Accu-caps for certified reference material (CRM) masses of ≈1, ≈2 and ≈4 mg per sample.

Spiking Level	CRM	Mean Recovery ± Std. Dev., %
≈4 mg	NIST SRM 1648	96.1 ± 1.6 (n=7)
	Arizona Road Dust	96.7 ± 2.8 (n=4)
≈2 mg	NIST SRM 1648	93.1 ± 6.2 (n=6*)
	Arizona Road Dust	97.4 ± 1.3 (n=4)
≈1 mg	NIST SRM 1648	91.6 ± 9.0 (n=7)
	Arizona Road Dust	102 ± 3.2 (n=4)
*One statistical outlier omitted (Q-test, p=0.05)		

Table 4. Sample weights for Arizona Road Dust and PVC capsules obtained by NIOSH vs. independent gravimetric laboratory results reported by Bureau Veritas North America (BVNA).

Sample	NIOSH wt. (g)	BVNA wt. (g)	Δ (g)	% Δ
Arizona Road Dust				
≈4 mg #1	0.00418	0.00408	-0.00010	-2.4
≈4 mg #2	0.00394	0.00379	-0.00015	-3.8
≈4 mg #3	0.00374	0.00361	-0.00013	-3.5
≈2 mg #1	0.00221	0.00210	-0.00011	-5.0
≈2 mg #2	0.00185	0.00188	+0.00003	+1.6
≈2 mg #3	0.00185	0.00186	+0.00001	+0.54
≈2 mg #4	0.00187	0.00178	-0.00093	-4.8
≈1 mg #1	0.00100	0.00105	+0.00005	+5.0
≈1 mg #2	0.00114	0.00116	+0.00002	+1.7
≈1 mg #3	0.00098	0.00094	-0.00004	-4.1
≈1 mg #4	0.00097	0.00098	+0.00001	+10
≈0.5 mg #1	0.00036	0.00038	+0.00002	+5.6
≈0.5 mg #2	0.00041	0.00042	+0.00001	+2.4
≈0.5 mg #3	0.00044	0.00047	+0.00003	+6.8
≈0.5 mg #4	0.00051	0.00056	+0.00005	+9.8
≈0.1 mg #1	0.00032	0.00031	-0.00001	-0.97
≈0.1 mg #2	0.00008	0.00009	+0.00001	+13
≈0.1 mg #3	0.00010	0.00003	-0.00007	-70
≈0.1 mg #4	0.00008	0.00008	-0-	
PVC capsule media blanks				
#1	0.28019	0.28036	+0.00017	+0.061
#2	0.29177	0.29195	+0.00018	+0.062
#3	0.28419	0.28436	+0.00017	+0.060
#4	0.30745	0.30762	+0.00017	+0.055
#5	0.31677	0.31698	+0.00021	+0.066
#6	0.32792	0.32812	+0.00020	+0.061
#7	0.33002	0.33018	+0.00016	+0.048
#8	0.23151	0.23165	+0.00014	+0.060
#9	0.26775	0.26792	+0.00017	+0.063
#10	0.30639	0.30659	+0.00020	+0.065
#11	0.32832	0.32853	+0.00021	+0.064
#12	0.32177	0.32197	+0.00020	+0.062

Table 5. Summary of field gravimetric data from paired PVC Accu-cap samplers housed in closed-face cassettes (CFCs) (n=15) and Institute of Occupational Medicine IOM samplers (n=12) obtained in metal foundries. (Results courtesy of M. Demange, Institut National de Recherche et de Sécurité [INRS], Vandoeuvre, France)

Data set	Accu-cap (mg/m3)	IOM (mg/m3)	Ratio (Accu-cap/IOM x 100%)
1	9.0	9.7	
	9.1	10.8	
	avg. = 9.1	avg. = 10.3	88
2	3.9	5.2	
	4.0	5.5	
	avg. = 4.0	avg. = 5.4	74
3	9.3	12.4	
	8.7	5.8	
	avg. = 9.0	avg. = 9.1	99
4	10.3	11.0	
	9.8	11.1	
	6.6	8.1	
	9.0		
	avg. = 9.0	avg. = 10.1	89
5	4.7	5.4	
	4.8	6.0	
	4.6	3.8	
	4.9		
	5.1		
	avg. = 4.8	avg. = 5.1	94
mean overall ratio (Accu-cap / IOM) = 89% (±9%)			

Appendix 1

These statistical calculations were provided by Amy Feng (DART/NIOSH).

The CV_{Total} was calculated taking into account the 5% pump error. The equation used was : CV_total =Sqrt(CV1**2+0.05)**2) =sqrt(0.031**2+0.05**2)=0.059, was then used to calculate the Accuracy of the Methods. The updated accuracy is now 0.15466.

Two sets of dust source: AZ and NIST were used for this study. The NIST dust had some problems with moisture so that set of data was not included in the statistical analysis.

1. The bias was defined as the difference between the NIOSH total dust weight on day 1 and BVNA adjusted dust weight on day 28. The following steps were taken for the calculation (see Appendix Table 1):
   a. Tare28_wt = NIOSH_twt28 - dwt_D0 NIOSH tare weight on day 28 is the difference between total weight on day 28 and the dust weight on day 1.
   b. BVNA_dwt = BVNA_twt28 - Tare28_wt ; Adjust BVNA total dust weight by subtracting off the NIOSH tare weight.
   c. Scale = the average blank of NIOSH – the average blank of BVNA on day 28. Calculate scale difference between NIOSH and BVNA using the blank samples on Day 28.
   d. BVNA_adj=BVNA_dwt-scale; Adjust BVNA dust weight by subtracting off the scale difference.
   e. Pt_bias=dwt_D0-BVNA_adj; Point bias is calculated as the difference between NIOSH Day 0 dust weight and BVNA adjusted dust weight.
2. The data at level 0.1 was below LOQ so was excluded from the subsequent analysis. Homogeneity of bias was tested using the ANOVA procedure. The test result indicated the bias was not homogenous. To take a conservative approach, the maximum mean bias value was used for the evaluation for the accuracy. Homogeneity of precision was tested using the Bartlett's test. The Bartlett's test suggested that the precision was poolable across the tested levels; therefore the pooled RSD was used for the accuracy evaluation (see Appendix Table 2). The NIOSH method Accuracy and 95% upper limit of the Accuracy was estimated and listed in Appendix Table 3.

Table 1. Data listing

Source = AZ level	sample	NIOSH_ twt28	BVNA_ twt28	NIOSHdwt_ D0	tare28_ wt	BVNA_ dwt	scale	BVNA_adj	pt_bias
0.1	1	0.25091	0.25108	.00032	0.25059	.00049	.000181667	.000308333	-0.03646
0.1	2	0.28280	0.28299	.00008	0.28272	.00027	.000181667	.000088333	0.10417
0.1	3	0.26069	0.26080	.00010	0.26059	.00021	.000181667	.000028333	-0.71667
0.1	4	0.26153	0.26171	.00008	0.26145	.00026	.000181667	.000078333	-0.02083
0.5	1	0.32152	0.32172	.00036	0.32116	.00056	.000181667	.000378333	0.05093
0.5	2	0.31611	0.31630	.00041	0.31570	.00060	.000181667	.000418333	0.02033
0.5	3	0.31734	0.31755	.00044	0.31690	.00065	.000181667	.000468333	0.06439
0.5	4	0.31176	0.31199	.00051	0.31125	.00074	.000181667	.000558333	0.09477
1.0	1	0.31949	0.31972	.00100	0.31849	.00123	.000181667	.001048333	0.04833
1.0	2	0.27512	0.27532	.00114	0.27398	.00134	.000181667	.001158333	0.01608
1.0	3	0.25899	0.25913	.00098	0.25801	.00112	.000181667	.000938333	-0.04252
1.0	4	0.32531	0.32550	.00097	0.32434	.00116	.000181667	.000978333	0.00859
2.0	1	0.31342	0.31349	.00221	0.31121	.00228	.000181667	.002098333	-0.05053
2.0	2	0.30589	0.30610	.00185	0.30404	.00206	.000181667	.001878333	0.01532
2.0	3	0.25327	0.25346	.00185	0.25142	.00204	.000181667	.001858333	0.00450
2.0	4	0.26232	0.26241	.00187	0.26045	.00196	.000181667	.001778333	-0.04902
4.0	1	0.29227	0.29235	.00418	0.28809	.00426	.000181667	.004078333	-0.02432
4.0	2	0.26984	0.26987	.00394	0.26590	.00397	.000181667	.003788333	-0.03849
4.0	3	0.30441	0.30446	.00374	0.30067	.00379	.000181667	.003608333	-0.03520

Table 2. List of data for the Accuracy Estimation

Sourcer = AZ level	pt_bias	m_bias	est_bias	pool_TRSD*
0.5	0.050926	0.057604*	0.057604	0.031388
0.5	0.020325	0.057604	0.057604	0.031388
0.5	0.064394	0.057604	0.057604	0.031388
0.5	0.094771	0.057604	0.057604	0.031388
1.0	0.048333	0.007622	0.057604	0.031388
1.0	0.016082	0.007622	0.057604	0.031388
1.0	-0.042517	0.007622	0.057604	0.031388
1.0	0.008591	0.007622	0.057604	0.031388
2.0	-0.050528	-0.019932	0.057604	0.031388
2.0	0.015315	-0.019932	0.057604	0.031388
2.0	0.004505	-0.019932	0.057604	0.031388
2.0	-0.049020	-0.019932	0.057604	0.031388
4.0	-0.024322	-0.032674	0.057604	0.031388
4.0	-0.038494	-0.032674	0.057604	0.031388
4.0	-0.035205	-0.032674	0.057604	0.031388

*The conservative approach took the maximum mean bias across levels as the bias estimation.

Table 3. NIOSH 0501 Gravimetric Method, estimation of NIOSH Accuracy and 95% upper limit of the Accuracy

source	n	k	est_bias	est_rsd	CV_total	accuracy	Acc_U95
AZ	4	4	0.057604	0.031388	0.059	0.15466	0.21657

Filename: Gravimetric_AZ_accuracy_based on CVTotal.docx 6/2/2014

Gravimetric_AZ_accuracy dated 4/25/2014.