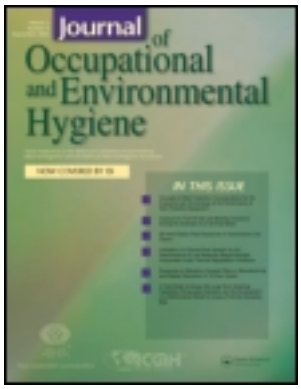

Journal of Occupational and Environmental Hygiene
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uoeh20

Acid-Soluble Internal Capsules for Closed-Face Cassette Elemental Sampling and Analysis of Workplace Air

Martin Harper [a] & Kevin Ashley [b]

[a] National Institute for Occupational Safety and Health, Health Effects Laboratory Division, Morgantown, West Virginia

[b] National Institute for Occupational Safety and Health, Division of Applied Research & Technology, Cincinnati, Ohio

Accepted author version posted online: 25 Feb 2013.Version of record first published: 02 Apr 2013.

To cite this article: Martin Harper & Kevin Ashley (2013): Acid-Soluble Internal Capsules for Closed-Face Cassette Elemental Sampling and Analysis of Workplace Air, Journal of Occupational and Environmental Hygiene, 10:6, 297-306

To link to this article: http://dx.doi.org/10.1080/15459624.2013.777310

Journal of Occupational and Environmental Hygiene, 10: 297–306
ISSN: 1545-9624 print / 1545-9632 online
DOI: 10.1080/15459624.2013.777310

Acid-Soluble Internal Capsules for Closed-Face Cassette Elemental Sampling and Analysis of Workplace Air

Martin Harper[1] and Kevin Ashley[2]

[1]National Institute for Occupational Safety and Health, Health Effects Laboratory Division, Morgantown, West Virginia
[2]National Institute for Occupational Safety and Health, Division of Applied Research & Technology, Cincinnati, Ohio

Airborne particles that are collected using closed-face filter cassettes (CFCs), which are used widely in the sampling of workplace aerosols, can deposit in places other than on the filter and thereby may not be included in the ensuing analysis. A technique for ensuring that internal non-filter deposits are included in the analysis is to collect airborne particles within an acid-soluble internal capsule that, following sampling, can be dissolved along with the filter for subsequent elemental analysis. An interlaboratory study (ILS) was carried out to evaluate the use of cellulosic CFC capsule inserts for their suitability in the determination of trace elements in airborne samples. The ILS was performed in accordance with an applicable ASTM International standard practice, ASTM E691, which describes statistical procedures for investigating interlaboratory precision. Performance evaluation materials consisted of prototype cellulose acetate capsules attached to mixed-cellulose ester filters. Batches of capsules were dosed with Pb-containing materials (standard aqueous solutions, and certified reference material soil and paint). Also, aerosol samples containing nine target analyte elements (As, Cd, Co, Cr, Cu, Fe, Pb, Mn, and Ni) were generated using a multiport sampler; various concentrations and sampling times were employed to yield samples fortified at desired loading levels. Triplicates of spiked capsules at three different loadings were conveyed to each volunteer laboratory; loading levels were unknown to the participants. The laboratories were asked to prepare the samples by acid dissolution and to analyze aliquots of extracted samples by atomic spectrometry in accordance with applicable ASTM International Standards. Participants were asked to report their results in units of μg of each target element per sample. For the elements investigated, interlaboratory precision and recovery estimates from the participating laboratories demonstrated the utility of the cellulosic capsule inserts for the measurement of sampled trace elements.

Keywords aerosol sampling, elemental analysis, internal capsule, occupational hygiene

Correspondence to: Martin Harper, National Institute for Occupational Safety and Health, Health Effects Laboratory Division, 1095 Willowdale Road, Morgantown, WV 26505; e-mail: zzg7@cdc.gov.

INTRODUCTION

For over 50 years, aerosol sampling methods for workplace air monitoring in the United States and many other countries have relied on the use of closed-face filter cassette (CFC) samplers.[1] Established occupational exposure monitoring practice based on CFC sampling generally entails the use of a battery-powered personal sampling pump, which pulls air via vacuum through a filter housed within the cassette.[2] For personal monitoring of airborne particles to measure their elemental content, such filter sampling is ordinarily carried out using membrane[3] or depth[4] filters. Subsequently, the filter deposit is normally analyzed by atomic spectrometric techniques after acid dissolution of the filter medium plus collected particles.[3–5] Unfortunately, analysis of the filter deposit alone does not always adequately measure worker exposures to airborne metals and metalloids because it can underestimate the concentration of airborne particles, thus potentially giving a false assurance of protection from overexposure. This underestimation results from accumulations of sampled aerosol particles on internal sampler surfaces, a contribution to exposure that has not always been included in analytical procedures.[6] Significant amounts of particulate matter up to and even exceeding quantities of material captured on the filter can be deposited on the internal surfaces of CFCs during sample collection, transport, and handling.[6–13] This accumulation can be substantial and yet invisible to cursory inspection, so that its significance is not always recognized.

Collection of airborne dust samples in occupational environments using CFC samplers requires the evaluation of all aerosol particles that enter the sampler, whether or not they are deposited on the filter.[6,8,14] Methods for incorporating this material along with the filter for subsequent analysis include rinsing,[13] wiping,[8] and within-cassette dissolution.[4] However, these procedures can be labor intensive and may result in increased experimental uncertainty as well as uncorrectable systematic errors.

An internal capsule (fused to a filter) that would contain all collected airborne particles, and that could be digested easily without compromising the analysis through high background or matrix interferences, could be used in lieu of the above-mentioned labor-intensive procedures. Currently, CFC internal capsules made of polyvinyl chloride (PVC) and used for gravimetric analysis of collected particulate matter are commercially available.[2,15] However, PVC is extremely difficult to solubilize without sizable dilution, and thus, CFC insert capsules fabricated from this polymer are not appropriate for elemental analysis by means of standardized acid digestion and atomic spectrometric detection methods. Efforts have been undertaken recently to produce CFC capsule inserts made out of material that is more easily solubilized (at the request of the ASTM International Subcommittee on Workplace Air Quality);[16] a prototype internal capsule made entirely of cellulosic material has been developed. Such a cellulosic capsule, when inserted into a CFC sampler, can be used to collect the entire aerosol sample, which is aspirated through the inlet of the cassette. Thereafter, the cellulosic insert can be completely digested in the same strong acid solutions that are customarily employed to dissolve mixed cellulose ester (MCE) filters, which historically have been widely used for airborne elemental sampling and analysis.

The overall goal of this effort was to evaluate and validate a method that accounts for all aerosol particles that enter the CFC sampler, thereby including material that is not otherwise measured by filter-only analysis procedures. A principal aim of this work was to carry out an interlaboratory study (ILS) to evaluate the analytical suitability of cellulosic capsule inserts for their use with traditional plastic air sampling cassettes. The ILS analysis entailed fortifying the filter capsule inserts with various loadings of metal-containing aerosols and sending them to volunteer laboratories. The inserts were then acid digested and analyzed for their elemental content by atomic spectrometry.

Tests performed on presumably identical materials in presumably identical circumstances do not, in general, yield identical results. This is attributed to unavoidable random errors inherent in every test procedure; the factors that may influence the outcome of a test cannot all be completely controlled. In the practical interpretation of test data, this inherent variability has to be taken into account. For instance, the difference between a test result and some specified value may be within that which can be expected to be due to unavoidable random errors, in which case a real deviation from the specified value has not been demonstrated. Similarly, the difference between test results from two batches of material will not indicate a fundamental quality difference if the difference is no more than that which can be attributed to inherent variability in the test procedure. Many different factors (apart from random variations between supposedly identical specimens) may contribute to the variability in application of a test method, including: (1) the operator, (2) equipment used, (3) calibration of instrumentation, and (4) environment (temperature, humidity, level of background contamination, and so on). Changing laboratories changes each of the above factors. The two practical extremes of precision are the repeatability (within-laboratory) and reproducibility (between-laboratory) conditions. This project yields data on both conditions by providing multiple test materials simultaneously to several laboratories. The protocol for this type of project has been codified in an ASTM International standard, ASTM E691,[17] which describes procedures for determining method precision by means of inter-laboratory testing.

Preliminary Laboratory Studies

One thousand prototype cellulose acetate internal capsules, fused to 0.8 μm pore size 37-mm MCE filters (cellulosic filter capsules), were provided by SKC Inc. (Eighty Four, Pa.) at cost. The cellulosic filter capsules are designed to be inserted into 37-mm plastic CFC samplers on top of cellulose support pads, as illustrated in Figure 1.

While MCE filters are generally considered to have negligible background for metals and metalloids, the cellulosic material from which the capsules of the cellulosic filter capsules are made is different from the MCE filter material, and the amount of material to be solubilized is greater. Thus, there was a need to check for background levels of metals in the cellulosic insert materials. In addition, while the MCE filters dissolve readily in concentrated nitric acid, it was not known if the corresponding cellulosic inserts also would be put into solution easily. Thus, preliminary experiments were done to investigate the suitability of cellulose acetate material for further consideration.

Prior to the manufacture of cellulosic filter capsules, approximately 5 cm $\times$ 5 cm squares of the raw cellulose acetate material for the capsules were analyzed by three different laboratories. One laboratory (Wisconsin Occupational Health Laboratory [WOHL], Madison, Wis.) analyzed three pieces of the unweighed material using inductively coupled plasma atomic emission spectrometry (ICP-AES).[18] Dissolution was carried out with 50:50 nitric acid/hydrochloric acid (concentrated) on a 90°C hot block. Mean reported elemental values in μg/sample were as shown in Table I (Laboratory 1). Note that the only elements in any major background abundance are Ca, Mg, and P. These are elements not commonly analyzed as they are not often encountered at levels considered harmful, although species containing them (e.g., calcium hydroxide, magnesium oxide, and phosphorous oxides) may be encountered in certain workplace situations, and occupational exposure limits (OELs) for these compounds do exist. A separate laboratory (Centers for Disease Control and Prevention/National Institute for Occupational Safety and Health [CDC/NIOSH], Cincinnati, Ohio) also analyzed 10 cellulose acetate squares after dissolution with nitric acid (concentrated) alone on a 120°C hot plate and measurement by ICP-AES,[3] and the results shown in Table I (Laboratory 2) were obtained. Ca, Mg, and P background abundances that had been observed by WOHL were confirmed. While the NIOSH laboratory found some background of Pb, this was not the experience of WOHL.

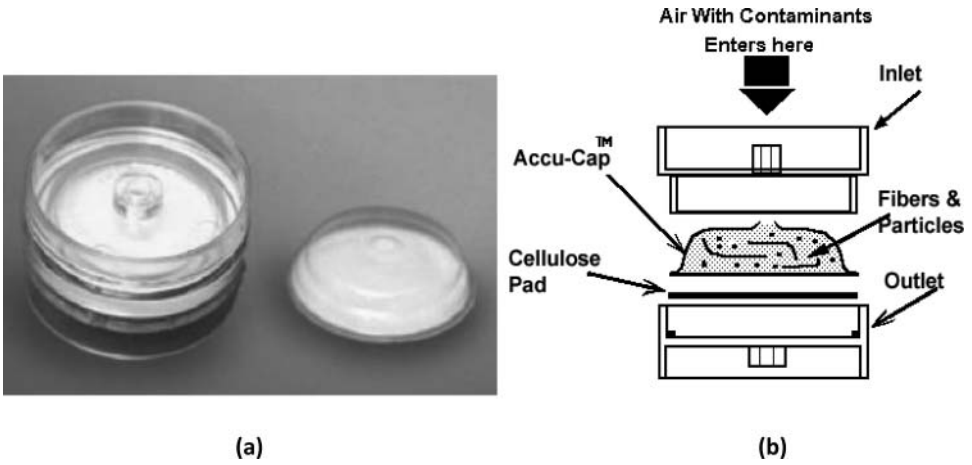

FIGURE 1. (a) Photograph of a 37-mm diameter plastic close-face cassette sampler (left) and a cellulosic filter capsule internal capsule (right); (b) schematic of the CFC sampler showing placement of the cellulosic filter capsule (shaded portion) and cellulose back-up pad within the cassette.

Otherwise, the elemental analysis results from these two laboratories were very similar.

Elsewhere, another laboratory (Health and Safety Laboratory [HSL], Buxton, England) used four different digestion procedures as described in ISO 15202-2.[19] This International Standard was followed to treat six cellulose acetate squares using each sample dissolution method, with subsequent analysis by inductively coupled plasma mass spectrometry (ICP-MS).[20] The dissolution procedures tested were: (a) 50% nitric acid (aqueous) on a 95°C hot block; (b) 50% sulfuric acid (aqueous) with a few drops of hydrogen peroxide on a 140°C hot plate; (c) nitric acid (concentrated) followed by perchloric acid (also concentrated) on a 95°C hot block; and (d) nitric acid and hydrofluoric acid (both concentrated) by microwave digestion at 180°C. Solutions for analysis were made up in dilute hydrochloric acid after dissolution, prior to aspiration into the ICP-MS instrument. The results are not presented here, but no obvious differences were observed between the different dissolution procedures. Many of the elements listed above were not determined, and for those that were measured, only Cu (0.6 μg/sample) and Fe (1.3 μg/sample) were significantly above background; these results were compatible with those presented in Table I. No background Pb was found, suggesting the possibility of contamination in the samples analyzed by NIOSH.

Lastly, a contract laboratory (Bureau Veritas North America, Novi, Mich.) digested prototype cellulosic filter capsules using nitric acid with hydrogen peroxide on a 140°C hot plate[19] and analyzed five sample extracts by ICP-AES[18] (Table II) and five by ICP-MS[20] (Table II). The lower numbers observed for Ca, Mg, and P in Table II compared with those in Table I are consistent with a smaller mass of plastic in the actual cellulosic filter capsules than in the 5 cm × 5 cm squares of raw cellulosic polymer. Some of the samples yielded higher levels of Pb compared with others, the highest levels being 1.7 μg by ICP-AES and 1.4 μg by ICP-MS.

The above studies demonstrate that background levels of metals and metalloids in the cellulose acetate media are for the

TABLE I. Mean Reported Elemental Values (μg/Sample) After Dissolution of Cellulose Acetate Media and Analysis by ICP-AES

Laboratory 1: HCl/HNO_3, 90°C (n = 3)														
Element	Al	Sb	As	Ba	Be	Bi	B	Cd	Ca	Cr	Co	Cu	Fe	Pb
$\bar{x}$, μg/sample	0.7	0.2	0.4	ND[A]	ND	0.3	0.1	ND	60	ND	ND	0.8	1.0	0.1
Element	Li	Mg	Mn	Mo	Ni	P	K	Se	Sr	Tl	Sn	Ti	V	Zn
$\bar{x}$, μg/sample	ND	5.7	0.0	0.0	0.1	12	1.6	0.7	0.1	ND	0.2	0.2	0.0	0.2
Laboratory 2: HNO_3 only, 120°C (n = 10)														
Element	Al	Sb	As	Ba	Be	Bi	B	Cd	Ca	Cr	Co	Cu	Fe	Pb
$\bar{x}$, μg/sample	1.1	ND[A]	ND	0.2	ND	—[B]	—[B]	ND	75	0.0	ND	0.6	2.0	2.8
Element	Li	Mg	Mn	Mo	Ni	P	K	Se	Sr	Tl	Sn	Ti	V	Zn
$\bar{x}$, μg/sample	ND	5.7	0.0	ND	0.1	13	2.6	ND	0.2	ND	0.1	0.2	ND	1.1

[A]ND = not detected (level varies by element). If a result is above the detection limit and less than 0.05 μg/sample it has been listed as 0.0.
[B]Not determined.

TABLE II. Mean Reported Elemental Values After Hot Plate Digestion of Cellulosic Filter Capsules and Analysis by ICP-AES and ICP-MS

Element	Al	Sb	As	Ba	Be	Bi	B	Cd	Ca	Cr	Co	Cu	Fe	Pb
ICP-AES	—	ND	0	0.2	ND	—	—	ND	—	0.8	ND	0.2	—	1.0
ICP-MS	0.1	0.2	ND	0.1	ND	—	—	ND	36	0.1	ND	0.2	1.6	0.8
Element	Li	Mg	Mn	Mo	Ni	P	K	Se	Sr	Tl	Sn	Ti	V	Zn
ICP-AES	—	—	ND	ND	ND	—	—	ND	—	ND	—	—	0.2	0.5
ICP-MS	0.1	2.2	0.1	0.0	0.0	6.4	1.3	ND	0.1	ND	0.7	0.2	ND	0.4

Note: (μg/Sample; N = 5).

most part insignificant, although for certain elements (e.g., Pb) correction might be required during analysis. Pb was therefore selected as the element of interest in a preliminary ILS that has been reported on previously,[14] and which is summarized in more detail in the following section. The results of that study suggest that, in practice, background levels of Pb should not be a problem in the analysis. These experiments confirm that significant levels of metals and metalloids that could potentially interfere with analyses are generally absent, although ongoing quality control is required to maintain low elemental background and to prevent laboratory contamination from commonly found metals such as Pb. The different digestion and extraction techniques investigated did not appear to affect the analysis, as complete dissolution was observed with all procedures tested.

Interlaboratory Studies

Elemental sample recovery was tested by using certified reference materials (CRMs) for Pb (RTI International, Research Triangle Park, N.C.) and metal-containing aerosols generated at the Norwegian Statens Arbeidsmiljøinstitutt (STAMI, Oslo, Norway), which has the capacity to generate precise replicates of more than forty 37-mm cassette samples at a time of different airborne metals in different combinations. A similar generation system that affords extremely uniform loadings (3–5% relative standard deviations [RSDs]) has been described in the literature.[21] Multiple batches of samples from various multi-element aerosol concentrations were generated and then disseminated to participating laboratories for interlaboratory analysis. A minimum of six laboratories is required for evaluation per the ASTM E691.[17] The participating laboratories, many of which have been part of previous interlaboratory evaluations,[22] included those listed in Table III.

These laboratories used different procedures for sample dissolution for metals, particularly in the combinations and concentrations of acids used and in the manner in which dissolution is facilitated (e.g., hot block, ultrasound, hot plate heating at different temperatures, microwave-assisted, and so on). Further, laboratories differed in their use of analytical instrumentation (e.g., atomic absorption spectrometry, ICP-AES and ICP-MS). Even where laboratories used the same detection technique, the method of sample introduction (e.g., by nebulization of extract solution) into the analytical measurement instrument area may have differed. The presence of additional organic material in the filter capsule inserts compared with filters alone may affect the digestion (e.g., by requiring additional acid or oxidizer for complete dissolution), the nebulization (e.g., by altering the viscosity of the solution), or the analysis (e.g., by introducing additional spectral interferences). It was believed that these differences are not significant and that the filter capsule inserts would not interfere with the analyses. That is, it was anticipated that the laboratories would be able to fully digest the capsule inserts using their standard procedure(s) and that results from the analyses would have variance similar to results from dosing of filters only, as has already been established within proficiency testing schemes.[23]

ASTM E691[17] states that an ILS should include 30 or more laboratories but recognizes that this may not be practical and allows that interlaboratory studies be run with fewer laboratories. It is important that enough laboratories be included in the ILS to be a reasonable cross-section of the population of qualified laboratories, that the loss or poor performance of a few will not

TABLE III. Volunteer Participants in One or More Interlaboratory Studies

Laboratory and Location
Bureau Veritas North America (BVNA), Novi, Michigan
Forensic Analytical Services, Hayward, California
Health and Safety Laboratory (HSL), Buxton, England
Institut National de Recherche et de Sécurité (INRS), Vandœuvre-lès-Nancy, France
Institut de Recherche Robert Sauvé et en Sécurité du Travail (IRSST), Montréal, PQ, Canada
Occupational Safety and Health Administration (OSHA), Sandy, Utah
Research Triangle Institute (RTI International), Research Triangle Park, North Carolina
Savannah River National Laboratory (SRNL), Savannah River Site, South Carolina
Statens Arbeidsmiljøinstitutt (STAMI), Oslo, Norway
Wisconsin Occupational Health Laboratory (WOHL), Madison, Wisconsin

TABLE IV. Rationale for Target Cellulosic Filter Capsule Sample Loadings

Loading (Sampling @ 2.0 L/min)	Loading Time in Hours	Target Loading Mass in μg Element								
		Fe	Ni	Cr	Mn	Co	Cu	Cd	Pb[A]	As
0.1 × OEL	1	12	1.2	6	2.4	0.24	2.4	0.12	10	0.12
0.5 × OEL	2	120	12	60	24	2.4	24	1.2	50	1.2
2 × OEL	4	960	96	480	192	19.2	192	9.6	100	9.6
ACGIH® TLV®,[B] mg/m^3	8-Hour TWA[C]	1	0.1	0.5	0.2	0.02	0.2	0.01	0.05	0.01

[A]Pb loadings were increased in consideration of background issues. Target loading is fraction of OEL multiplied by loading time.
[B]Threshold limit value.
[C]Time-weighted average.

be fatal to the study, and to provide a reasonably satisfactory estimate of the reproducibility. It is strongly recommended that an ILS include acceptable results from a minimum of no less than six laboratories.[17] ASTM E691 further states that it is generally sound to limit the number of test results on each material in each laboratory to a small number, such as three or four, and that the minimum number of test results per laboratory will normally be three for a chemical test.

In the first set of experiments, samples were spiked with various matrices containing certified levels of Pb. RTI International provided cellulosic filter capsules spiked with two different mass levels of each of three matrices (solution, soil, and paint). Standard Pb solutions of known, certified concentration were used for liquid spikes. CRM soil materials used previously in the AIHA® Environmental Lead Proficiency Analytical Testing (ELPAT) program[24] were collected mainly from the yards of older North Carolina homes (pre-1950). At RTI International, these materials were dried, ground in a ball mill, and sieved through a 150-μm screen; Pb concentration was verified by ultrasonic extraction and ICP-AES analysis. Paint materials also used in the ELPAT program were collected from several venues (hospitals in Athens, Ohio, and Raleigh, N.C., and a factory in Winston-Salem, N.C.), and from old boards and paint scraping operations. They were sieved through a 2-mm screen to remove debris, ground in a ball mill, and sieved again through a 150-μm screen, with Pb concentration verified by microwave digestion and ICP analysis. The conduct and results of the ILS study involving Pb measurements on these materials have been reported.[14]

In a different ILS, various target elements in solution (Spectrapure Standards, Oslo, Norway) were converted to aerosols using an ultrasonic nebulizer with a desolvation unit. Aerosols were introduced into a 114-port "Sputnik"-type aerosol dosing chamber[25] at STAMI. Plastic 37-mm diameter cassettes (Millipore, Inc., Billerica, Mass.) containing cellulosic filter capsules (supplied by SKC and then conveyed to STAMI by NIOSH) were placed into the multi-port aerosol sampling chamber and connected to air sampling pumps. Samples were collected from the chamber using critical orifices to ensure a similar flow through each cassette. The actual flow rate through each cassette was measured and recorded (to the nearest 0.01 L/min). The metals solutions were adjusted to give target sampler loadings in accordance with the values listed in Table IV.

Elemental contents of the digests from a single sample at each level were measured at STAMI by ICP-AES (Optima 3000; PerkinElmer Inc., Waltham, Mass.). The cellulosic filter capsules were digested in Teflon autoclaves with a mixture of 2 mL aqua regia and 0.2 mL hydrofluoric acid. A known quantity of beryllium chloride solution was added as an internal spectrometric standard before acid digestion. The autoclaves were heated in a microwave unit (MLS 1200, Teflon Container SV140, 10 bar pressure; Milestone, Sorisole, Italy). Fourteen mL of deionized water was added to make up the total sample volume. The results showed deviations from the desired target of Level 1: 115–125%, Level 2: 120–130%, Level 3: 75–80%. The deviations are confirmed through the approximate mean values reported by the participating laboratories listed in Table V.

After preparation, the dosed cellulosic filter capsule samples, loaded into 37-mm plastic cassettes (SKC, Inc.), were delivered to NIOSH; three replicates at each loading level were later distributed to the participating laboratories. The participants were asked to carry out digestion and analysis of the cellulosic filter capsules using their preferred procedure(s) in accordance with the applicable ASTM International standards.[18,20] Following analysis, the participants were asked to report their results to the coordinator of the study in units of micrograms per sample. These results were recalculated as concentrations using the measured flow rates through the individual cassettes to remove the effect of minor variations in the flow rates. Concentration values were then used in the statistical evaluations. For data presentation, laboratories are identified by code to ensure confidentiality.

RESULTS AND DISCUSSION

Reported results have been evaluated in accordance with ASTM E691.[17] The analysis and treatment of the ILS test results have three purposes: (1) to determine whether the

TABLE V. Elemental Loadings of Aerosol-Dosed Cellulosic Cellulosic Filter Capsule Analyzed in the ILS

	Loading Mass (approx.), μg/Sample Element								
Loading Level	**Fe**	**Ni**	**Cr**	**Mn**	**Co**	**Cu**	**Cd**	**Pb**	**As[A]**
L1	15	1.5	7.0	3.0	0.3	3.0	0.15	12	0.15
L2	150	15	75	30	3	30	1.5	60	1.5
L3	750	75	350	150	15	150	7.5	75	7.5

Note: Elemental loadings were approximate, based on participant data.
[A]Data for As showed significantly higher uncertainties than the remaining elements.

collected data are adequately consistent to form the basis for a test method precision statement, (2) to investigate and act on any data considered to be inconsistent, and (3) to obtain the precision statistics on which the precision statement can be based. The statistical analysis of the data for estimates of the precision statistics is simply a one-way analysis of variance (within- and between-laboratories) carried out separately for each level (material). The procedure to be followed is that detailed in the standard.[17] The fundamental precision statistics of the ILS are the repeatability standard deviation and the reproducibility standard deviation. Other statistical parameters may then be calculated from these standard deviations. The repeatability standard deviation is calculated from

$$s_r = \sqrt{\sum_1^p s^2/p}$$

where

s_r = the repeatability standard deviation
s = the cell standard deviation (p of them from Eq. 2 in Reference 16), and
p = the number of laboratories.

A provisional value ($(s_R)^*$) for the reproducibility standard deviation (s_R) is computed from

$$(s_R)^* = \sqrt{(s_{\bar{x}})^2 + (s_r)^2(n-1)/n}$$

where

$s_{\bar{x}}$ = the standard deviation of the tabulated cell averages, and
n = the number of reported results.

The provisional value is then compared with the repeatability standard deviation, and whichever value is larger is taken to be the repeatability standard deviation (and thus the same value can appear in both columns). Whereas such an analysis can be invalidated by the presence of severe outliers, it is necessary to first examine the consistency of the reported data as detailed in Part 17 of ASTM E691, "Flagging Inconsistent Results," using the critical values of the h and k consistency statistics (calculated according to Paragraph 15.7, Eqs. 8 and 9 of ASTM E691) at the 0.5% significance level. After removal of outliers by this procedure, values of s_r and s_R are recalculated and then used to derive the 95% repeatability and reproducibility limits (r and R) according to $r = 2.8s_r$ and $R = 2.8s_R$. The final form of the precision statement is prepared in accordance with ASTM E177.[26]

ILS results for measurements of cellulosic filter capsules spiked with Pb-containing performance evaluation materials, which appeared in different form in a preliminary report,[14] are presented again in Table VI. Repeatability values were all at about 16% and below, reproducibility estimates ranged from about 5% to 24%, and recoveries were generally

TABLE VI. ILS Precision Statistics and Recoveries for Pb-Spiked Cellulosic Filter Capsules ($p = 6$)

Sample Matrix	$\bar{x}$,[A] μg Pb	$s_{\bar{x}}$[B]	**Reference, μg Pb**	R[C]	r[D]	**% Recovery (% RSD[E])**
Liquid spike	18.2	0.90	18.0	5.1	5.1	101 (5.0)
Ground paint	22.2	0.42	21.3	4.7	4.7	104 (1.9)
Ground soil	21.6	2.20	22.1	4.5	6.2	97.7 (10.2)
Liquid spike	37.5	1.75	42.1	16	24	89.1 (4.7)
Ground paint	49.2	1.20	51.8	6.1	6.1	95.0 (2.3)
Ground soil	49.8	2.39	54.5	6.8	7.8	91.2 (4.8)

[A]Overall mean for six reporting laboratories (n = 3 for each sample matrix at each spike level).
[B]Standard deviation of individual laboratory means about overall mean $\bar{x}$.
[C]Repeatability.
[D]Reproducibility.
[E]Relative standard deviation.

TABLE VII. Multi-Element ILS Precision Statistics for Aerosol-Dosed Cellulosic Filter Capsules

Element and Approx. Loading Level	p^A	$\bar{x}$,^{B} μg/m^3	$s_{\bar{x}}{}^C$	$s_{\bar{x}}/\bar{x}$ ^{D}	r^E	R^F	$r/\bar{x}$	$R/\bar{x}$
Cd L2 (1.5 μg)^G	8	6.0	0.79	0.13	2.6	3.0	0.43	0.51
Cd L3 (7.5 μg)	8	5.5	0.53	0.096	1.0	1.7	0.19	0.31
Cr L1 (7.0 μg)	7	41	2.3	0.057	2.7	6.8	0.07	0.17
Cr L2 (75 μg)	6	340	18	0.052	17	51	0.05	0.15
Cr L3 (350 μg)	8	290	14	0.049	51	58	0.17	0.20
Co L1 (0.3 μg)	8	1.5	0.06	0.040	0.11	0.20	0.07	0.13
Co L2 (3.0 μg)	7	13	0.42	0.032	0.61	1.3	0.05	0.10
Co L3 (15 μg)	8	12	0.79	0.068	1.9	2.7	0.16	0.23
Cu L1 (3.0 μg)	6	18	0.98	0.056	1.6	3.1	0.09	0.17
Cu L2 (30 μg)	8	140	6.2	0.045	17	22	0.12	0.16
Cu L3 (150 μg)	8	110	6.0	0.053	22	25	0.19	0.22
Fe L1 (15 μg)	7	80	5.0	0.062	10	16	0.13	0.20
Fe L2 (150 μg)	7	630	44	0.070	41	130	0.07	0.20
Fe L3 (750 μg)	8	590	46	0.078	120	160	0.21	0.28
Pb L1 (12 μg)	8	67	4.5	0.068	5.0	13	0.07	0.20
Pb L2 (60 μg)	8	260	15	0.058	24	47	0.09	0.18
Pb L3 (75 μg)	8	58	4.2	0.073	11	15	0.19	0.26
Mn L1 (3.0 μg)	8	16	1.4	0.090	1.6	4.1	0.10	0.27
Mn L2 (30 μg)^G	8	130	11	0.084	11	32	0.09	0.24
Mn L3 (150 μg)	7	120	4.1	0.035	23	23	0.20	0.20
Ni L1 (1.5 μg)	8	8.5	1.5	0.18	0.68	4.1	0.08	0.48
Ni L2 (15 μg)	8	67	7.1	0.11	7.0	21	0.10	0.31
Ni L3 (75 μg)	8	59	7.0	0.12	8.0	21	0.14	0.35

^{A}Number of reporting laboratories minus outliers.
^{B}Overall mean airborne concentration for p reporting laboratories (n = 3 for each element at each dosing level).
^{C}Standard deviation of laboratory means about overall mean $\bar{x}$.
^{D}Relative standard deviation about overall mean.
^{E}Repeatability.
^{F}Reproducibility.
^{G}Results where removal of outliers led to additional outliers, so outliers were not removed.

quantitative within ±10% of target values. The values for the high Pb aqueous spike are discussed in the reference.[14] Overall, the ILS performance data for Pb demonstrate that cellulosic internal capsules attached to MCE filters can be used in place of wiping and/or rinsing techniques that are otherwise required to account for CFC internal non-filter deposits. However, data from two international laboratories could not be used in the analysis because the intense jostling in international transportation had caused the loose soil and paint materials to escape from the interior of the cellulosic filter capsules.

All nine participating laboratories in the multi-element study returned results that are presented in Table VII. The samples were collected by filtration from an aerosol atmosphere, and the results are presented in terms of air concentrations. The loadings, however, are a function of both concentration and sampling time. One laboratory neglected to follow provided instructions and separated the filters from their capsules and analyzed only the filters. While this laboratory later also analyzed the capsules, this was considered too far removed from the standard procedure being evaluated for the results to be included; thus, these results were not used.

Multi-element data from the ILS round are presented in Table VII; eight participants returned acceptable results for most elements, as has been explained above. Reported results returned from the laboratories were provided in units of mass (μg) per filter. These results were recalculated as air concentrations (μg/m^3) using the measured flow rates through the individual samplers to remove the effect of minor variations in flow rates. Concentration values were then used in succeeding statistical computations. Results are provided for the evaluation of all eight laboratories unless outlier laboratories were removed as was indicated by h and k statistics.[17] Two cases where outliers were identified but could not be removed were indicated. Overall means are given in units of elemental concentration in air (μg/m^3).

Not all laboratories analyze As on a routine basis, so not every laboratory reported values for this element. The results

from those laboratories that did report As were highly variable, and given that the minimum number of six participants was not reached, the As data were not included in the ASTM E691 statistical analysis. For the lowest As level, the reported values varied from 0.07 to 3.0 μg/sample, for the second level from 0.99 to 5.0 μg/sample, and for the highest level from 5.0 to 10 μg/sample. The target loadings at each level were anticipated to be 0.15, 1.5, and 7.5 μg/sample, respectively, and thus, the reported range of As values included the target values. However, the large variations encountered here were not anticipated, since such variability was not obvious in a prior round-robin study where As loading levels were 0.25, 5, and 100 μg/sample.[22] However, the As levels in this study are similar to the two lowest levels in the previous study and high variation was encountered at the very lowest level in that work. Previously, two laboratories had analyzed blank cellulosic filter capsules from the same batch as used here and had reported all samples with arsenic < 0.8 or < 1.4 μg As per sample, respectively. While these reporting limits are higher than the lowest level of anticipated sample loading provided, they are at least an indication that background was not a contributor to variance in the higher loadings.

The lowest level in this study for Cd was also problematic, being below the reporting limit for two of the participating laboratories. A third laboratory reported Cd results ranging from <0.06 to 0.11 μg/sample, and this laboratory could have been classified as an outlier. Since removing this laboratory would have left only five laboratories in the study (less than the minimum of six specified by ASTM E691), these results were also not included in the evaluation. However, the range for all the other Cd values (0.11 to 0.14 μg/sample, compared with an expected 0.15 μg/sample) suggests that the outcome would probably have been within acceptable limits. Nevertheless, these results were not used.

Finally, several laboratories were identified as outliers in the analysis of one or more levels of one or more elements using critical values of the h and k statistics, as per the ASTM E691 procedure.[17] This finding was spread fairly evenly among the laboratories, and no one laboratory was consistently an outlier in any one element. Identified outlier laboratories were removed and the statistics recalculated. In two cases, this was a meaningless procedure, as removal of suspected outliers led to yet additional outliers. This situation is especially prevalent when the variance in the inter-sample analysis is very tight and considerably smaller than the between-laboratory variance. Hence, the results in these cases are given for all laboratories and the issue is noted. In the other cases, removal of the outlier laboratory or laboratories generally (but not always) improved the variance, and this is how the results are reported, with a notation that outliers were removed. No more than two laboratories have been removed from any level for any particular element, so that the final statistics are provided for at least the ASTM E691-specified minimum of six laboratories in every case.

The repeatability standard deviation (r) and reproducibility standard deviation (R) are functions of the absolute value of the mean, which is typical for results away from the limit of detection. In the final columns of Table VII, r and R are divided by the overall mean to give more meaningful estimates of variability. With one exception (i.e., Cd Level 2), all results for repeatability are considered acceptable (i.e., $r/\bar{x} < 0.25$). The low loading level (<5 μg Cd per sample) explains the higher variability for this sample. The RSD for reproducibility ($R/\bar{x}$) can be used as an estimate of the overall variance of the method. Most of the observed ILS elemental analysis results for reproducibility (Table VII) are acceptable (i.e., <0.30). We cannot postulate an explanation for the higher interlaboratory variability observed for Ni measurements. All values of $s_{\bar{x}}/\bar{x}$ are <0.20 and compare favorably with variabilities typically observed in interlaboratory multi-element analysis of air samples.[22–25,27]

In carrying out this work it was observed that some CFCs, as provided by the manufacturer, were found not to fit tightly together, or else the cassettes fit tightly but sealed above the edge of the internal capsule. Also, about 3% of the assembled cassettes with support pads and cellulosic filter capsules had very high pressure drops and were thus unusable. This was believed to result from regions within the cellulose ester membrane filter with limited porosity. A similar problem with MCE filters has been reported previously,[28] and such matters highlight the need for ongoing quality assurance. Even if these (and other) quality issues are corrected by the manufacturer, it is recommended that all assembled CFCs with or without internal capsule inserts be checked by the laboratory assembling the cassettes (or by the user in the field) to ensure that (a) the internal capsule is securely sealed within the cassette (this can be checked by pulling air through a condensation nucleus counter in line with the CFC, as has been proposed for all sampling cassettes)[29]; and (b) that the CFC inlet plug fits both the entry orifice of the cassette and the insert so as to properly seal the internal capsule. Assembled capsule inserts that do not meet these checks should be rejected for further use. Also, to ensure that the seal remains good after sampling, it is further recommended that the specific plug/cassette combination be retained for reassembly by, for example, placing the plug in a secure labeled container to match the cassette while sample collection is underway.

CONCLUSION

To ensure that personal exposures to aerosols are fully quantified, it is necessary to account for all particles crossing the plane of aspiration of the sampler, whether they eventually reside on the filter or elsewhere within the sampler. Several methods have been proposed for accounting for internal nonfilter deposits, including within-cassette dissolution, rinsing and/or wiping of the surfaces, and an internal capsule that will contain all particles. Through the experiments described here, we have demonstrated the potential of acid-soluble cellulose acetate capsules bound to mixed-cellulose ester filters for the collection and analysis of aerosols containing metal particles entering the 37-mm CFCs. These particular capsules are not

suitable for gravimetric analysis because of high variability in mass associated with changes in humidity.

We have shown that the background levels of many metals important in industrial hygiene, together with any matrix effects from the capsule material, are sufficiently low to allow repeatable and reproducible analyses down to levels approaching typical limits of quantitation for MCE filters. Internal capsules have advantages over rinsing or wiping in that they are less labor intensive and less likely to show variability due to variation in individual manual technique. Should acid-soluble cellulose acetate capsules bound to MCE filters of appropriate quality become commercially available, they can be used for sampling and analysis of many elements according to NIOSH procedures. It is anticipated that the results from this and subsequent studies will be used in methods that are or will be published in the *NIOSH Manual of Analytical Methods* and through consensus standards bodies such as ASTM International and the International Organization for Standardization (ISO).

ACKNOWLEDGMENTS

We are extremely grateful to the volunteer laboratories for their participation in this study. The authors thank Ronnee Andrews (NIOSH), Owen Butler (HSL), and LeRoy Dobson (WOHL) for their technical assistance with preliminary experiments; David Bartley (Consultant) for his insights into the ASTM International ILS procedure; and Eli Smyrloglou (ES Consulting) for his work with and knowledge of filters. Finally, we would like to thank David Binstock (RTI International) and Yngvar Thomassen (STAMI) for their discussions and assistance in preparing the test samples. This work was carried out under the auspices of a CDC/NIOSH National Occupational Research Agenda (NORA) exposure assessment project.

Mention of company names or products does not constitute endorsement by the Centers for Disease Control and Prevention. The findings and conclusions in this article are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

REFERENCES

1. **Raynor, P.C., D. Leith, K.W. Lee, and R. Mukund:** Sampling and analysis using filters. In *Aerosol Measurement: Principles, Techniques and Applications,* 3rd ed. P. Kulkarni, P.A. Baron, and K. Willeke (eds.). New York**:** Wiley, 2011.
2. **Volkwein, J.C., A.D. Maynard, and M. Harper:** Workplace aerosol measurement. In *Aerosol Measurement: Principles, Techniques and Applications,* 3rd ed. P. Kulkarni, P.A. Baron, and K. Willeke (eds.). New York**:** Wiley, 2011.
3. **National Institute for Occupational Safety and Health (NIOSH):** "NIOSH Manual of Analytical Methods." Methods 7300, 7301, 7303. Available at http://www.cdc.gov/niosh/nmam (accessed August 23, 2012).
4. **Institut National de Recherche et de Sécurité (INRS):** Fiche 003. In *Méthodes de Prélèvement et d'Analyse de l'Air* [Methods of Air Sampling and Analysis] Paris**:** INRS, updated periodically. [In French]
5. **Wang, J., P.D. Siegel, D.M. Lewis, et al.:** Spectroscopic techniques in industrial hygiene. In *Encyclopedia of Analytical Chemistry*, R.A. Myers (ed.). Chichester, U.K.: Wiley, 2000. pp. 4783–4824.
6. **Harper, M., and M. Demange:** Analytical performance criteria—Concerning sampler wall deposits in the chemical analysis of airborne metals. *J. Occup. Environ. Hyg. 4*:D81–D86 (2007).
7. **Chisholm, W.P., T. Lee, J.S. Slaven, J. Nelson, and M. Harper:** Comparison of filter and wall deposits from samplers used to collect airborne lead-containing dusts at field sites. *Aerosol Sci. Technol. 46*:411–418 (2012).
8. **Hendricks, W., F. Stones, and D. Lillquist:** On wiping the interior walls of 37-mm closed-face cassettes—An OSHA perspective. *J. Occup. Environ. Hyg. 6*:732–734 (2009).
9. **Demange, M., J.C. Gendre, B. Hervé-Bazin, B. Carton, and A. Peltier:** Aerosol evaluation difficulties due to particle deposition on filter holder inner walls. *Ann. Occup. Hyg. 34*:399–403 (1990).
10. **Puskar, M.A., J.M. Harkins, J.D. Moomey, and L.H. Hecker:** Internal wall losses of pharmaceutical dusts during closed-face, 37-mm polystyrene cassette sampling. *Am. Ind. Hyg. Assoc. J. 52*:280–286 (1991).
11. **Demange, M., P. Görner, J-M. Elcabache, and R. Wrobel:** Field comparison of 37-mm closed-face cassettes and IOM samplers. *Appl. Occup. Environ. Hyg. 17*:200–208 (2002).
12. **Dobson, L., L. Reichmann, and D. Popp:** Evaluation of quartz residue on cassette interiors of AIHA proficiency samples. *J. ASTM Int. 2*(*4*):1–6 (2005).
13. **Ashley, K., R. Andrews, L. Cavazos, and M. Demange:** Ultrasonic extraction as a sample preparation technique for elemental analysis by atomic spectrometry. *J. Anal. At. Spectrom. 16*:1147–1153 (2001).
14. **Harper, M., and K. Ashley:** Analytical performance issues—Preliminary studies on the use of acid-soluble cellulose acetate internal capsules for workplace metals sampling and analysis. *J. Occup. Environ. Hyg. 9*:D125–D129 (2012).
15. **Ashley, K., G.T. Applegate, T.J. Wise, J.E. Fernback, and M.J. Goldcamp:** Evaluation of a standardized micro-vacuum sampling method for collection of surface dust. *J. Occup. Environ. Hyg. 4*:215–223 (2007).
16. **ASTM International:** "D22 on Air Quality. Subcommittees and Standards." Available at http://www.astm.org/COMMIT/SUBCOMMIT/D2204.htm (accessed August 23, 2012).
17. **ASTM International:** *Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method* (ASTM E691). [Standard] West Conshohocken, Pa.: ASTM International, 2011.
18. **ASTM International:** *Standard Test Method for the Determination of Metals and Metalloids in Workplace Air by Inductively Coupled Plasma Atomic Emission Spectrometry* (ASTM D7035). [Standard] West Conshohocken, Pa.: ASTM International, 2009.
19. **International Organization for Standardization (ISO):** *Workplace Air—Determination of Metals And Metalloids in Airborne Particulate Matter by Inductively Coupled Plasma Atomic Emission Spectrometry—Sample Preparation* (ISO 15202-2). [Standard] Geneva: ISO, 2012.
20. **ASTM International:** *Standard Test Method for the Determination of Metals and Metalloids in Workplace Air by Inductively Coupled Plasma Mass Spectrometry* (ASTM D7439). [Standard] West Conshohocken, Pa.: ASTM International, 2007.
21. **Balázs, B., D.G. Ellingsen, M. Náray, G. Záray, and Y. Thomassen:** A study of the bio-accessibility of welding fumes. *J. Environ. Monit. 10*:1448–1453 (2008).
22. **Ashley, K., S.A. Shulman, M.J. Brisson, and A.M. Howe:** Interlaboratory evaluation of trace element determination in workplace air samples by inductively coupled plasma mass spectrometry. *J. Environ. Monit. 14*:360–367 (2012).
23. **Stacey, P., and O.T. Butler:** Performance of laboratories analysing welding fume on filter samples—Results from the WASP Proficiency Testing Scheme. *Ann. Occup. Hyg. 52*(*4*):287–295 (2008).
24. **AIHA:** "Environmental Lead Proficiency Analytical Testing (ELPAT) Program." Available at http://www.aihapat.org/ProficiencyTestingPrograms/elpat (accessed July 31, 2012).

25. **Gerboles, M., D. Buzica, R.J.C. Brown, et al.:** Interlaboratory comparison exercise for the determination of As, Cd, Ni and Pb in PM_{10} in Europe. *Atmos. Environ. 45*:3488–3499 (2011).
26. **ASTM International:** *Standard Practice for Use of the Terms Precision and Bias in ASTM Test Methods* (ASTM E177). [Standard] West Conshohocken, Pa: ASTM International, 2010.
27. **Butler, O.T., and A.M. Howe:** Development of an international standard for the determination of metals and metalloids in workplace air using ICP-AES: Evaluation of sample dissolution procedures through an interlaboratory trial. *J. Environ. Monit. 1*:23–32 (1999).
28. **Breuer, D.:** Analytical performance criteria—Flow resistance of samplers for personal monitoring in work areas and requirements for sampling pump performance. *J. Occup. Environ. Hyg. 9*:D25–D32 (2012).
29. **Baron, P.A., A. Khanina, A.B. Martinez, and S.A. Grinshpun:** Aerosol sampling cassettes. *Aerosol. Sci. Technol. 36*:857–865 (2002).