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Article in Journal of Occupational and Environmental Hygiene - June 2013
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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

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

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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, 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 employed to yield samples fortified at desired loading levels. Triplicates of spiked capsules at three different loadings were employed to yield samples fortified at desired loading levels. Triplicates of spiked capsules at three different loadings were employed to yield samples fortified at desired loading levels. Triplicates of spiked capsules at three different loadings were employed to yield samples fortified at desired loading levels. Triplicates of spiked capsules at three different loadings were employed to yield samples fortified at desired loading levels. Triplicates of spiked capsules at three different loadings were employed to yield samples fortified at desired loading levels. Triplicates of spiked capsules at three different loadings were employed to yield samples fortified at desired loading levels.

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 membrane³ or depth⁴ 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.¹⁴ However, these procedures can be labor intensive and may result in increased experimental uncertainty as well as uncorrectable systematic errors.

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

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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. 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), 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, 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 × 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). 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,(13) 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.
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. 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). 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 cellulose 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/HNO₃, 90°C (n = 3) | Element | Al  | Sb  | As  | Ba  | Be  | Bi  | B   | Cd  | Ca  | Cr  | Co  | Cu  | Fe  | Pb  |
|--------------------------------------|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| x , μg/sample                        |         | 0.7 | 0.2 | 0.4 | ND  | ND  | 0.3 | 0.1 | ND  | 60  | ND  | 0.8 | 1.0 | 0.1 |
| x , μg/sample                        |         | Li  | Mg  | Mn  | Mo  | Ni  | P   | K   | Se  | Sr  | Ti  | Sn  | Ti  | V   | Zn  |
| Laboratory 2: HNO₃ only, 120°C (n = 10) | Element |     |     |     |     |     |     |     |     |     |     |     |     |     |
| x , μg/sample                        | Al  | Sb  | As  | Ba  | Be  | Bi  | B   | Cd  | Ca  | Cr  | Co  | Cu  | Fe  | Pb  |
| x , μg/sample                        | ND  | ND  | 0.8 | 1.6 | 0.7 | 0.1 | ND  | 0.2 | 0.2 | 0.0 | 0.0 |
| x , μg/sample                        | Li  | Mg  | Mn  | Mo  | Ni  | P   | K   | Se  | Sr  | Ti  | Sn  | Ti  | V   | Zn  |
| x , μg/sample                        | ND  | ND  | 0.1 | 3.0 | 0.1 | 2.8 | ND  | 0.2 | 0.2 | 0.0 | 0.0 |

aND = 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.

bNot 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 | Ti | Sn | Ti | V  | Zn |
| ICP-AES | —  | ND | ND | ND | —  | 6.4| 1.3| ND | 0.1| ND | 0.7| 0.2| ND | 0.4|
| 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 | 0.2|

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. 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) 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 |
| 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 (IRSSST), 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 |
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 cellulose 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; 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; Pb concentration was verified by microwave digestion and ICP-AES analysis. The conduct and results of the ILS study involving Pb measurements on these materials have been reported.(18,20) Following analysis, the participants were asked in accordance with the applicable ASTM International standards.(18,20) The analysis and treatment of the ILS reported results have been evaluated in accordance with the Australian/New Zealand standard for Pb concentration verified by microwave digestion and ICP-AES analysis. The deviations are confirmed through the approximate mean values reported by the participating laboratories listed in Table V.

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 cellulose filter capsules (supplied by SKC, Inc.) were later distributed to the participating laboratories. The participants were asked to carry out digestion and analysis of the cellulose filter capsules using their preferred procedure(s) 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 IV. Rationale for Target Cellulosic Filter Capsule Sample Loadings

| Loading (Sampling @ 2.0 L/min) | Loading Time in Hours | Target Loading Mass in μg |
|-------------------------------|-----------------------|--------------------------|
|                              |                       | Fe | Ni | Cr | Mn | Co | Cu | Cd | Pb<sup>a</sup> | 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<sup>a</sup> TLV<sup>b</sup>, mg/m<sup>3</sup> | 8-Hour TWA<sup>c</sup> | 1  | 0.1 | 0.5 | 0.2 | 0.02 | 0.2 | 0.01 | 0.05 | 0.01 |

<sup>a</sup>Pb loadings were increased in consideration of background issues. Target loading is fraction of OEL multiplied by loading time.

<sup>b</sup>Threshold limit value.

<sup>c</sup>Time-weighted average.
TABLE V. Elemental Loadings of Aerosol-Dosed Cellulosic Cellulosic Filter Capsule Analyzed in the ILS

| Loading Level | Fe  | Ni  | Cr  | Mn  | Co  | Cu  | Cd  | Pb  | As  |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 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 provisional value \((s_R)^*\) for the reproducibility standard deviation \((s_R)\) is computed from

\[
(s_R)^* = \sqrt{(s_x)^2 + (s_y)^2(n-1)/n}
\]

where

- \(s_x\) = the repeatability standard deviation
- \(s_y\) = the cell standard deviation
- \(n\) = the number of reported results.

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

| Sample Matrix   | \(\bar{x}\) \(\mu g\) Pb | \(s_x\) | Reference, \(\mu g\) Pb | \(R\) | \(r\) | % Recovery \((% \text{ RSD})\) |
|-----------------|--------------------------|------|------------------------|------|------|--------------------------|
| 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.
and 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/m³) 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/m³).

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

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

| Element and Approx. Loading Level | $p^A$ | $\bar{x}^B$, µg/m³ | $s^C_\text{r}$ | $s^D_\bar{x}$ | $r^E$ | $R^F$ | $r/\bar{x}$ | $R/\bar{x}$ |
|----------------------------------|------|-----------------|----------------|----------------|--------|--------|--------|--------|
| 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.
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 \( \mu g/\)sample, for the second level from 0.99 to 5.0 \( \mu g/\)sample, and for the highest level from 5.0 to 10 \( \mu g/\)sample. The target loadings at each level were anticipated to be 0.15, 1.5, and 7.5 \( \mu g/\)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 \( \mu g/\)sample.\(^{23}\) 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 cellulose filter capsules from the same batch as used here and had reported all samples with arsenic \(< 0.8\) or \(< 1.4 \mu g\) 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 \( \mu g/\)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 \( \mu g/\)sample, compared with an expected 0.15 \( \mu g/\)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 (\(< 5 \mu g\) 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 \( s_1/\bar{x} \) are \(< 0.20 \) and compare favorably with variabilities typically observed in interlaboratory multi-element analysis of air samples.\(^{12-25,27}\)

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 cellulose 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 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 non-filter 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

W e 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.

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