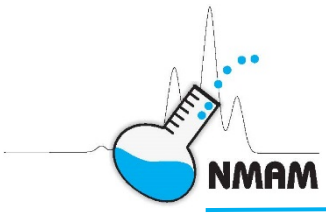

BACKUP DATA REPORT
NIOSH Method No. 7306

Title: Elements by Cellulosic Internal Capsule

Analyte: 33 elements

Author/developer: Kevin Ashley, Ronnee N. Andrews, and H. Amy Feng

Date: 9/10/2015

Elements by cellulosic internal capsule samplers and ICP-AES: Backup data report for NIOSH method 7306

Summary

Performance evaluation materials for the interlaboratory study (ILS) consisted of cellulose acetate capsules attached to mixed-cellulose ester (MCE) filters (37 mm, 0.8 µm pore size). Batches of capsules were dosed with 33 elements from standard aqueous solutions. Triplicates of spiked capsules at three different loadings, plus blank media, 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 ICP-AES in accordance with applicable NIOSH 7300-series methods [1-4]. Participants were asked to report their results in units of µg of each target element per sample. For the majority of the elements investigated, interlaboratory precision and recovery estimates from the participating laboratories amply demonstrated the utility of the cellulosic internal capsules for the measurement of sampled trace elements.

Introduction

Airborne particles that are collected using closed-face filter cassettes (CFCs), which are used widely to sample workplace aerosols, can deposit in places other than on the filter, notably on the inside walls of the cassette [5]. If only the filter is then analyzed, these particulate wall deposits will not be included in the ensuing elemental analysis, potentially leading to underestimation of exposure [6]. An effective technique for ensuring that internal non-filter deposits are included in the analysis is to collect airborne particles within an acid-soluble internal capsule which, following sampling, can be dissolved along with the filter for subsequent elemental analysis [7]. The schematic of the CFC with an internal capsule is illustrated in Figure 1. In this project, an interlaboratory study (ILS) was carried out to evaluate the use of cellulosic CFC internal capsules for their suitability in the determination of trace elements in airborne samples from workplaces.

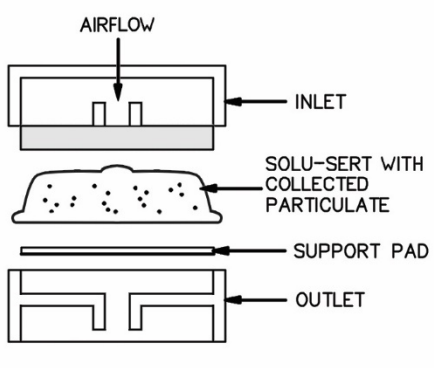

Figure 1. Schematic of closed-face filter cassette (CFC) aerosol sample collection using an internal capsule (Used with permission of Zefon International, Inc. [8])

The overall goal of this effort was to evaluate and validate a method that accounts for all aerosol particles entering the inlet of the CFC sampler, thereby including material that would not otherwise be 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 internal capsules for their use with traditional plastic air sampling cassettes. The ILS entailed fortifying the filter of the internal capsule with various loadings of metals and metalloids of interest and sending them to volunteer laboratories for analysis. The inserts were subjected to acid dissolution and analyzed by the participating laboratories for their elemental content by inductively coupled plasma – atomic emission spectrometry (ICP-AES). The procedure described is meant to replace the practice of filter-based sample collection and subsequent filter-only analysis using CFCs.

Experimental

The performance evaluation materials used in this ILS consisted of Solu-Sert™ cellulosic acid-soluble capsules, which were obtained from Zefon International (Ocala, FL). The Solu-Sert™ capsules were spiked with 33 elements of interest by High-Purity Standards (Charleston, SC), in order to prepare certified reference materials (CRMs) having desired loading levels of the metals and metalloids of concern in occupational exposure assessment (Table 1). The values listed in Table 1 include the impurity in the filter. Certificates of analysis for the CRMs, provided by the vendor, provided certified reference values for each element at each loading level. The target loading levels of the 33 elements within the Solu-Sert™ capsules (Table 1) were chosen based upon reasonable assumptions of what a variety of laboratories could confidently measure. Spiking of Solu-Sert™ capsules was carried out using standard solutions (containing the elements of interest) traceable to national standards, i.e., National Institute for Standards and Technology (NIST).

Table 1: Elements and nominal spiking levels (in µg) on internal capsule (Solu-Sert™)

Element (Symbol)	Level 1 (Low level)	Level 2 (Medium level)	Level 3 (High level)
Silver (Ag)	5.0 ± 0.1	10.1 ± 0.2	20.1 ± 0.4
Aluminum (Al)	10.6 ± 0.2	30.9 ± 0.6	60.8 ± 1.2
Arsenic (As)	5.0 ± 0.1	20.2 ± 0.4	40.1 ± 0.8
Barium (Ba)	2.21 ± 0.04	7.3 ± 0.1	15.2 ± 0.3
Beryllium (Be)	2.01 ± 0.02	7.0 ± 0.1	14.9 ± 0.1
Calcium (Ca)	114 ± 2	165 ± 3	215 ± 4
Cadmium (Cd)	2.01 ± 0.02	7.0 ± 0.1	14.9 ± 0.1
Cobalt (Co)	2.01 ± 0.02	7.0 ± 0.1	14.9 ± 0.1
Chromium (Cr)	2.91 ± 0.04	7.9 ± 0.2	15.8 ± 0.3
Copper (Cu)	3.16 ± 0.06	15.1 ± 0.3	29.9 ± 0.6
Iron (Fe)	21.3 ± 0.4	41.0 ± 0.8	80.5 ± 1.6
Indium (In)	5.04 ± 0.05	14.9 ± 0.1	39.7 ± 0.4
Potassium (K)	10.6 ± 0.2	15.7 ± 0.3	20.7 ± 0.4
Lanthanum (La)	3.01 ± 0.03	10.1 ± 0.1	20.1 ± 0.2
Lithium (Li)	2.01 ± 0.02	7.0 ± 0.1	14.9 ± 0.1
Magnesium (Mg)	12.7 ± 0.1	27.9 ± 0.3	103 ± 1
Manganese (Mn)	2.01 ± 0.02	7.0 ± 0.1	14.9 ± 0.1
Molybdenum (Mo)	2.01 ± 0.02	7.1 ± 0.1	15.0 ± 0.2
Nickel (Ni)	2.01 ± 0.02	7.0 ± 0.1	14.9 ± 0.1
Phosphorus (P)	10.1 ± 0.2	24.9 ± 0.5	99 ± 2
Lead (Pb)	10.0 ± 0.2	25.2 ± 0.5	100 ± 2
Antimony (Sb)	5.0 ± 0.1	25.1 ± 0.5	40.2 ± 0.8
Selenium (Se)	3.0 ± 0.2	15.1 ± 0.3	30.1 ± 1.5
Tin (Sn)	2.01 ± 0.04	7.0 ± 0.1	14.9 ± 0.3
Strontium (Sr)	2.01 ± 0.02	7.1 ± 0.1	15.0 ± 0.2
Tellurium (Te)	3.0 ± 0.1	12.6 ± 0.3	20.1 ± 0.4
Titanium (Ti)	2.01 ± 0.04	7.0 ± 0.1	14.9 ± 0.3
Thallium (Tl)	3.0 ± 0.1	10.1 ± 0.2	20.1 ± 0.4
Vanadium (V)	3.02 ± 0.06	7.0 ± 0.1	14.9 ± 0.3
Tungsten (W)	10.1 ± 0.2	25.1 ± 0.5	40.2 ± 0.8
Yttrium (Y)	2.01 ± 0.04	7.1 ± 0.1	15.0 ± 0.3
Zinc (Zn)	5.2 ± 0.1	25.1 ± 0.5	59.7 ± 1.2
Zirconium (Zr)	2.01 ± 0.04	7.0 ± 0.1	14.9 ± 0.3

The Solu-Sert™ CRMs were conveyed to volunteer laboratories, which were requested to carry out sample dissolution and ICP-AES analysis in accordance with NIOSH methods (7300 methods series). Triplicates of Solu-Sert™ samples spiked at each loading level, plus media blanks (also in triplicate), were conveyed to each participant. Loading levels were unknown to the participants. Sampling chain-of-custody procedures were followed throughout the ILS, in accordance with ASTM D4840 [9].

Laboratories that participated in the ILS and reported analytical results included: CDC/NIOSH, Cincinnati, OH; Occupational Safety and Health Administration (OSHA) Salt Lake Technical Center, Sandy, UT; Bureau Veritas North America (BVNA), Novi, MI; ALS Laboratories, Salt Lake City, UT; Institut National de Recherche et de Sécurité (INRS), Vandoeuvre-lès-Nancy, France; Forensic Analytical Services, Hayward, CA; BWXT Y-12 National Security Organization, Oak Ridge, TN; and the Wisconsin Occupational Health Laboratory (WOHL), Madison, WI. The sample preparation methods used by the participating laboratories are summarized in Table 2. For data presentation, laboratories are identified by code to maintain confidentiality.

Table 2. Sample preparation methods used by laboratories participating in internal capsule (Solu-Sert™) interlaboratory study

Laboratory No.	Sample dissolution procedure
1	hot block extraction; HNO_3, 90-95 ^oC (NIOSH 7303)
2a[1]	hot plate digestion; $HNO_3/HClO_4$, 120-130 ^oC (NIOSH 7300)
2b[1]	microwave digestion; HNO_3, 150 ^oC (NIOSH 7302)
3	hot block extraction; HNO_3/HCl, 95 ^oC (NIOSH 7303)
4	microwave digestion; HNO_3/H_2O_2, 210 ^oC (modified NIOSH 7302)
5	hot block extraction; HNO_3, 95 ^oC (NIOSH 7303)
6	hot block extraction; HNO_3/HCl, 95 ^oC (NIOSH 7303)
7	hot block extraction; HNO_3/HCl, 95 ^oC (NIOSH 7303)
8	hot plate digestion; $HNO_3/H_2SO_4/H_2O_2$, 120-130 ^oC (modified NIOSH 7300)

[1]This lab used two different procedures (i.e., hot plate and microwave digestion treatment) and it was treated as a separate laboratory for the data analysis.

After sample dissolution by means of hot plate, hot block or microwave treatment in acid solutions, each laboratory analyzed sample extracts for multielement analysis by ICP-AES. Five participating laboratories used hot block extraction, two used hot plate digestion, and two used microwave digestion (Table 2). One of the above laboratories used two different procedures, where hot plate or microwave digestion was used on separate sets of Solu-Sert™ CRMs. For the purposes of the ILS, results from these two different sample dissolution procedures from the same laboratory were treated as being from separate laboratories. The participating laboratories were requested to report their results in units of micrograms per sample of each element analyzed.

Results

Reported results from the participating laboratories are presented in Table 3a for media blanks and in Tables 3b-d for three different Solu-Sert™ CRM elemental loadings, Levels 1 (low), 2 (medium) and 3 (high). The results presented are as reported and no rounding of the values was done. Not all laboratories reported results for all elements. Some laboratories reported results above the estimated method detection limit (MDL), while others only reported results above their reporting limit (RL). Laboratory-reported results that were below the MDL or RL are indicated by a (<) sign in table entries, with the MDL or RL value listed in each instance. The MDL or RL values were determined using the laboratory's usual procedure.

Table 3a. Internal capsule (Solu-Sert™) interlaboratory study - Elemental determination by ICP-AES: Media blank results

Element	Lab 1 (µg/sample) (RL)			Lab 2a (µg/sample) (MDL)			Lab 2b (µg/sample) (MDL)			Lab 3 (µg/sample) (MDL)			Lab 4[3] (µg/sample) (MDL)	
Ag	<0.250	<0.250	<0.250	<0.017	<0.017	<0.017	0.102	0.056	0.022	<0.03	<0.03	<0.03	<4.2	<4.2
Al	<5.00	<5.00	<5.00	2	<1.	<1.	1.7	1.2	1.1	<2	<2	<2	0.78	0.387
As	<2.50	<2.50	<2.50	0.14	0.12	<0.098	0.885	0.852	0.610	<2	<2	<2	<0.83	<0.83
Ba	<0.250	<0.250	<0.250	0.218	0.203	0.235	0.345	0.220	0.230	<0.6	<0.6	<0.6	0.205	0.332
Be	<0.0130	<0.0130	<0.0130	<0.0040	<0.0040	<0.0040	<0.0090	<0.0090	<0.0090	0.016	<0.001	<0.001	<0.0053	<0.0053
Ca	<15.0	<15.0	<15.0	16.5	13.8	15.7	17.3	14.9	14.3	<3	<3	<3	11.10	12.1
Cd	<0.0750	<0.0750	<0.0750	<0.22	<0.22	<0.22	0.0364	0.0263	0.013	<0.03	<0.03	<0.03	<0.022	<0.022
Co	<0.0750	<0.0750	<0.0750	<0.0099	<0.0099	<0.0099	0.0541	0.0351	0.013	<0.03	<0.03	<0.03	<0.049	<0.049
Cr	<1.30	<1.30	<1.30	0.288	0.269	0.398	0.421	0.387	0.792	<0.4	<0.4	<0.4	1.01	0.82
Cu	<0.500	<0.500	<0.500	0.19	0.15	0.353	0.12	0.16	0.084	<0.8	<0.8	<0.8	<0.046	<0.038
Fe	<5.00	<5.00	<5.00	1	1.2	1.3	2.38	1.55	3.20	1.1	1.9	1.2	1.91	1.04
In	NA[2]	NA	NA	<0.11	<0.11	<0.11	1.01	0.699	0.31	<0.3	<0.3	<0.3	<0.17	<0.17
K	<13.0	<13.0	<13.0	2	2	1	1.29	1.00	0.823	<6	<6	<6	<0.15	<0.15
La	NA	NA	NA	<0.047	<0.047	<0.047	0.298	0.194	0.107	<0.02	<0.02	<0.02	<0.017	<0.014
Li	<0.500	<0.500	<0.500	<0.019	<0.019	<0.019	0.013	0.0073	<0.0062	<0.02	<0.02	<0.02	<0.0050	<0.0068
Mg	<1.40	<1.40	<1.40	2.65	2.21	2.55	3.86	3.17	2.88	<1	<1	<1	2.42	2.60
Mn	<0.130	<0.130	<0.130	<0.012	<0.012	<0.012	<0.020	<0.020	<0.020	0.024	0.062	<0.02	<0.031	<0.026
Mo	<0.380	<0.380	<0.380	<0.012	0.014	<0.012	0.0861	0.0769	0.0432	<0.1	<0.1	<0.1	<0.12	<0.12
Ni	<0.130	<0.130	<0.130	0.0375	0.022	0.0457	0.194	0.154	0.0867	<0.1	0.1	<0.1	<0.30	<0.26
P	<5.00	<5.00	<5.00	0.67	0.73	<0.62	2.20	2.12	1.67	<2	<2	<2	<0.49	<0.49
Pb	<1.30	<1.30	<1.30	<0.40	<0.40	<0.40	0.495	0.393	0.243	<1	<1	<1	0.085	<0.082
Sb	<1.50	<1.50	<1.50	<0.7	<0.7	<0.7	0.750	0.588	0.346	<1	<1	<1	<0.41	<0.41
Se	<2.50	<2.50	<2.50	0.064	<0.055	<0.055	1.27	1.15	0.744	<5	<5	<5	<0.51	<0.84
Sn	<2.50	<2.50	<2.50	<0.2	<0.2	<0.2	0.457	0.462	0.321	<0.4	<0.4	<0.4	<0.14	<0.14
Sr	<0.380	<0.380	<0.380	0.0456	0.0385	0.0427	0.0599	0.0496	0.0453	0.010	<0.009	<0.009	0.0389	0.0427
Te	<1.30	<1.30	<1.30	<0.09	0.1	<0.09	0.942	0.774	0.376	<0.6	<0.6	<0.6	<0.42	<0.44
Ti	<0.0750	<0.0750	<0.0750	0.033	0.031	0.033	0.116	0.0982	0.0766	0.024	<0.02	<0.02	0.1039	0.0830
Tl	<1.30	<1.30	<1.30	<0.025	<0.025	<0.025	0.496	0.426	0.282	<1	1.1	<1	NA	NA
V	<0.230	<0.230	<0.230	<0.011	<0.011	<0.011	0.0644	0.0454	0.019	<0.02	<0.02	<0.02	<0.025	<0.025
W	<1.30	<1.30	<1.30	<0.43	<0.43	<0.43	0.175	0.260	0.055	<0.1	<0.1	<0.1	<0.30	<0.30
Y	<0.0750	<0.0750	<0.0750	<0.0083	<0.0083	<0.0083	0.0319	0.014	<0.0049	0.018	<0.005	<0.005	<0.0053	<0.0053
Zn	<0.500	<0.500	<0.500	<0.74	<0.74	<0.74	0.485	0.1	0.2	<0.1	0.84	0.53	<0.089	<0.089
Zr	<0.500	<0.500	<0.500	<0.072	<0.072	<0.072	0.0656	0.0477	0.029	0.053	<0.02	<0.02	0.018	0.023

Note: RL=Reporting Limit; MDL=Method Detection Limit

[2]NA: Not applicable; not reported by the laboratory

[3]one sample lost; not reported by the laboratory

Table 3a con't. Internal capsule (Solu-Sert™) interlaboratory study - Elemental determination by ICP-AES: Media blank results

Element	Lab 5 (µg/sample) (RL)			Lab 6 (µg/sample) (RL)			Lab 7 (µg/sample) (RL)			Lab 8 (µg/sample) (RL)		
Ag	<0.15	<0.15	<0.15	< 0.5	< 0.5	< 0.5	< 0.3	< 0.3	< 0.3	NA[2]	NA	NA
Al	<10	<10	<10	< 5	< 5	< 5	NA	NA	NA	NA	NA	NA
As	<0.75	<0.75	<0.75	< 5	< 5	< 5	< 0.6	< 0.6	< 0.6	NA	NA	NA
Ba	0.38	0.2	0.2	0.225	0.159	0.169	< 0.5	< 0.5	< 0.5	NA	NA	NA
Be	<0.013	<0.013	<0.013	< 0.012	< 0.012	< 0.012	< 0.08	< 0.08	< 0.08	<0.1	<0.1	<0.1
Ca	29	<20	<20	15.3	15.3	14.5	17	18	26	NA	NA	NA
Cd	<0.25	<0.25	<0.25	< 0.25	< 0.25	<0.25	< 0.6	< 0.6	< 0.6	<0.5	<0.5	<0.5
Co	<0.25	<0.25	<0.25	< 0.5	< 0.5	< 0.5	< 0.3	< 0.3	< 0.3	<2.5	<2.5	<2.5
Cr	<4	<4	<4	< 0.5	< 0.5	0.505	< 0.9	< 0.9	< 0.9	<10	<10	<10
Cu	<1.5	<1.5	<1.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	<2.5	<2.5	<2.5
Fe	<5	<5	<5	1.37	< 1.2	< 1.2	< 20	< 20	< 20	<25	<25	<25
In	NA	NA	NA	NA	NA	NA	< 0.6	< 0.6	< 0.6	NA	NA	NA
K	<7.5	<7.5	<7.5	< 50	< 50	< 50	NA	NA	NA	NA	NA	NA
La	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Li	<0.5	<0.5	<0.5	< 0.25	< 0.25	< 0.25	NA	NA	NA	NA	NA	NA
Mg	5.1	<5	<5	< 5	< 5	< 5	NA	NA	NA	NA	NA	NA
Mn	<0.25	<0.25	<0.25	< 0.12	< 0.12	< 0.12	< 0.8	< 0.8	< 0.8	<2.5	<2.5	<2.5
Mo	<0.5	<0.5	<0.5	< 0.5	< 0.5	< 0.5	< 2	< 2	< 2	<25	<25	<25
Ni	<1	<1	<1	< 1.2	< 1.2	< 1.2	< 0.3	< 0.3	< 0.3	<25	<25	<25
P	NA	NA	NA	< 12	< 12	< 12	NA	NA	NA	NA	NA	NA
Pb	<1.8	<1.8	<1.8	< 2.5	< 2.5	< 2.5	< 0.8	< 0.8	< 0.8	<5	<5	<5
Sb	<1.5	<1.5	<1.5	< 5	< 5	< 5	< 0.5	< 0.5	< 0.5	<25	<25	<25
Se	<1.3	<1.3	<1.3	< 5	< 5	< 5	< 0.9	< 0.9	< 0.9	NA	NA	NA
Sn	<5	<5	<5	NA	NA	NA	< 30	< 30	< 30	NA	NA	NA
Sr	<0.15	<0.15	<0.15	< 0.12	< 0.12	< 0.12	NA	NA	NA	NA	NA	NA
Te	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ti	<0.5	<0.5	<0.5	< 1.2	< 1.2	< 1.2	NA	NA	NA	NA	NA	NA
Tl	<2.5	<2.5	<2.5	< 5	< 5	< 5	< 3	< 3	< 3	NA	NA	NA
V	<0.25	<0.25	<0.25	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	<1.5	<1.5	<1.5
W	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Y	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Zn	<1.8	<1.8	<1.8	< 1.2	< 1.2	< 1.2	< 0.8	< 0.8	< 0.8	<25	<25	<25
Zr	NA	NA	NA	< 5	< 5	< 5	NA	NA	NA	NA	NA	NA

Note: RL=Reporting Limit; MDL=Method Detection Limit

[2]NA: Not applicable; not reported by the laboratory

Table 3b. Internal capsule (Solu-Sert™) interlaboratory study - Elemental determination by ICP-AES: Level 1 (Low loading) results

Element	Lab 1 (µg/sample)			Lab 2a (µg/sample)			Lab 2b (µg/sample)			Lab 3 (µg/sample)			Lab 4 (µg/sample)			Lab 5 (µg/sample)			Lab 6 (µg/sample)			Lab 7 (µg/sample)			Lab 8 (µg/sample)		
Ag	5	5.07	4.67	4.46	4.34	4.62	4.82	4.82	4.75	6.5	2.9	6.9	<4.2	<4.2	<4.2	4.9	4.9	5	3.15	3.07	2.81	5.1	5.1	5	NA[2]	NA	NA
Al	10.4	10.5	8.97	11	10	11	11.3	11.0	11.0	9.8	8.9	9.3	9.33	9.35	9.59	10	10	11	10.2	10.4	10.7	NA	NA	NA	NA	NA	NA
As	4.59	5.21	4.59	4.72	4.47	4.82	5.62	5.63	5.66	4.5	5.3	4.8	4.42	4.68	4.60	5.4	5	5.1	< 5	< 5	< 5	5	5.2	5.1	NA	NA	NA
Ba	2.07	2.1	1.92	2.12	2.09	2.13	2.17	2.17	2.12	1.8	1.8	1.8	2.41	2.38	2.43	2.4	2.2	2.3	2.14	2.17	2.12	2.2	2.2	2.2	NA	NA	NA
Be	2.06	2.08	1.79	1.94	1.88	1.99	2.15	2.14	2.14	2.0	2.0	2.1	2.14	2.17	2.21	2.1	2	2.1	1.93	1.91	1.88	2	2	2	1.99	1.98	2.00
Ca	101	102	93.7	109	107	112	116	115	114	73	73	73	111.8	110.8	111.4	140	120	120	110	110	108	130	130	130	NA	NA	NA
Cd	2.07	2.07	1.8	1.86	1.80	1.96	2.09	2.09	2.05	2.0	2.0	2.0	2.02	2.03	2.06	2.2	2	2.1	2.06	2.02	2.01	2.1	2.1	2.1	2.09	2.07	2.10
Co	2.09	2.12	1.84	1.83	1.79	1.89	2.17	2.18	2.16	2.0	2.0	2.0	2.07	2.05	2.09	2.4	2.3	2.3	2.06	1.99	2.02	2.2	2.2	2.2	2.08	2.03	2.08
Cr	2.21	2.19	1.95	2.27	2.17	2.24	2.58	2.86	3.28	1.8	1.5	1.5	2.45	2.40	2.51	<4	<4	<4	2.41	2.48	2.38	2.8	2.5	2.3	2.40	2.45	2.40
Cu	3.29	3.28	2.82	3.10	5.53	3.61	3.29	3.41	3.21	3.0	2.9	2.9	3.02	3.03	3.15	3.2	3.1	3.2	3.17	3.11	3.11	3.2	3.2	3.1	3.38	3.32	3.50
Fe	22.2	21.8	18.7	21.2	20.0	21.3	22.9	25.7	23.3	21	21	22	21.8	23.2	21.9	46	23	24	21.1	21	20.6	20	20	20	23.85	25.35	24.55
In	NA	NA	NA	4.78	4.66	4.94	6.40	6.35	6.22	5.2	5.0	5.1	4.47	4.40	4.98	NA	NA	NA	NA	NA	NA	2.2	2.2	2.2	NA	NA	NA
K	<13.0	<13.0	<13.0	13	12	12	11.8	11.9	11.6	11	6.9	10	4.66	3.44	3.29	9	11	10	< 50	< 50	< 50	NA	NA	NA	NA	NA	NA
La	NA	NA	NA	2.80	2.73	2.90	3.40	3.39	3.30	2.9	2.9	2.9	3.07	3.12	3.17	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Li	2.09	2.06	1.88	1.84	1.66	1.71	1.64	1.64	1.62	1.8	1.8	1.8	1.87	1.85	1.82	2	2.1	2.1	2.02	1.97	1.99	NA	NA	NA	NA	NA	NA
Mg	9.66	9.63	8.91	11.3	11.1	11.7	13.3	13.1	12.9	10	10	9.9	12.78	12.85	13.33	17	13	14	12.1	12.1	11.8	NA	NA	NA	NA	NA	NA
Mn	2.1	2.09	1.82	1.92	1.89	1.99	1.67	1.68	1.62	2.1	2.1	2.1	2.16	2.17	2.21	2.2	2	2.1	2	1.97	1.95	2	2.1	2	2.09	2.05	2.08
Mo	2.13	2.12	1.94	1.80	1.80	1.95	2.28	2.29	2.24	1.9	2.0	1.9	1.99	2.01	2.02	2.2	2.1	2.1	2.01	1.89	1.85	2	2	2	2.05	2.00	2.05
Ni	2.22	2.21	1.94	1.89	1.84	1.95	2.35	2.83	2.33	2.0	2.0	2.1	2.20	2.13	2.26	2.1	2.1	2	2.04	1.98	2	2.5	2.5	2.4	2.30	2.30	2.25
P	10.6	10.5	9.08	9.91	9.37	10.1	12.0	12.1	12.2	11	11	9.8	9.9	10.0	9.9	NA	NA	NA	< 12	< 12	< 12	NA	NA	NA	NA	NA	NA
Pb	10.4	10.3	9.82	9.11	8.87	9.51	11.1	11.2	11.0	10	10	10	9.55	9.45	9.74	10	9.8	9.9	9.77	9.7	9.51	11	11	11	10.26	10.02	10.42
Sb	4.7	4.94	4.86	4.5	4.3	4.7	5.56	5.65	5.56	5.2	4.8	4.7	5.15	5.19	5.17	5	4.8	4.8	< 5	< 5	< 5	5.1	5.1	5	4.70	4.70	4.75
Se	3.18	2.83	<2.50	2.70	2.50	2.77	4.03	4.12	4.11	<5	<5	<5	3.03	3.32	3.51	3.9	3.5	3.5	< 5	< 5	< 5	3.5	3.6	3.5	NA	NA	NA
Sn	<2.50	<2.50	<2.50	2.0	2.0	2.1	2.56	2.60	2.58	2.1	2.0	2.0	1.26	1.26	1.39	<5	<5	<5	NA	NA	NA	< 30	< 30	< 30	NA	NA	NA
Sr	2.04	2.04	1.91	1.99	1.96	2.02	2.10	2.09	2.08	2.0	2.0	2.0	2.25	2.29	2.34	2	2	2	2.03	2.01	1.99	NA	NA	NA	NA	NA	NA
Te	2.97	3.01	2.68	2.8	2.6	2.9	4.04	4.04	3.98	4.0	2.9	3.0	2.65	2.66	2.72	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ti	2.08	2.11	1.8	1.97	1.97	2.00	2.29	2.28	2.28	2.0	2.0	2.1	2.19	2.15	2.20	2.2	2.2	2.3	2.08	2.06	2.04	NA	NA	NA	NA	NA	NA
Tl	3.09	2.77	3.12	2.79	2.68	2.85	3.44	3.42	3.35	3.2	2.8	3.7	NA	NA	NA	3.1	2.9	3.1	< 5	< 5	< 5	3	3	3	NA	NA	NA
V	3.15	3.17	2.74	3.04	3.01	3.10	3.34	3.34	3.28	3.0	3.0	3.0	3.03	3.04	3.11	3.2	3.2	3.3	2.99	2.95	2.91	2.7	2.7	2.7	3.07	3.01	3.07
W	7.47	8.41	7.68	6.12	6.73	8.09	9.36	9.64	9.69	9.2	8.4	8.5	8.51	8.66	9.32	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Y	2.09	2.11	1.94	1.92	1.88	1.95	2.14	2.13	2.09	2.0	2.0	2.0	2.03	2.04	2.09	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Zn	5.33	5.35	4.71	4.96	5.10	5.65	5.68	5.65	5.65	5.1	5.1	5.1	4.78	4.65	4.76	5.9	5.2	5.4	5.17	4.98	4.89	5.1	5.1	5	5.60	5.60	5.75
Zr	2.02	2.07	1.75	1.99	1.97	2.03	2.20	2.20	2.17	1.9	1.9	1.9	2.13	2.12	2.17	NA	NA	NA	< 5	< 5	< 5	NA	NA	NA	NA	NA	NA

[2]NA: not applicable; not reported by the laboratory

Table 3c. Internal capsule (Solu-Sert™) interlaboratory study - Elemental determination by ICP-AES: Level 2 (Medium loading) results

Element	Lab 1 (µg/sample)			Lab 2a (µg/sample)			Lab 2b (µg/sample)			Lab 3 (µg/sample)			Lab 4 (µg/sample)			Lab 5 (µg/sample)			Lab 6 (µg/sample)			Lab 7 (µg/sample)			Lab 8 (µg/sample)		
Ag	10	10.2	9.96	9.01	9.10	9.25	9.67	9.93	9.95	13	2.6	1.5	<4.2	<4.2	<4.2	9.6	9.7	8.9	2.54	9.67	2.58	10	9.9	10	NA[2]	NA	NA
Al	30.2	30.3	29.8	29	29	30	28.8	29.7	29.7	28	28	28	29.2	29.5	29.5	31	31	31	29.6	29.8	29.6	NA	NA	NA	NA	NA	NA
As	20	20.7	20	18.5	19.2	19.0	22.2	23.0	22.7	21	20	21	20.9	21.8	21.9	21	22	21	19.9	20.6	20.1	21	21	21	NA	NA	NA
Ba	7.06	7.32	7.13	6.67	6.79	6.84	7.02	7.17	7.15	6.9	6.9	6.9	8.18	8.37	8.37	7.3	7.3	7.2	7.12	7.17	7.16	7.2	7.1	7.2	NA	NA	NA
Be	6.97	7.07	6.98	6.25	6.46	6.51	7.43	7.61	7.62	6.9	7.1	7.0	7.83	8.01	8.10	6.9	7.1	7.1	6.54	6.6	6.58	7.1	7.1	7.2	6.86	6.70	6.75
Ca	150	154	151	157	161	159	167	174	172	110	110	110	168	170	169	180	180	180	158	158	158	190	180	190	NA	NA	NA
Cd	6.91	7.12	7.01	6.32	6.80	6.53	7.10	7.36	7.34	7.1	7.1	7.1	7.45	7.59	7.73	6.9	6.9	6.9	6.85	6.92	6.92	7	7.1	7.1	7.14	7.03	7.04
Co	6.96	7.21	7.13	6.45	6.59	6.62	6.86	7.06	7.04	7.0	7.0	7.0	7.52	7.64	7.81	7.7	7.8	7.8	6.81	6.85	6.84	7.3	7.4	7.4	6.87	6.77	6.77
Cr	7.17	7.38	7.29	7.18	7.43	7.40	8.00	7.97	8.29	6.8	7.0	6.9	8.89	8.65	8.81	7.3	7.6	7.9	7.49	7.62	7.81	7.1	7.7	7.3	7.50	7.30	7.55
Cu	15.6	15.9	15.6	14.6	14.7	14.6	15.6	16.0	15.9	15	15	15	15.7	16.0	16.3	15	15	15	14.7	14.8	14.8	14	14	15	15.83	15.57	15.75
Fe	41.5	42.4	42.3	39.1	39.5	41.2	42.0	42.4	42.7	42	41	42	44.8	45.4	48.3	45	46	46	40.3	41	40.5	40	40	40	44.65	43.10	44.45
In	NA	NA	NA	14.1	14.3	14.2	16.6	17.2	17.1	15	15	15	14.0	14.4	14.4	NA	NA	NA	NA	NA	NA	7.2	7.1	7.3	NA	NA	NA
K	14.9	15.8	15.5	20	18	21	17.3	18.1	17.8	13	15	15	9.6	8.9	8.8	16	17	15	< 50	< 50	< 50	NA	NA	NA	NA	NA	NA
La	NA	NA	NA	9.40	9.57	9.62	10.6	10.8	10.8	9.9	10	9.9	10.99	11.23	11.29	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Li	6.95	7.21	7.1	6.39	6.33	6.84	5.64	5.76	5.78	6.5	6.5	6.5	6.76	6.85	6.93	7	7.1	7	6.81	6.8	6.77	NA	NA	NA	NA	NA	NA
Mg	23.5	24.4	23.8	26.0	26.1	26.4	28.2	29.5	29.1	26	26	26	30.5	31.1	31.3	30	30	30	26.7	26.8	26.9	NA	NA	NA	NA	NA	NA
Mn	7.01	7.13	7.04	6.35	6.47	6.42	7.07	7.21	7.20	7.0	7.1	7.1	7.86	7.95	8.22	7	7	6.9	6.71	6.75	6.76	6.9	6.9	7	6.99	6.85	6.85
Mo	7.46	7.75	7.55	6.69	6.71	6.77	7.63	7.85	7.77	7.3	7.1	7.2	7.48	7.75	7.75	7.3	7.4	7.4	6.86	7.01	6.98	7	7	7	7.25	7.10	7.15
Ni	<3.80	<3.80	<3.80	6.36	6.51	6.56	7.35	7.33	7.37	7.2	7.2	7.1	7.98	8.19	8.47	6.9	7	7	6.73	6.81	6.84	7.8	7.9	7.9	7.10	6.90	7.05
P	7.35	7.59	7.46	21.6	22.1	20.9	27.5	28.6	28.3	27	26	26	26.3	27.2	28.0	NA	NA	NA	25.5	25.2	25.2	NA	NA	NA	NA	NA	NA
Pb	25.1	25.9	25.7	22.8	23.8	23.3	26.0	26.9	26.5	26	26	26	26.5	27.2	27.7	25	25	25	24.2	24.2	24.4	26	26	26	23.92	23.21	23.33
Sb	24.8	24.8	24.9	22	22	24	25.6	26.7	26.5	26	25	26	27.0	27.4	27.6	24	25	24	23.8	24.1	24.3	24	25	25	24.40	23.95	23.80
Se	14.8	15.3	14.7	13.5	14.7	14.5	18.1	19.0	18.6	17	15	15	17.1	17.7	18.2	17	17	17	16.5	16.3	16.4	17	17	17	NA	NA	NA
Sn	6.75	6.98	6.93	6.2	5.0	2.6	8.08	8.35	8.24	6.9	6.5	6.9	7.10	7.01	7.19	7.1	7.1	7.1	NA	NA	NA	< 30	< 30	< 30	NA	NA	NA
Sr	7.02	7.25	7.1	6.53	6.61	6.62	7.24	7.44	7.45	7.2	7.1	7.1	8.22	8.36	8.40	7	7.1	7.1	6.94	6.95	6.94	NA	NA	NA	NA	NA	NA
Te	12.5	12.9	12.5	11	12	12	13.7	14.4	14.3	14	13	14	12.2	12.7	13.4	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ti	7.08	7.18	7.09	6.29	5.72	4.67	7.46	7.63	7.60	6.9	7.0	7.1	7.65	7.74	7.83	7.6	7.6	7.5	6.91	6.96	6.93	NA	NA	NA	NA	NA	NA
Tl	9.49	10	9.8	9.24	9.44	9.43	10.9	11.2	11.1	9.4	10	10	NA	NA	NA	9.8	10	9.7	10.7	10.6	10.5	10	10	10	NA	NA	NA
V	7.15	7.28	7.18	6.91	6.95	7.00	7.72	7.89	7.89	7.1	7.0	7.1	7.46	7.58	7.75	7.4	7.4	7.3	6.72	6.74	6.76	6.4	6.4	6.4	6.98	6.84	6.84
W	24.1	24.3	24.4	21.9	20.3	18.9	24.8	25.6	25.7	24	25	24	27.2	28.1	29.2	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Y	7.3	7.41	7.25	6.44	6.57	6.60	7.22	7.40	7.38	7.1	7.2	7.1	7.57	7.74	7.78	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Zn	25.5	26.2	25.9	23.0	24.1	24.3	25.9	25.9	25.9	25	25	25	26.9	27.6	28.3	25	26	25	24	24.2	24.2	24	24	25	26.90	26.50	26.65
Zr	6.95	7.02	6.95	6.34	6.20	5.88	7.51	7.65	7.64	6.5	6.7	6.7	7.72	7.82	7.93	NA	NA	NA	6.6	6.63	6.66	NA	NA	NA	NA	NA	NA

[2]NA: not applicable; not reported by the laboratory

Table 3d. Internal capsule (Solu-Sert™) interlaboratory study - Elemental determination by ICP-AES: Level 3 (High loading) results; as reported

Element	Lab 1 (µg/sample)			Lab 2a (µg/sample)			Lab 2b (µg/sample)			Lab 3 (µg/sample)			Lab 4 (µg/sample)			Lab 5 (µg/sample)			Lab 6 (µg/sample)			Lab 7 (µg/sample)			Lab 8 (µg/sample)		
Ag	20.2	19.6	19.9	18.0	17.0	16.1	19.1	19.2	19.7	9.5	7.6	6.0	<4.2	<4.2	<4.2	6.9	11	11	2.63	2.63	2.08	20	20	20	NA[2]	NA	NA
Al	60.1	57.8	60.5	60	56	55	57.2	56.4	58.2	56	55	68	56.1	56.6	57.7	60	60	60	60.1	59.3	58.6	NA	NA	NA	NA	NA	NA
As	41	39.4	41.7	38.4	35.1	33.3	42.7	42.4	44.6	40	41	43	40.9	40.3	42.2	43	43	43	39.8	40.6	40.2	40	42	42	NA	NA	NA
Ba	15.5	15	15.3	14.9	14.1	13.7	14.5	14.6	15.0	15	15	15	16.7	16.7	17.1	16	15	15	15.3	15	15	15	15	15	NA	NA	NA
Be	15.1	15	15.2	14.4	13.8	13.1	15.1	14.8	15.7	15	15	15	16.2	16.4	16.8	15	15	15	14.2	14.2	14.1	15	15	15	14.49	14.60	14.64
Ca	201	196	200	203	197	189	216	216	226	15	15	16	210	211	212	230	230	230	209	205	205	230	240	240	NA	NA	NA
Cd	15.1	14.9	15.1	13.9	13.3	12.4	15.1	15.0	15.6	150	150	150	15.4	15.7	16.2	15	15	15	14.8	14.9	14.8	15	16	15	15.23	15.35	15.23
Co	15.4	15.2	15.5	13.9	13.4	12.9	15.0	14.9	15.6	15	15	16	15.5	15.7	16.2	17	16	16	14.7	14.7	14.7	16	16	16	14.62	14.74	14.68
Cr	15.4	15.4	15.1	15.1	14.3	14.1	16.2	15.6	16.3	15	15	16	16.1	16.2	16.8	16	15	15	15.3	14.9	15.3	15	15	15	15.30	14.82	15.35
Cu	31.7	31.9	31	29.3	28.1	27.4	30.6	30.1	31.6	30	30	30	29.7	30.1	30.6	30	30	30	30	29.2	29.2	29	29	29	30.19	30.57	30.41
Fe	83.6	82.9	83.6	75.7	73.8	72.0	83.7	82.7	87.7	85	84	84	85.2	85.8	87.6	89	88	88	80.4	79.9	79.8	80	80	80	86.25	87.05	87.80
In	NA	NA	NA	36.3	35.5	34.0	41.6	41.3	43.0	41	41	42	36.7	37.6	38.2	NA	NA	NA	NA	NA	NA	15	15	15	NA	NA	NA
K	22.1	20.7	21.4	30	27	29	23.6	24.0	24.3	17	23	22	16.3	14.5	15.2	21	22	21	< 50	< 50	< 50	NA	NA	NA	NA	NA	NA
La	NA	NA	NA	18.7	17.8	17.2	20.8	20.8	21.6	20	20	20	21.2	21.1	21.8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Li	15.5	15.3	15.3	15.2	14.3	14.6	13.0	12.9	13.3	15	15	16	14.5	14.9	15.1	15	15	15	14.8	14.4	14.4	NA	NA	NA	NA	NA	NA
Mg	96.4	94.2	95.6	97.1	93.5	87.2	107	108	112	110	110	110	107.7	107.4	110.7	110	110	110	101	101	101	NA	NA	NA	NA	NA	NA
Mn	15.2	15.3	14.9	13.7	13.4	12.6	15.4	15.3	15.9	15	15	15	16.2	16.3	16.7	15	15	15	14.5	14.5	14.4	15	15	15	14.62	14.72	14.58
Mo	16.1	15.5	16.3	14.2	13.5	13.7	16.0	16.0	16.8	15	16	16	15.5	15.3	16.0	16	16	16	14.9	14.9	14.9	14	15	15	14.70	15.00	14.95
Ni	16	15.8	16.1	13.9	13.4	12.7	15.5	15.2	16.1	15	15	16	16.5	16.6	17.2	15	15	15	14.5	14.5	14.6	16	17	17	14.90	15.10	14.90
P	99.5	99.8	102	81.8	73.9	75.4	99.7	98.4	104	100	100	110	100.9	102.7	104.2	NA	NA	NA	99.4	99	98.6	NA	NA	NA	NA	NA	NA
Pb	104	100	105	91.7	88.3	84.0	101	101	106	110	110	110	102.1	102.0	105.0	100	98	98	98.3	99.2	98.5	100	110	110	86.59	90.49	91.96
Sb	39.9	39.8	40.2	33	25	29	40.7	40.4	41.7	41	42	43	41.3	42.2	44.0	39	39	39	39.2	38.8	38.2	39	40	40	39.48	37.74	39.46
Se	29.7	29.3	30.6	27.6	24.9	23.2	35.0	35.0	36.9	28	30	30	32.2	31.7	33.2	33	33	33	31.6	32.2	32.1	32	34	34	NA	NA	NA
Sn	15.1	14.8	15	1.6	1.1	1.6	16.5	16.3	17.1	15	15	16	14.3	14.6	15.1	15	15	15	15	14.7	14.7	< 30	< 30	< 30	NA	NA	NA
Sr	15.2	14.9	15.2	14.4	13.8	13.5	14.6	14.6	15.2	15	15	16	16.8	16.8	17.3	15	15	15	NA	NA	NA	NA	NA	NA	NA	NA	NA
Te	19.8	19.8	20	18	17	15	21.8	21.4	22.5	23	22	24	19.3	19.7	20.4	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ti	15.2	15.2	14.9	4.26	4.83	10.5	15.5	15.2	16.0	15	15	15	15.7	15.8	16.2	16	16	16	14.8	14.7	14.6	NA	NA	NA	NA	NA	NA
Tl	19.8	19	19.9	17.7	17.0	16.4	21.2	21.2	22.0	20	21	22	NA	NA	NA	19	19	19	20.3	20.8	20.8	19	20	20	NA	NA	NA
V	15.6	15.6	15.3	14.5	14.1	13.6	16.5	16.3	17.0	15	16	15	15.4	15.7	16.1	16	16	16	14.6	14.4	14.4	14	14	14	14.89	15.00	14.95
W	38.3	38.3	39.8	23.9	31.2	28.7	43.1	42.6	44.6	41	40	40	42.4	42.8	44.4	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Y	15.6	15.2	15.9	14.6	13.8	13.4	15.0	15.0	15.7	15	15	15	15.6	15.6	16.1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Zn	61.9	61.2	62.1	58.6	55.1	51.0	59.6	58.9	62.3	60	61	60	62.4	62.9	65.3	61	60	60	58.2	57.7	57.4	58	59	58	64.30	64.45	64.30
Zr	15	15	14.7	8.15	6.08	11.6	15.4	15.2	15.9	14	14	14	15.8	15.9	16.4	NA	NA	NA	14.3	14.1	14	NA	NA	NA	NA	NA	NA

[2]NA: not applicable; not reported by the laboratory

Mean overall laboratory-reported results and standard deviations are shown in Table 4a for media blanks and in Tables 4b-d for the three different Solu-Sert™ CRM elemental loadings, i.e., Levels 1 (low loading), 2 (medium loading) and 3 (high loading). For elements with 1 or 2 results reported <MDL or <RL, half of the MDL or RL was used to calculate the mean blank results. If all results reported were <MDL or <RL, the average MDL or RL was reported as a less than value. Also for each loading level, relative standard deviations and recoveries, the latter computed with respect to CRM reference values, are presented in Tables 4b-d. Calculations were performed before the results were rounded to 3 significant figures. For a few of the data sets in Tables 4b-d, outliers (identified by means of Grubbs' test) were removed prior to carrying out subsequent statistical computations.

Table 4a. Blank Internal capsule (Solu-Sert™) media – Mean laboratory results & certified reference values

Element	No. Labs[4]	Mean[5] (µg)	Std. Dev.[6] (µg)	Reference value (µg)[7]
Ag	1	0.060	-	<0.01
Al	3	1.1	0.49	0.6
As	2	0.44	0.48	<0.01
Ba	5	0.24	0.037	0.2
Be	1	0.0085	-	<0.01
Ca	6	17	4.6	14
Cd	1	0.025	-	<0.01
Co	1	0.034	-	<0.01
Cr	4	0.57	0.25	0.9
Cu	2	0.18	0.077	0.14
Fe	5	1.5	0.48	1.2
In	1	0.67	-	<0.01
K	2	1.4	0.44	0.6
La	1	0.20	-	<0.01
Li	1	0.0078	-	<0.01
Mg	4	3.3	1.2	2.7
Mn	1	0.032	-	<0.01
Mo	2	0.041	0.039	<0.01
Ni	3	0.093	0.055	<0.01
P	2	1.3	1.0	<0.01
Pb	2	0.22	0.22	<0.01
Sb	1	0.56	-	<0.01
Se	2	0.56	0.70	<0.01
Sn	1	0.41	-	<0.01
Sr	4	0.036	0.018	<0.01
Te	2	0.40	0.43	<0.01
Ti	4	0.061	0.039	<0.01
Tl	2	0.73	0.46	<0.01
V	1	0.043	-	<0.01
W	1	0.16	-	<0.01
Y	2	0.014	0.0033	<0.01
Zn	2	0.37	0.15	0.2
Zr	3	0.035	0.014	<0.01

[4]Number of laboratories reporting at least one result >MDL (or RL)
[5]values based only on reported results above MDL (or RL);
[6]standard deviation (if *p*>1);
[7]as reported by the CRM provider

Table 4b. Internal capsule (Solu-Sert™) interlaboratory study laboratory means vs. certified reference values – Level 1 (Low Loading)

Element	No. Labs[4]	Mean(µg)	Std. Dev. (µg)[6]	RSD[8]	Reference value (µg)[7]	Uncertainty in ref. value (µg)[7]	Recovery (%)
Ag	7	4.66	0.78	0.17	5.0	0.1	93.2
Al	7	10.1	0.62	0.061	10.6	0.2	95.7
As	7	4.97	0.36	0.073	5.0	0.1	99.4
Ba	8	2.14	0.18	0.084	2.21	0.04	97.0
Be	9	2.03	0.090	0.044	2.01	0.02	100.8
Ca	8	109.	18	0.16	114	2	95.8
Cd	9	2.03	0.070	0.036	2.01	0.02	101.1
Co	9	2.08	0.14	0.068	2.01	0.02	103.4
Cr	8	2.33	0.38	0.16	2.91	0.06	80.2
Cu	8[#]	3.16	0.14	0.045	3.16	0.06	100.1
Fe	9	22.9	3.4	0.15	21.3	0.4	107.4
In	5	4.61	1.5	0.33	5.0	0.1	92.1
K	5	9.44	3.4	0.36	10.6	0.2	89.0
La	4	3.05	0.25	0.081	3.01	0.03	101.3
Li	7	1.87	0.16	0.085	2.01	0.02	93.0
Mg	7	11.9	1.9	0.16	12.7	0.1	93.9
Mn	9	2.01	0.15	0.076	2.01	0.02	99.8
Mo	9	2.02	0.13	0.062	2.01	0.02	100.7
Ni	9	2.18	0.21	0.096	2.01	0.02	108.2
P	5	10.5	0.94	0.090	10.1	0.2	103.9
Pb	9	10.1	0.63	0.062	10.0	0.2	100.9
Sb	8	4.95	0.33	0.067	5.0	0.1	99.1
Se	6	3.37	0.50	0.15	3.0	0.2	112.2
Sn	4	1.98	0.52	0.26	2.01	0.04	98.7
Sr	6[#]	2.01	0.040	0.019	2.01	0.02	100.2
Te	5	3.13	0.55	0.18	3.0	0.1	104.3
Ti	7	2.11	0.12	0.057	2.01	0.04	104.9
Tl	6	3.07	0.22	0.071	3.0	0.1	102.4
V	9	3.04	0.17	0.057	3.02	0.06	100.7
W	5	8.39	0.99	0.12	10.1	0.2	83.0
Y	5	2.03	0.080	0.038	2.01	0.04	100.8
Zn	9	5.23	0.31	0.060	5.2	0.1	100.6
Zr	5	2.03	0.13	0.062	2.01	0.04	101.2

[4]Number of laboratories reporting at least one result >MDL (or RL)
[6]standard deviation (if $p>1$);
[7]as reported by the CRM provider
[8]RSD: relative standard deviation
[#]excludes outlier (Grubbs' test)

Table 4c. Internal capsule (Solu-Sert™) interlaboratory study laboratory means vs. certified reference values – Level 2 (Medium Loading)

Element	No. Labs[4]	Mean (µg)	Std. Dev. (µg)[6]	RSD[8]	Reference value (µg)[7]	Uncertainty in ref. value (µg)[7]	Recovery (%)
Ag	7	8.43	2.2	0.26	10.1	0.2	83.5
Al	7	29.6	0.91	0.031	30.9	0.6	95.7
As	8	20.8	1.1	0.053	20.2	0.4	103.0
Ba	7[#]	7.08	0.18	0.025	7.3	0.1	96.9
Be	9	7.05	0.48	0.068	7.0	0.1	100.7
Ca	8	161	24	0.15	165	3	97.4
Cd	9	7.05	0.28	0.040	7.0	0.1	100.7
Co	9	7.12	0.40	0.057	7.0	0.1	101.7
Cr	9	7.60	0.55	0.072	7.9	0.2	96.3
Cu	9	15.2	0.61	0.040	15.1	0.3	100.8
Fe	9	42.5	2.3	0.055	41.0	0.8	103.7
In	5	13.5	3.7	0.27	14.9	0.1	90.8
K	6	15.4	3.6	0.24	15.7	0.3	98.0
La	4	10.4	0.75	0.072	10.1	0.1	102.4
Li	7	6.64	0.46	0.070	7.0	0.1	94.9
Mg	7	27.5	2.5	0.091	27.9	0.3	98.7
Mn	9	7.03	0.43	0.061	7.0	0.1	100.4
Mo	9	7.27	0.35	0.048	7.1	0.1	102.4
Ni	9	7.26	0.54	0.074	7.0	0.1	103.7
P	6	25.7	2.3	0.089	24.9	0.5	103.1
Pb	9	25.3	1.4	0.053	25.2	0.5	100.4
Sb	9	24.9	1.4	0.057	25.1	0.5	99.0
Se	8	16.4	1.4	0.087	15.1	0.3	108.8
Sn	6	6.78	1.2	0.18	7.0	0.1	96.9
Sr	7	7.22	0.54	0.075	7.1	0.1	101.7
Te	5	13.0	1.0	0.077	12.6	0.3	102.8
Ti	7	7.07	0.73	0.10	7.0	0.1	101.0
Tl	7	10.1	0.58	0.058	10.1	0.2	99.6
V	9	7.12	0.44	0.062	7.0	0.1	101.7
W	5	24.5	2.8	0.12	25.1	0.5	97.6
Y	5	7.20	0.43	0.059	7.1	0.1	101.5
Zn	9	25.4	1.3	0.049	25.1	0.5	101.2
Zr	6	6.97	0.64	0.092	7.0	0.1	99.5

[4]Number of laboratories reporting at least one result >MDL (or RL)
[6]standard deviation (if $p>1$);
[7]as reported by the CRM provider
[8]RSD: relative standard deviation
[#]excludes outlier (Grubbs' test)

Table 4d. Internal capsule (Solu-Sert™) interlaboratory study laboratory means vs. certified reference values – Level 3 (High Loading)

Element	No. Labs[4]	Mean (µg)	Std. Dev. (µg)[6]	RSD[8]	Reference value (µg)[7]	Uncertainty in ref. value (µg)[7]	Recovery (%)
Ag	7	13.7	7.1	0.52	20.1	0.4	68.2
Al	7	58.5	1.4	0.024	60.8	1.2	96.2
As	8	40.8	2.4	0.058	40.1	0.8	101.8
Ba	8	15.2	0.75	0.050	15.2	0.3	99.9
Be	9	14.9	0.76	0.051	14.9	0.1	100.1
Ca	8	206	27	0.13	215	4	95.8
Cd	8[#]	15.2	0.28	0.019	14.9	0.1	102.2
Co	9	15.2	0.87	0.058	14.9	0.1	102.0
Cr	9	15.4	0.55	0.035	15.8	0.3	97.2
Cu	9	30.0	0.96	0.032	29.9	0.6	100.2
Fe	9	83.1	4.5	0.054	80.5	1.6	103.2
In	5	34.2	11	0.32	39.7	0.4	86.2
K	6	21.9	4.4	0.20	20.7	0.4	105.8
La	4	20.1	1.6	0.079	20.1	0.2	99.9
Li	7	14.7	0.77	0.052	14.9	0.1	98.6
Mg	7	104	7.4	0.072	103	1	100.8
Mn	9	14.9	0.85	0.057	14.9	0.1	100.2
Mo	9	15.3	0.80	0.052	15.0	0.1	102.1
Ni	9	15.4	1.1	0.070	14.9	0.1	103.0
P	5[#]	101	1.8	0.017	99	2	102.2
Pb	9	100.	7.3	0.073	100	2	100.0
Sb	8[J]	40.2	1.5	0.036	40.2	0.8	100.0
Se	8	31.3	3.2	0.10	30.1	1.5	104.1
Sn	5[#]	15.3	0.76	0.050	14.9	0.3	102.8
Sr	7	15.1	0.92	0.061	15.0	0.2	100.9
Te	5	20.2	2.5	0.12	20.1	0.4	100.5
Ti	6[#]	15.4	0.52	0.034	14.9	0.3	103.2
Tl	7	19.8	1.5	0.075	20.1	0.4	98.3
V	9	15.2	0.89	0.058	14.9	0.3	101.9
W	5	38.7	6.4	0.16	40.2	0.8	96.4
Y	5	15.1	0.72	0.048	15.0	0.3	100.6
Zn	9	60.2	2.9	0.048	59.7	1.2	100.8
Zr	6	13.9	2.7	0.19	14.9	0.3	93.1

[4]Number of laboratories reporting at least one result >MDL (or RL)
[6]standard deviation (if $p>1$);
[7]as reported by the CRM provider
[8]RSD: relative standard deviation
[#]excludes outlier (Grubbs' test)

Estimates of bias, precision and accuracy, computed statistically in accordance with established NIOSH guidelines [10,11], are presented in Table 5. For each data subset, Grubbs' test at 1% confidence level was used to identify outliers which, if identified, were removed prior to further statistical calculations. Bias, precision and accuracy estimates were computed based on results from all three Solu-Sert™ loading levels. All calculations were based on the original data and not the mean laboratory results presented in Tables 4b-d. Analysis of Variance procedure was used to test for homogeneity of bias; Bartlett's test was used for testing homogeneity of RSD (precision) on the data sets for each element. Where results were homogeneous across spiking levels, pooled estimates of bias and precision were used to compute method accuracy for each element. If homogeneity tests failed to pass, the most conservative, i.e. largest, estimates of precision and bias were used to estimate accuracy for each element. It must be pointed out that the accuracy estimates presented in Table 5 also include a conservative imprecision component of ±5% sampling pump error, in accordance with recommended guidelines [10].

Discussion

The laboratory-reported data from the ILS shown in Tables 3a-d demonstrated no statistically significant differences due to sample preparation procedure regardless of loading level. Using SAS Mixed model procedure, statistical tests of data subsets for heating method (hot plate, hot block or microwave) and acid mixture sample treatment yielded no statistically significant differences in the reported multielement analysis results at 5% significance level ($p=0.23$ for heating method, $p=0.73$ for acid mixure). The test factors included heating method, acid mixture, level and element as the fixed factor and lab and sample nested with lab and level as the random factors. The interactions of heating method with element and acid mixture with element were also included. Thus the implication is that, for the Solu-Sert™ samples evaluated, the various sample preparation procedures performed equivalently. These results are consistent with previous reports entailing elemental analysis of soluble capsules for use as cassette inserts [7,12].

It is important to note that lab-to-lab differences were taken into account in the above statistical calculations. Some differences in the sample preparation methods may have been found had such variations not had to be considered. The presence and identity of the outliers may prove valuable in that regard. Of particular importance are the less than quantitative recoveries for Sb, Sn, and Ti using the hot plate method of Lab 2a. This sample preparation method may not be amenable to the analysis of Sb, Sn and Ti.

It can be seen from the reference values listed in Table 4a that appreciable media background levels were found for several elements, notably Al, Ca, Cr, Fe, K, and Mg. Trace media background levels of a few other elements, i.e., Ba, Cu and Zn, were also obtained. Additionally, appreciable (>0.5 µg) media background levels of In, P, Sb, Se, and Tl were reported by the participating laboratories. However, it is noted that only a few laboratories had MDLs or RLs low enough to report measurable elemental analysis results for media blanks (Table 4a). For Levels 1, 2 and 3, the reported results for laboratory means compared to certified values yielded quantitative recoveries (i.e., within 100% ± 10% of the reference value) for the vast majority of elements and spike levels (Tables 4b-d). Mean overall recoveries below 90% were found only for Cr, K, and W at low loadings and for Ag at medium and high spike levels and for In at the high spike level. The significant media background levels reported for certain elements did not negatively affect recoveries. Most values for precision (expressed as RSD) were <0.20 (Tables 4b-d), which compare favorably with the variability typically observed in interlaboratory multielement analysis of air filter samples by atomic spectrometric methods [13].

While there was measurable background for certain elements (mentioned above; see Table 4a), this background was effectively corrected for, as evidenced by the quantitative recoveries obtained for the vast majority of elements and loading levels (Tables 4b-d). Where the background levels may pose a greater influence is in the calculation of the method LOD. In Table 6 method LODs are calculated using the responses of 7 respective sample types: reagent blank solutions, MCE filters and Solu-serts™ taken through the sample preparation steps of NIOSH 7302 (microwave digestion). The standard deviation of the results is multiplied by 3.143 to give the method LOD. For many elements, the method LOD is greater when using the internal capsule. Care should be taken in choosing the appropriate media in concert with the expected sample concentrations. Please note: the MCE filter calculations did not include a wipe or rinse of the sampling cassette as is currently recommended [5]. This may increase the method LOD using MCE filters and lessen the difference between the method LODs of MCE filters and Solu-Sert™ samplers.

Table 5. Internal capsule (Solu-Sert™) interlaboratory study – Estimates of bias, precision and accuracy

Element	Bias	n[9]	$\check{S}$[10]	$\hat{S}_{rT}$[11]	Accuracy	A_{U95}[12]
Ag	-0.184	21	0.041	0.065	0.290	0.314
Al	-0.0414	21	0.006	0.050	0.124	0.143
As	0.0141	23	0.016	0.052	0.107	0.124
Ba	-0.0206	23	0.036	0.062	0.128	0.149
Be	0.00536	27	0.025	0.056	0.110	0.127
Ca	-0.0367	24	0.001	0.050	0.119	0.136
Cd	0.0133	26	0.022	0.055	0.111	0.127
Co	0.0238	27	0.036	0.062	0.129	0.149
Cr	-0.0281	26	0.046	0.068	0.144	0.166
Cu	0.00347	26	0.017	0.053	0.104	0.119
Fe	0.0476	27	0.011	0.051	0.132	0.148
In	-0.103	15	0.056	0.075	0.226	0.260
K	-0.0239	17	0.029	0.058	0.123	0.147
La	0.0119	12	0.025	0.056	0.112	0.140
Li	-0.0447	21	0.039	0.064	0.149	0.173
Mg	-0.0219	21	0.012	0.051	0.109	0.128
Mn	0.00127	27	0.039	0.063	0.124	0.143
Mo	0.0169	27	0.032	0.060	0.121	0.140
Ni	0.0498	27	0.055	0.074	0.172	0.196
P	0.0310	16	0.010	0.051	0.115	0.137
Pb	0.00439	27	0.006	0.050	0.099	0.114
Sb	-0.00631	25	0.013	0.052	0.102	0.118
Se	0.0864	22	0.055	0.075	0.209	0.236
Sn	-0.00541	15	0.117	0.128	0.250	0.304
Sr	0.00930	20	0.011	0.051	0.102	0.120
Te	0.0256	15	0.063	0.081	0.166	0.201
Ti	0.0305	20	0.032	0.059	0.131	0.154
Tl	0.00128	20	0.030	0.058	0.114	0.135
V	0.0143	27	0.020	0.054	0.109	0.126
W	-0.0240	15	0.010	0.051	0.110	0.134
Y	0.00971	15	0.020	0.054	0.107	0.130
Zn	0.00873	27	0.013	0.052	0.103	0.118
Zr	-0.0206	17	0.033	0.060	0.124	0.149

[9]Number of reported results minus outliers (Grubbs' test, 1% confidence level)

[10]precision, $\breve{S}$ = (true) relative standard deviation (TRSD)

[11]overall precision precision = $\sqrt{\breve{S}^2 + (0.05)^2}$

[12]upper 95% confidence limit of accuracy estimate

Table 6. Method limits of detection (LOD) calculated using different media

Sample	Reagent Blanks (µg/sample)	MCE Filters (µg/sample)	Solu-Serts™ (µg/sample)	Solu-Sert™ / MCE Filter
Ag	0.022	0.017	0.020	1
Al	0.72	0.12	0.38	3
As	0.069	0.099	0.099	1
Ba	0.0052	0.010	0.55	56
Be	0.0094	0.0036	0.0064	2
Ca	0.35	0.59	3.9	7
Cd	0.0073	0.0061	0.0052	1
Co	0.011	0.0078	0.0090	1
Cr	0.012	0.042	0.28	7
Cu	0.058	0.0087	0.15	17
Fe	0.30	1.0	5.3	5
In	0.15	0.15	0.26	2
K	0.25	0.34	0.70	2
La	0.023	0.026	0.026	1
Li	0.0065	0.0016	0.010	6
Mg	0.12	0.11	1.1	10
Mn	0.022	0.047	0.031	1
Mo	0.0093	0.011	0.021	2
Ni	0.020	0.057	0.56	10
P	0.16	0.12	0.27	2
Pb	0.063	0.056	0.062	1
Sb	0.10	0.085	0.11	1
Se	0.16	0.13	0.14	1
Sn	0.017	0.21	0.065	0
Sr	0.0012	0.0027	0.014	5
Te	0.11	0.087	0.22	3
Ti	0.0055	0.0045	0.042	9
Tl	0.042	0.049	0.046	1
V	0.013	0.010	0.0091	1
W	0.020	0.041	0.055	1
Y	0.0052	0.0066	0.0039	1
Zn	0.076	0.27	0.69	3
Zr	0.0093	0.0051	0.0099	2

The results for accuracy summarized in Table 5 demonstrate the suitability of Solu-Sert™ samplers for multielement analysis by acid dissolution and ICP-AES. For a method to be deemed unbiased and accurate with 95% probability of results ±25% of the actual concentration, the accuracy estimates

should be ≤0.25 and the bias should be ≤0.10 [10]. The mean accuracy estimate is ≥0.25 for only two elements: Ag and In. The upper 95% confidence limit for the accuracy estimate exceeds ±0.25 for only three elements: Ag, In and Sn. Bias estimates beyond ±0.10 are obtained only for two elements: Ag and In. Estimates of precision and overall precision are >0.10 for only one element: Sn. For 30 of the 33 elements evaluated, accuracy estimates of 0.25 or better demonstrate that the method is valid for quantitative multielement analytical determination.

Difficulties with atomic spectrometric interlaboratory analysis of Ag have been observed previously [13]. Since Ag^+ ions are light-sensitive and subject to photoreduction, it is recommended to carry out sample preparation in light-protected vessels if this element is to be analyzed [14]. ILS results reported here for In (Table 5) are limited, unfortunately, since many participants did not report results for this element. It is anticipated that better estimates for tighter precision and lesser bias would be obtained with a larger number of participating laboratories. The somewhat higher estimates for ILS variability and accuracy for Sn (Table 5) may be improved with data from additional laboratory participants [15], especially for low-level samples.

Disclaimer: Mention of any company or product does not constitute endorsement by the National Institute for Occupational Safety and Health.

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