



Impaction collection and slurry sampling for the determination of arsenic, cadmium, and lead in sidestream cigarette smoke by inductively coupled plasma-mass spectrometry

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The slurry sampling technique has been applied for the determination of arsenic, cadmium and lead in sidestream cigarette smoke condensate (SS CSC) by inductively coupled plasma mass spectrometry (ICP-MS). The smoke collection system consists of a “fishtail” chimney in conjunction with an impaction trap and a mixed cellulose ester (MCE) backup filter for the SS CSC collection. The smoke condensates, collected at three different regions of the system (*i.e.* the inner wall of the chimney, the impaction trap and the MCE filter), were individually prepared and analyzed and showed that about 70 and 20% of Cd and Pb, respectively, were trapped by the impaction trap and the MCE filter with less than 5% trapped by the chimney. In contrast, about 60% of As was trapped by the impactor and a relatively high percentage of As, about 30%, was deposited onto the inner wall of the chimney. The uneven distribution of trace metals at each collection stage strongly suggested that the composition of smoke aerosol and the associated physical form of the analytes may be different. The yields of As, Cd and Pb for the sidestream cigarette smoke of the 1R4F reference cigarette were 29.5 ± 2.4 , 421 ± 6.6 and 46.4 ± 0.9 ng cigarette⁻¹ ($n = 3$) respectively, when the cigarette was smoked according to the smoking regime: 45 mL puff volume of 2-s puff duration at an interval of 30 s with 50% ventilation holes covered. The analytical results for the slurry sampling technique were also compared with other sample preparation techniques and show good agreement.

Introduction

Recently, there has been an increase in attention towards sidestream cigarette smoke due to the reported health risks of passive smoking of environmental tobacco smoke (ETS) on the human respiratory system.^{1–3} Cigarette smoke released from the combustion of tobacco is usually classified into mainstream and sidestream smoke. ETS is composed of both the aged and diluted sidestream smoke and the exhaled mainstream smoke from the smoker. Sidestream smoke is a major contributor to ETS. Mainstream smoke refers to the smoke coming out of the mouth end of a cigarette during smoking, while sidestream smoke is that which comes from the lit end between puffs. The compositions of mainstream and sidestream cigarette smoke are qualitatively similar but quantitatively different.⁴ Methods for smoke collection and analyses of mainstream cigarette smoke have been significantly developed and well established, but relatively few studies have been reported for sidestream cigarette smoke, especially those that involve determining trace metals in sidestream smoke.

For mainstream cigarette smoke, a smoke collection device is placed directly behind a burning cigarette, along with an additional device that is needed to confine and channel sidestream smoke to the smoke collection device. The major criterion for designing such an apparatus that confines and channels sidestream smoke is its ability to supply fresh air continuously during the process of cigarette combustion without changing the characteristics of the normal combustion of mainstream cigarette smoke. Therefore a variety of apparatus, along with procedures, have been designed and employed for sidestream smoke collection which have been described in detail and references cited therein.^{4–8} Of these devices, the “fishtail” chimney was first described by Proctor *et al.*⁶ and

it can be adapted to the commercially available smoking machines without any difficulty. The main advantage of the “fishtail” chimney is the capability of providing a constant supply of fresh air. Also, small particles of fresh sidestream smoke can travel longer before sample collection. This improves the collection efficiency because the smoke aerosol particles can agglomerate and coagulate to form larger aerosol particles. It is believed that the “fishtail” chimney, in combination with a regular smoke trap, has the potential to become a standard device for routine sidestream cigarette smoke collection. Perfetti *et al.*⁹ compared the yields of a few selected components in mainstream smoke with and without the “fishtail” chimney in place. Their analytical results further support the suitability of the “fishtail” chimney for sidestream cigarette smoke collection.

Filtration, electrostatic precipitation, cryogenic collection and inertial impaction are commonly used to collect cigarette smoke. Glass and quartz filter pads are not suitable to collect cigarette smoke for trace metals analysis because of their intrinsic trace impurity, although quartz filters contain much less contamination of trace metals compared to glass fiber filters. Electrostatic precipitation has been recognized as the most preferred technique for the collection of mainstream cigarette smoke for trace metal analysis. However, application of electrostatic precipitation for sidestream cigarette smoke collection is not feasible because the high air flow rate needed to draw sidestream smoke through the electrostatic precipitator causes poor collection efficiency. Cryogenic collection is not often used because water vapor in the smoke matrix (~13% or higher) must be removed first to avoid the clogging of traps. The inertial impactor (or jet impactor) has been broadly studied for use in size-selective collections of aerosol particles in ambient air because of its relatively inexpensive and user-

friendly aspects.^{10–12} Numerous cascade impactors are commercially available and have been adopted as standard sampling devices for the classification of particle size distribution in environmental aerosols. Although Mathewson^{13,14} introduced the jet impactor for mainstream cigarette smoke collection, it is seldom used as a method to collect tobacco smoke in the tobacco industry. The lack of interest in using the impaction trap is mainly due to its relatively low collection efficiency, about 95%, when compared with that of the glass fiber filter. Nevertheless, cascade impactors have been used by environmental researchers for particle size distribution study in cigarette smoke.^{15–18} Sneddon has developed the impaction-electrothermal atomization atomic absorption spectrometry (I-ETAAS), using a graphite furnace tube as an impactor surface for the direct introduction and collection of an aerosol for near real-time determination of trace metals in atmospheric aerosols^{19–23} and cigarette smoke.²⁴ The major obstacle for its practical application is its inability to accurately calibrate the instrument, thus limiting its application to qualitative or semi-quantitative analysis.

Recently, a jet impactor, in conjunction with a “fishtail” chimney, has been applied to sidestream cigarette smoke collection in order to minimize background contamination for trace metals determination.²⁵ The preliminary results have resolved the issue of high background levels of trace metals occurring when the filtration media were used to collect sidestream smoke. However, the sample preparation procedure for the collected smoke sample is a tedious, time-consuming and labor-intensive process. It has been our interest to simplify the sample preparation, in order to enhance productivity, by reducing the sample preparation time without compromising accuracy and precision. In our previous work,²⁶ the slurry sampling technique was successfully applied for the determination of trace metals in mainstream cigarette smoke condensate by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Graphite Furnace Atomic Absorption Spectrometry (GFAAS). Furthermore, mainstream cigarette smoke has been introduced directly into the ICP-MS for trace elements analysis.²⁷ In this report, the slurry sample preparation was further extended to the sidestream cigarette smoke condensate collected by a “fishtail” chimney in conjunction with a jet impactor. The sidestream cigarette smoke condensate (SS CSC) slurry sample was then analyzed by ICP-MS for the determination of As, Cd and Pb. The analytical results were compared with those of different sample collections and preparation techniques.

Experimental

Instrumentation and procedure

An Elan 6000 ICP-MS instrument (Perkin-Elmer SCIEX, Concord, Ontario, Canada) with a cross-flow nebulizer, Scott-type spray chamber and a 2.0 mm (i.d.) alumina injector was used in conjunction with a Perkin-Elmer AS-91 autosampler for this work. The experimental operating conditions are given in Table 1. The optimization and tuning of the instrument were performed in accordance with the manufacturer's recommendation. The nebulizer flow rate was optimized to obtain maximum signals of As, Cd and Pb by aspirating a 10 µg L⁻¹ solution of As, Cd and Pb in 0.5% (m/v) Triton X-100, 5% (v/v) methanol and 0.5% (v/v) nitric acid. The solution was delivered to the nebulizer at a flow rate of 1.2 ml min⁻¹ via a peristaltic pump. The internal standard was directly added into the sample stream via a mixing tee fitting. The pump tubing for the sample and the internal standard were 0.076 mm i.d. and 0.038 mm i.d., respectively.

The sidestream smoke collection apparatus has been previously described.²⁵ A five-port linear smoking machine (KC Automation Inc., Richmond, VA, USA) was used to generate

Table 1 Instrumental operating conditions for the ICP-MS

RF power	1350 W	
Plasma argon flow	15 L min ⁻¹	
Carrier gas flow	0.92 L min ⁻¹	
Sample uptake flow	1.2 mL min ⁻¹	
Dwell time per AMU	Internal standard ¹¹⁵ In ⁺ 65 ms	Analyte ⁷⁵ As ⁺ 100 ms ¹¹⁴ Cd ⁺ 65 ms ²⁰⁸ Pb ⁺ 65 ms
Resolution	0.7 amu	
Sweeps/reading	15	
Reading/replicate	1	
Replicates	3	
Nebulizer	Cross-flow II Rytan	
Sampler and skimmer cone	Nickel	
Scan mode	Peak hopping	
Autolens	On	

the smoke. The sidestream smoke collection system consisted of a quartz “fishtail” chimney (Research Glass, Richmond, VA, USA) which confines and channels sidestream smoke to a quartz jet impactor (Research Glass, Richmond, VA, USA), followed by a mixed cellulose ester (MCE) backup filter with a 37 mm diameter and a 0.8 µm pore size (Environmental Express, Mt. Pleasant, SC, USA). In the system, sidestream smoke was collected sequentially by the impaction trap and the backup MCE filter, in which the jet impactor was the primary smoke trap, with the MCE filter serving as a secondary trap that collected smoke passing through the jet impactor. In addition, smoke also deposits onto the inner wall of the chimney due to condensation. A few modifications have been carried out. An 11-mL quartz impaction tube was used in place of the larger sized 25-mL pear-shaped impaction tube. The dimension of the capillary tip was 5-mm long with a 0.56-mm diameter of orifice. A 24/40 glass adapter with a curved outlet glass tube connected the impaction trap to the top outlet of the chimney by a 12/5 ball glass joint connector. The curved adapter positioned the impaction trap at an angle perpendicular to the effluent of cigarette smoke, which enabled the liquid portion of the smoke condensate to dribble down to the lower part of the impaction trap. This reduced the build-up of smoke condensate on the impaction surface, which could clog the impaction orifice. The outlet of the impaction trap was then connected to a MCE filter using a short piece of silicone sleeve. Vacuum was used to draw up the sidestream smoke from a burning cigarette at an air flow rate of 2.5 L min⁻¹, which was regulated by a mass flow controller (Model HFC-202, Hastings, Hampton, VA, USA).

For the sidestream cigarette smoke condensate collected by filtration, a filter cassette containing two 37-mm quartz filter pads (Pall Gelman Sciences, Ann Arbor, MI, USA) was directly attached to the top outlet of the chimney. A CEM MARS 5 equipped with the HP 500 Plus vessels (CEM Corp., Matthews, NC, USA) was used for microwave-assisted sample digestion. The details of the preparation procedure were described in a previous paper.²⁶

Chemical and reagents

High purity double de-ionized water (18 MΩ cm⁻¹), generated from a Milli-Q® Plus Total Water System (Millipore Corp., Bedford, MA, USA), was used to prepare all solutions. Optima grade concentrated nitric acid from Fisher Scientific (Atlanta, GA, USA) was further purified in a double distillation apparatus (Hans Kurner Analysentechnik, Rosenheim, Germany). The double-distilled hydrofluoric acid was from GFS Chemicals, Inc. (Columbus OH, USA). ULTREX hydrogen peroxide

(30%) (J. T. Baker, Philipsburg, NJ, USA) and high purity methanol stored in a Teflon-lined container (Burdick & Jackson, McGraw Park, IL, USA) were used. Triton X-100 (Fisher Scientific, Atlanta, GA, USA) was used as a wetting agent. Calibration standards were prepared by mixing single element standard solutions (SPEX Industries Inc, Metuchen, NJ, USA). All labware was cleaned by being soaked in 20% nitric acid (aqueous) for a minimum of 24 hours. After soaking, the labware was rinsed thoroughly with double de-ionized water, dried in a Class 100 clean bench and stored in a Class 100 clean room until needed.

Sample collection and preparation

The 1R4F reference cigarette was purchased from the University of Kentucky Tobacco and Health Research Institute (Lexington, KY, USA). The test cigarettes were conditioned at $22 \pm 1^\circ\text{C}$ and $60\% \pm 3\%$ relative humidity for a minimum of 48 hours and smoking was conducted in a room controlled at $22 \pm 2^\circ\text{C}$ and $60 \pm 5\%$. After conditioning, the cigarettes were stored in a closed polypropylene container until tested. A pre-determined number of cigarettes were smoked sequentially following the "Massachusetts" smoking regime: 45 ± 0.5 mL puff volume with 2 ± 0.1 s puff duration once every 30 ± 1 s with 50% of the cigarette ventilation holes covered, as defined by the Massachusetts Department of Health.²⁸ The "Massachusetts" smoking regime increases mainstream smoke delivery per cigarette relative to the standard International Organization for Standardization (ISO) smoking regime.²⁹ The cigarette was smoked to a butt length of tipping plus 3 mm. Cigarette smoking termination was manually performed when the burning line reached the butt length. The SS CSC collected was prepared in a Class 100 laminar flow hood as follows.

Preparation of SS CSC collected on quartz filters

The unreliability for the determination of trace metals collected on glass fiber filters has been realized for decades because of the high level of trace metal impurities.³⁰ Therefore, a quartz filter was used instead of a glass fiber filter to trap sidestream cigarette smoke condensate. The sidestream cigarette smoke condensate collected by two quartz filter pads was prepared in three different manners as follows: The first sample preparation, modified from the draft method for Health Canada in 1998,³¹ will be referred to as to the quartz filter-methanol extraction henceforth. The SS CSC that condensed on the inner wall of the chimney was sequentially washed off with small aliquots of methanol (a total of about 10 mL per cigarette smoked) into a centrifuge tube. The quartz filters were then folded and submerged in the chimney methanol rinsate and sonicated for approximately 5 minutes until the SS CSC dissolved into methanol in an ultrasonic bath (FS 400 W ultrasonic cleaner, Fisher Scientific, Atlanta, GA, USA). The methanol extract was then transferred to a microwave digestion vessel and the methanol was evaporated by passing nitrogen gas through at ambient temperature. The almost-dried smoke condensate was subsequently microwave-digested with hydrogen peroxide and nitric acid.

The second sample preparation method will be referred to as to the quartz filter-Triton X-100 extraction henceforth. A prepared 0.5% (m/v) Triton X-100, 5% (v/v) methanol and 0.5% (v/v) HNO_3 solution, referred to as to the Triton X-100 solution throughout unless otherwise stated, was used in place of methanol to rinse the chimney and to extract the quartz filters with the assistance of ultrasound. A 50 W, VC 50 ultrasonic processor (Sonics and Materials, Danbury, CT, USA) equipped with a 2-mm titanium probe was used to sonicate the quartz filter pads until the filter fiber was broken

into a white chunky slurry. The suspension was centrifuged and an aliquot of the supernatant was used for analysis.

The third sample preparation will be referred to as the quartz filter-hydrofluoric acid digestion henceforth. The SS CSC condensed on the inner wall of the chimney was washed off with aliquots of methanol into a graduated sample vial, followed by the evaporation of methanol to near dryness at 65°C in a hot block. The quartz filter pads were then folded and placed into the sample vial. A 1 mL aliquot of HF was added to dissolve the quartz filters with the aid of heating, followed by 4 mL of HNO_3 . The solution was evaporated to almost dryness and then 5% nitric acid was used to bring it to the final volume.

Preparation of SS CSC collected by the impaction collection system

Two sample preparation procedures were used for cigarette smoke condensate collected by the impaction collection system. The first procedure has been described elsewhere²⁵ and will be referred to as to the impactor-methanol extraction henceforth. In brief, the smoke condensate collected by the chimney and the impactor was initially extracted with methanol, followed by the evaporation of methanol. Both the methanol-free smoke condensate and the MCE filter were acid-digested in a digestion block at 95°C for about an hour.

The second procedure is the proposed method and will be referred to as the impactor-Triton X-100 slurry sample preparation henceforth. Methanol was used to extract the smoke condensate collected in the impaction trap with the aid of sonication in an amount of 0.5 mL per cigarette smoked. The smoke condensate dissolves into methanol instantly when sonicated. Then, 5 mL of the 0.5% (m/v) Triton X-100 in 0.5% (v/v) HNO_3 solution was added to the methanol extract and sonicated for another minute. The sample solution was transferred to a 50 mL graduated polypropylene vial and brought up to the final volume with a solution of 0.5% (m/v) Triton X-100 in 0.5% (v/v) HNO_3 , at 10 mL per cigarette smoked. In this manner, the sample solution has the same solvent concentration as the calibration standards, 0.5% (m/v) Triton X-100, 5% (v/v) methanol and 0.5% (v/v) nitric acid. This procedure was experimentally found to facilitate smoke condensate removal more easily than using the Triton X-100 solution directly. The smoke condensate deposited on the wall of chimney was rinsed out with the Triton X-100 solution (10 mL per cigarette smoked). To evaluate the rinsing efficiency, two equal aliquots of the Triton X-100 solution were used to rinse the chimney in sequence. These two rinsates were then analyzed individually, with the results showing that the first rinsate was capable of extracting 99% of the analytes of interest from the chimney. The MCE filter was dissolved into 2-mL of nitric acid at 95°C , then evaporated to near dryness, and brought up to a final volume of 10 mL per cigarette smoked with the Triton X-100 solution.

Results and discussion

The effect of jet-to-plate distance on the collection efficiency of impaction trap

The collection efficiency of the impaction trap is dependent on particle sizes, aerosol velocity, and the physical configuration of the impactor (*e.g.* diameter of the nozzle orifice, distance of the jet-to-plate distance, and the capillary jet length).¹⁴ The particle size distribution of mainstream smoke reaches a maximum ranging from 0.3 to 0.4 μm particle diameter; the mass median diameter of smoke aerosol ranges somewhere between 0.2 and 0.6 μm depending on the age of the smoke and the sampling dilution factor. Fresh sidestream cigarette smoke is composed of slightly finer particles than that of mainstream cigarette smoke.³² However, the particle size of sidestream

smoke aerosol can be enlarged through agglomeration and coagulation within the long traveling distance of the chimney, before collection by impaction. In order to obtain high collection efficiency, the diameter of the nozzle orifice for the jet impactor should be maintained as small as possible but without creating a significant pressure drop between the capillary and the impaction plate. Otherwise, an optimum downstream flow rate cannot be achieved. It was observed that a 2.5 L min^{-1} flow rate could not be maintained if the nozzle orifice was smaller than a 0.56-mm diameter. Therefore, a round orifice with a 0.56-mm diameter with a 5-mm capillary jet length was chosen for this study.

Mathewson¹⁴ has observed that a 1–2 mm of jet-to-plate distance for 0.4–0.8 mm diameter of orifice provided high collection efficiency for undiluted mainstream cigarette smoke generated under a smoking condition of 35 mL puffing volume per 2 s. Sneddon²³ found that the jet-to-plate distance, ranging from 0.1 to 10 mm, was not a critical parameter for the collection of aerosols and analysis of trace metals by I-ETAAS. In this work, jet-to-plate distances over a range of 0.4–1.5 mm were investigated on the sidestream smoke collection efficiency of impaction traps by smoking five 1R4F reference cigarettes under the smoking conditions mentioned previously. Fig. 1 shows the relative collection efficiency for the impaction trap and the MCE back-up filter as a function of jet-to-plate distance. The smoke condensate for the impaction trap and the MCE filter was normalized to the whole smoke condensate when using a jet-to-plate distance of 0.63 mm. The whole smoke condensate is the summation of smoke condensate collected by the impactor and the MCE filter. Each data point represents the average of three replicates, with the highest and the lowest values denoted with a vertical bar. Smoke deposited upon the inner wall of the chimney was not included because of the difficulty in gravimetrically measuring a small quantity of CSC out of a heavy chimney. As indicated in Fig. 1, the collection efficiency of the impaction trap was not significantly different over the 0.4 and 0.8 mm range of the jet-to-plate distance. The collection efficiency of the impaction trap begins to decrease as the gap exceeds 0.8 mm, along with an increase of smoke condensate collected by the MCE-filter. A 0.63 mm of jet-to-plate distance was chosen for further experiments to avoid possible blockage of the jet. In this manner, the ratio of the jet-to-plate distance to the diameter of the nozzle orifice is 1.1 for the impaction trap.

The effect of number of cigarettes smoked on the collection efficiency

The number of cigarettes that can be smoked per sample is strictly dependent on the amount of the sidestream cigarette

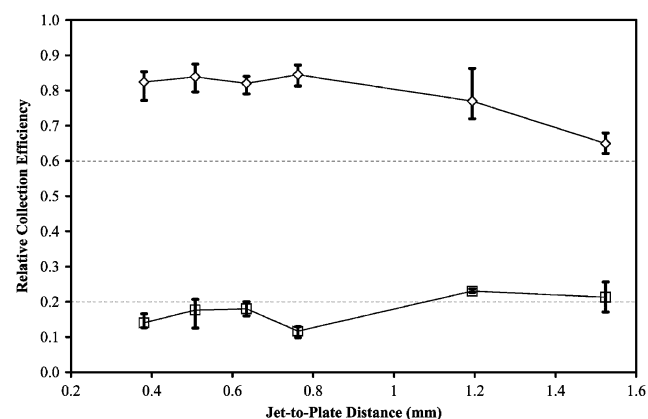


Fig. 1 Relative collection efficiency of the impaction trap (diamonds) and the MCE backup filter (squares) for the sidestream smoke condensate of 1R4F reference cigarette as a function of the jet-to-plate distance of impaction trap.

smoke generated per test cigarette and the withholding capacity of the smoke trap. The Cambridge filter pads of 44-mm and 92-mm diameters are capable of retaining up to 150 mg and 600 mg of total particulate matter, respectively. Proctor *et al.*⁶ reported that nicotine and tar yields were not additive when the number of cigarettes exceeded three while using a “fishtail” chimney in combination with a Cambridge filter pad for the collection of sidestream cigarette smoke. In order to discern the maximum number of cigarettes that could be smoked in our smoke trapping system, the effect of the number of smoked cigarettes on the collection efficiency of sidestream cigarette smoke was investigated by smoking one to five 1R4F reference cigarettes in three replicates. Fig. 2 shows the yield of Cd at three different collection regions and the total yield as a function of the number of cigarettes smoked. The yields of As, Cd and Pb at each collection stage were added together to give the total yields. Although not shown, similar relationships were also observed for As, Pb, SS CSC, and mainstream cigarette condensate (MS CSC). Each datum is the average of three replicates and the error bars represent the standard deviation. Table 2 shows the linear regression of total yields of SS CSC, Cd, Pb and As along with their yields at each distinct collection stage, as a function of the number of cigarettes smoked. The MS CSC was collected by a Cambridge filter and is also included for reference. As demonstrated by the correlation coefficient values in the table, the yields of MS CSC, total SS CSC and Cd, Pb and As collected by the impaction trap are linearly proportional to the number of cigarettes smoked. The correlation between the CSC collected on the MCE and the number of cigarettes smoked shows somewhat good linearity, but is slightly poorer than that of the impaction trap.

For the yield of trace metals, Cd shows a strong linear relationship in all aspects at every collection stage. This agrees with a report that the Cd yield was linearly proportional to the number of cigarettes smoked (up to eight cigarettes) for sidestream cigarette smoke collected from an environmental chamber.³³ Similar to Cd, Pb and As also demonstrated a linear relationship between their yields and numbers of cigarettes smoked, although with different degrees of linearity. The relatively poor linearity for Pb in the MCE filter and As in the chimney is probably due to the high background level of Pb present in the MCE filter and to the varying degrees of condensation of As compounds occurring on the wall of the chimney respectively. Overall, the yields of analyte are additive from one to five cigarettes for SS CSC, Cd, Pb and As. It is recommended that three test cigarettes be smoked for routine

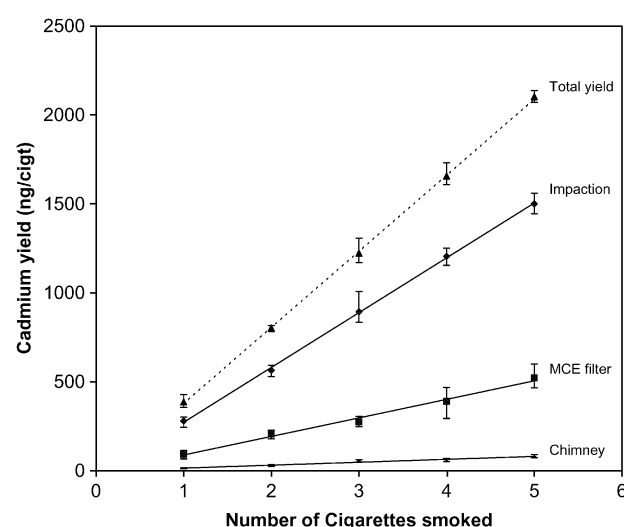


Fig. 2 The total and individual yields of Cd collected by the impaction trap, the MCE filter and the chimney, respectively, as a function of the number of cigarettes smoked.

Table 2 Linear regression data of smoke constituent delivery versus number of cigarettes smoked

Analyte		Slope/mg cigt ⁻¹	Correlation coefficient	Standard error/mg
Smoke condensate	MS CSC	29.2	0.999 45	1.76
	Impaction trap	22.9	0.999 01	1.86
	MCE filter	4.6	0.977 28	1.84
	Total SS CSC	27.5	0.999 34	1.83
		Slope/ng cigt ⁻¹		Standard error/ng
Cd	Chimney	16.3	0.991 15	4.0
	Impaction trap	308.2	0.999 77	12.1
	MCE filter	104.1	0.994 80	19.5
	Total	428.6	0.999 89	11.7
Pb	Chimney	1.0	0.985 14	0.3
	Impaction trap	37.0	0.997 44	4.8
	MCE filter	9.0	0.932 85	6.4
	Total	47.0	0.991 77	11.1
As	Chimney	8.9	0.977 29	3.5
	Impaction trap	19.7	0.993 77	4.0
	MCE filter	3.5	0.997 11	0.5
	Total	32.1	0.993 28	6.8

sample collection due to the compromise of precision of measurement and total smoking time.

Elemental distribution between three distinct regions of the collection system

The analytical results of As, Cd and Pb for the 1R4F reference cigarette are shown in Table 3, which includes the total yields and percentage distribution between the chimney, the impactor and the MCE filter. The limit of detection (LOD), defined as three times the standard deviation, was determined by analyzing ten replicates of the method blank. The amount of SS CSC and MS CSC collected were 28.5 ± 1.8 and 29.5 ± 1.2 mg cigt⁻¹ ($n = 3$), respectively. The MS CSC collected agrees well with that when the sidestream collection apparatus is not in place, indicating that our collection system does not change the characteristics of the normal combustion of mainstream cigarette smoke. The amount of smoke condensate collected in the impactor trap was about four times that collected in the MCE filter with a respective precision of 10 and 21% RSD ($n = 3$), respectively. The relatively imprecise measurement of the MCE filter is caused by the possibility that some moisture and volatile organics were evaporated and hence lost as continuous air flows through the MCE filter at a high velocity.

The analytical results in Table 3 show that about 70 and 20% of Cd and Pb are trapped by the impactor trap and the MCE filter, respectively, and less than 5% is trapped by the chimney. Wu *et al.*³³ used a 3.4-L glass container to confine and channel the sidestream smoke for the determination of Cd, and assumed that the fraction of Cd deposited onto the inner wall of the channeling device could be negligible. However, our results indicated that about 4% of Cd is collected by the “fishtail” chimney. In contrast to Cd and Pb, As has a larger portion collected by the chimney, about 30%. Cigarette smoke

is complex and composed of solid particles, gases and liquids. The fresh sidestream smoke is relatively warm, in contrast, to the mainstream smoke. Kaneki³⁴ reported that the temperature of sidestream smoke is about 70 °C at 10 cm above the cigarette and gradually drops to about 40 °C at 60 cm using a cylinder type of smoking chamber with 8-cm internal diameter. Recently, the existence of trace elements at various physical forms in cigarette smoke has been attributed to the behavioral differences in the time-dependent ICP-MS signal profiles of each element, as the mainstream cigarette smoke was directly introduced into ICP-MS for trace elements analysis.²⁷ Moreover, Proctor⁶ indirectly measured the concentration of nicotine collected in the chimney and the Cambridge filter pad by comparing the UV absorbance at 310 nm for the corresponding propanol extract, and reported that the amount of nicotine collected in the chimney was about 20% on average. All of these studies suggest that the physical and chemical characteristics for each smoke constituent could be different. We speculate that a certain portion of As exists in a type of liquid vapor form which condenses onto the cooler inner surface of chimney, whereas the majority of the Cd and Pb is believed to be present in the particulate phase of cigarette smoke. This may explain the difference in elemental distribution between chimney, impactor and MCE filter.

Comparison of sample collection and preparation methods

The analytical results of As, Cd and Pb for SS CSC of the 1R4F reference cigarette, collected by either impactor or quartz filter pad and followed by different manners of sample preparation, are displayed in Fig. 3. These data were obtained on different occasions by collecting the sidestream smoke of five 1R4F cigarettes in three replicates. All data were normalized to the SS CSC prepared as Triton X-100 slurry sample.

Table 3 Analytical results for As, Cd and Pb for the sidestream cigarette smoke of 1R4F cigarette smoked under the smoking condition of 45 mL puff volume of 2-s puff duration at an interval of 30 s with 50% of the ventilation holes covered

	Total yield/ng cigt ⁻¹	LOD/ng cigt ⁻¹	% in chimney	% in impactor	% in MCE filter
As	29.5 ± 2.4	0.5	28	62	10
Cd	421 ± 6.6	0.4	4	73	23
Pb	46.4 ± 0.9	0.4	2	78	20

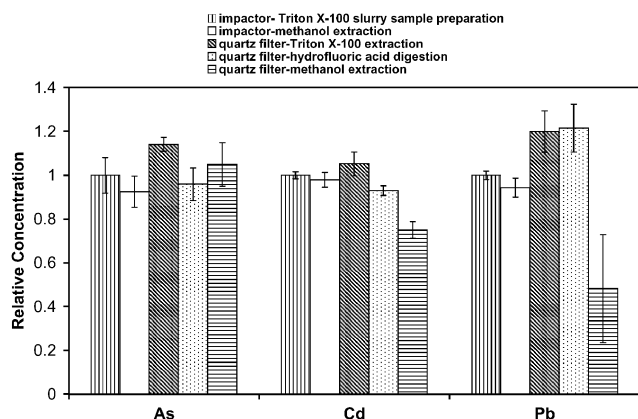


Fig. 3 Comparison of analytical results for As, Cd and Pb through five different combinations of sample collection and preparation.

The error bar stands for one standard of deviation. The use of HF in the quartz filter-hydrofluoric acid digestion may result in a loss of As through the formation of volatile arsenic fluoride during the evaporation process. However, As results are consistent regardless of the method applied for smoke collection and preparation, as shown in the figure. The quartz filter-methanol extraction method results in poor extraction efficiency for both Cd and Pb with respect to the other four methods, with a reduction of efficiency of about 70 and 40% respectively. It appears that a considerable amount of Cd and Pb could not be completely extracted out of the quartz filter by methanol. This suggests that the common method for extracting organic constituents from a filter pad by using an organic solvent is not appropriate for inorganic constituents, at least not for Cd and Pb. This might be the reason that a new and modified official test method for the determination of trace metals in sidestream cigarette smoke was issued by Health Canada later on,³⁵ which uses 10% nitric acid in conjunction with hydrogen peroxide to extract SS CSC collected for trace metals analysis on the chimney wall and the Cambridge filter. The relatively high recovery of Pb for the quartz filter-Triton X-100 slurry sample and the quartz filter-HF digestion could be due to the background contamination of the quartz filter pad.

Conclusion

A "fishtail" chimney was used to confine and direct sidestream cigarette smoke to an impaction trap followed by a MCE filter for smoke collection. The smoke condensates collected at three collection stages, *i.e.* chimney, impactor, and MCE filter in sequence, were prepared as Triton X-100 slurry samples and analyzed by ICP-MS for As, Cd and Pb. The analytical results for the 1R4F sidestream cigarette smoke condensate were compared with four other sample preparation techniques for smoke condensate collected by either the impaction trap or the quartz filter. All methods provide comparable analytical results except for the Cd and Pb condensates collected by the quartz filter-methanol extraction method, which provides lower yields of Cd and Pb. This suggests that the accuracy of the method for the determination of trace metals in cigarette smoke strongly depends on the choice of the sample preparation method. In this work, the slurry sample preparation using Triton X-100 has proved to be a suitable method for the determination of trace metals in sidestream cigarette smoke condensate by ICP-MS, which not only increases the sample throughput (by avoidance of lengthy sample preparation) but also avoids any possible contamination when using the filter pad. Moreover, the uneven distribution of trace metals at each collection stage indicates that the composition of smoke aerosol and the physical and chemical characteristics of an individual analyte could be different. It will be interesting for the

future to develop a method which can separate and identify the physical and chemical forms of the trace metals in cigarette smoke.

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