CRYOTRAPPING TECHNIQUE FOR THE ANALYSIS OF AEROSOLS SUCH AS MAINSTREAM SMOKE

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OBJECTIVE

A new cryogenic instrument was designed for the trapping of aerosols such as cigarette mainstream smoke at low temperature. The technique enabled the trapping of the mainstream smoke of a single cigarette and the particulate and vapour phases were trapped simultaneously. The instrument consisted of a copper chamber containing an adjustable quantity of liquid nitrogen and a heating system. The trap was kept in a helium atmosphere in the copper chamber and the temperature was controlled by balancing the volume of injected liquid nitrogen and the heating of the helium atmosphere. The cryogenic instrument was controlled by software which allowed the temperature of the copper chamber to be lowered and raised within a range of -190°C to room temperature. 2R4F reference cigarettes were smoked under ISO regime and trapped at low temperature using the cryogenic instrument. After trapping, the mainstream smoke of the 2R4F reference cigarette was diluted with a solvent and selected smoke components could be quantified using Gas Chromatography-Mass Spectrometry and Liquid Chromatography. The capability of the instrument for trapping the mainstream smoke is demonstrated. The feasibility of the procedure for the detection and the quantification of a large range of smoke components including aldehydes, olefins, aromatic compounds and poly-aromatic compounds in the mainstream of a single cigarette is also shown.

INTRODUCTION

The cold technique was used since 1950s for the collection of aerosols such as mainstream smoke at low temperature[1,2]. This technique was used in order to preserve the chemical composition of the smoke. Different trap shapes and designs were developed using liquid nitrogen as a low temperature bath. The major issues with the liquid nitrogen bath were: (i) lack of control of the puff volume (the volume of the puffs set on the smoking machine), and (ii) oxygen condensation in the trap. When the trap was placed in liquid nitrogen, it acted as a pump and started to draw and condense oxygen. When connecting the trap to the smoking machine (instrument used to smoke cigarettes), the puff volume could not be controlled and it increased the volume of each puff. In addition, liquid oxygen was condensed in the trap. Furthermore, the technique required a large number of cigarettes (up to 20) which was not convenient when testing hand-made prototypes. Therefore, for all these reasons, the cold trap technique using liquid nitrogen as a low temperature bath was abandoned. Consequently, a new instrument (Figure 1) was designed to resolve the issues observed with the use of the liquid nitrogen bath and avoid time-consuming use of a large number of cigarettes. This was achieved by decreasing the temperature to -183°C, which is just above the temperature of oxygen condensation. This temperature was obtained by heating the trap placed in the copper chamber over liquid N2. This permitted the control of the puff volume and prevented oxygen condensation. The technique is based on trapping the mainstream smoke at cryogenic temperature and it requires only a single cigarette for the collection of the particulate and the vapor phases simultaneously. After trapping, the condensed smoke was diluted with solvent and selected smoke components were quantified using Gas Chromatography-Mass Spectrometry and Liquid Chromatography. In this study, 17 compounds were analysed in 2R4F reference cigarette mainstream smoke and compared with the results of the collaborative study conducted by Chen et al.[3] using a Cambridge filter and impinger for the collection of smoke constituents in mainstream smoke. A further objective of this work was to determine the feasibility of using one single trapping solution for analyzing the mainstream smoke by simultaneously three different methods (GCMS, HPLC and Stir-Bar GCMS).

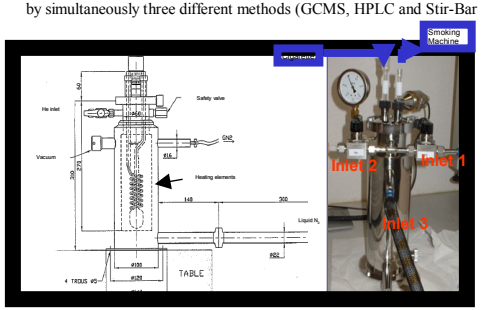

Figure 1: Cryogenic instrument

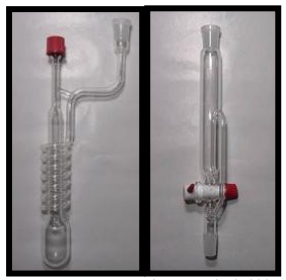

Figure 2: The trap

Figure 3: The bubbler

The bubbler with the trapping solution on the top of the trap (should be inside the instrument)

EXPERIMENTAL PART

The general procedure for trapping the mainstream smoke was as follows: a)The trap (Figure 2) was placed in the copper chamber of the cryo-instrument (Figure 1). b) A vacuum was obtained in the cryogenic chamber through inlet 1. c) The helium was injected into the cryogenic chamber through inlet 2. d) The liquid nitrogen was injected into the instrument through inlet 3 and the required temperature was programmed. e)When the temperature of -183°C was reached, the puff volume was adjusted, and the temperature remained stable throughout the whole smoking run. f)The external parts of the trap were connected to a smoking machine. g) At the end of the smoking process, the smoking machine was disconnected and the bubbler (Figure 3) containing the solvent solution was placed on the upper part of the trap while the other exit of the trap was closed with a stopper. h)The temperature of the chamber was increased to room temperature and the volatile fraction of the trapped smoke was collected in the bubbler. i) At the end of the bubbling, the trapping solution was introduced into the trap to collect the remaining non-volatile fraction, and then collected for analysis by the three afore-mentioned analytical methods.

RESULTS AND DISCUSSION

Initial tests were performed to determine the lowest temperature for which puff volume could be reliably adjusted. It was observed that a temperature of -183°C enabled precise adjustment of the puff volume. The puffing volume obtained with the cryotrapping instrument closely matched the puff volume shape obtained with a Cambridge filter (Figure 4). It was important to work at a temperature above that of liquid nitrogen condensation. It was observed when cooling the cryogenic instrument near these temperatures that the puff volume had a different shape, and oxygen condensation was observed. Using a linear smoking machine, one single 2R4F cigarette was smoked (according to ISO conditions) when the trap reached the temperature of -183°C. The bubbler was then placed at the top of the croytrap with 5mL of DPIH (2-diphenylacetyl-1,3-indandione-1-hydrazone) reagent in acetonitrile solution, and the temperature of the cryogenic instrument was increased to room temperature.

Immediately after raising the temperature, the condensed smoke escaped through the trap to reach the bubbler and bubbling of the DPIH solution was observed. It is to be noted that a fraction of the smoke remained in the trap, and probably this fraction essentially consisted of compounds with a lower volatility. A notable exception was the presence of formaldehyde, which although very volatile, remained in the trap. This bubbling was probably due to the high volatility of certain compounds which were present in the mainstream smoke such as CO_2 which evaporated through the bubbler, the other side of the trap being sealed. When the bubbling ceased, the valve was opened and 5mL of the DPIH solution was introduced into the cryotrap. The collected solution was then divided into three parts: 1mL was used for the analysis by direct GCMS; 0.5mL was used for the analysis of carbonyls by HPLC and 1mL for the analysis of volatile organic non-polar compounds using SBSE-GCMS. Each determination was performed on one single 2R4F cigarette.

Table 1 summarizes the results obtained in this study and includes the data for quantification of formaldehyde, acetaldehyde, acrolein, acetone and propionaldehyde, 1,3 butadiene, toluene, isoprene benzene, phenol, pyridine, styrene, nicotine, *o*-cresol, *m+p* cresol, Benzanthracene, and Benzo[a]pyrene. These compounds were selected because they cover the range of smoke components usually analyzed. The results were then compared with data obtained in an inter-laboratory study of six independent laboratories using a variety of analytical techniques[6]. The derivative agent DPIH was added to the trapping solution in order to trap the carbonyl compounds. The results obtained when trapping the mainstream smoke of the 2R4F reference cigarette at -183°C were compared with those obtained by the standard methods and a good agreement was observed.

Table 1: Analysis of 2R4F cigarette

compounds	Cryo-trapping 1st tests (n=5x1cig) Average µg/cig	CV %	Cryo-trapping 2nd tests (n=5x1cig) Average µg/cig	CV %	Standard methods Inter-laboratory test[6] Average µg/cig	CV(r) %	CV(R) %	p labs x q replic x n cig
Pyridine (GC-MS)	5	21	5.6	18	7.02	10	36	5x5x(5-20)
Styrene (GC-MS)	4.9	15	6	18	5.11	9	45	5x5x(5-20)
Nicotine (GC-MS)	775	7	695	11	750	5	6	6x8x5
o-cresol (GC-MS)	1.9	9	1.8	23	1.89	7	14	6x5x(5-20)
Phenol (GC-MS)	6.4	8	6.9	21	7.32	7	42	6x5x(5-20)
m+p-cresol (GC-MS)	5.7	9	5.2	19	5.84	15	25	6x5x(5-20)
1,3-Butadiene (GC-MS)	29.8	6	26.7	33	29.94	5	25	5x5x(5-20)
Isoprene (GC-MS)	364.8	11	291.3	17	297.68	4	26	5x5x(5-20)
Benzene (GC-MS)	48.6	2	37.4	10	43.39	3	17	5x5x(5-20)
Toluene (GC-MS)	73.6	5	68.9	12	64.91	4	33	5x5x(5-20)
Benzanthracene (GC-MS/MS)			0.013	24	0.0145	6	N/A	1x5x20
Benzo[a]pyrene (GC-MS/MS)			0.009	9	0.007	8	27	6x5x(5-20)
Formaldehyde (LC-Fluo)	24.7	21	22.2	23	21.61	10	14	5x5x(2-5)
Acetaldehyde (LC-Fluo)	513.3	15	459.2	14	560.48	5	15	5x5x(2-5)
Acetone (LC-Fluo)	308.3	4	244.6	11	264.74	5	5	5x5x(2-5)
Acrolein (LC-Fluo)	36	33	34	9	58.77	7	14	5x5x(2-5)
Propionaldehyde (LC-Fluo)	47	13	40.2	8	43.92	5	13	5x5x(2-5)

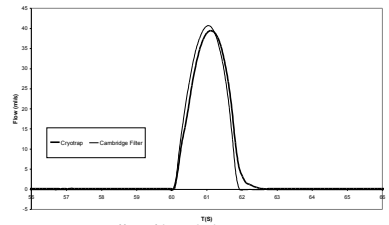

Figure 4: Puff profile with the cryogenic instrument and the Cambridge pad

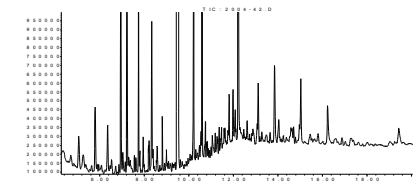

Figure 5: Mainstream profile of the GCMS fraction (Capillary Column DB-WAXetr)

CONCLUSIONS

The feasibility and the validation of the cryotrap for the collection of mainstream smoke were demonstrated. The cryotrap offers several advantages in the collection of tobacco smoke, among them: no solvent needs to be used during the trapping, the low temperature significantly reduces the rate of many chemical reactions, and finally, the method appears to minimize the formation of artifacts during the collection of smoke and the whole smoke can be collected in a single run. Furthermore, conventional methods such as the Cambridge pad, impinger or electrostatic precipitation might require a large number of cigarettes for the trapping. While using the cryotrap technique, only one single cigarette was sufficient.

Thus the development of the cryogenic instrument resolved issues previously observed namely oxygen condensation and lack of control over the puff volume. Furthermore, a minimal breakthrough of compounds was detected when trapping cigarette smoke. The recovery (93-102 %) of sample collection was satisfactory and the data were in good agreement with the smoke constituent results obtained from the 2003 inter-laboratory study.

ACKNOWLEDGMENT
The authors thank Air liquide Sessenage France and Carbagas Geneva Switzerland for their help in designing the cryogenic instrument.

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3) Chen P .X., Moldoveanu, S., *Beitrage Zur Tabakforshung int.* **2003**, *20*, 448