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Short communication

Direct determination of hydrogen cyanide in cigarette mainstream smoke by ion chromatography with pulsed amperometric detection

Zi-Wei Zhang[a,b], Ying-Bo Xu[c], Cheng-Hui Wang[c], Kai-Bo Chen[c], Hong-Wu Tong[a], Shao-Min Liu[a,b,*]

[a] Department of Chemistry, University of Science and Technology of China, Hefei 230026, China
[b] Research Center of Tobacco and Health, University of Science and Technology of China, Hefei 230052, China
[c] Technology Center of China Tobacco Anhui Industrial Corporation, Hefei 230088, China

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ABSTRACT

The determination of hydrogen cyanide in cigarette mainstream smoke has been achieved by ion chromatography (IC) with pulsed amperometric detection (PAD). The proposed method of totally trapping whole cigarette mainstream smoke by Cambridge filters, which are treated with sodium hydroxide/ethanol solution, possesses the advantage of fast analysis time over the widespread used solution absorption method. The possible co-existing interferents are evaluated under the optimized detection conditions and excellent recoveries of cyanide are obtained. The cyanide content of absorption solution can be directly determined by the optimized IC-PAD method without any pretreatments. The linear range is 0.0147–2.45 μg/mL with R^2 value of 0.9997. The limit of the detection is 3 μg/L for a 25 μL injection loop. The overall relative standard deviation of the method is less than 5.20% and the recovery range from 94.3% to 101.0%. The results obtained from the developed method are in good agreement with that of continuous flow analyzer (CFA) method.

1. Introduction

Hydrogen cyanide (HCN) in cigarette smoke is formed in the burning zone mainly from pyrolysis of various nitrogenous compounds such as protein and nitrate in tobacco at temperature higher than 700 °C, oxygen-deficient conditions [1]. It is one of the major ciliatoxic components when tobacco products such as cigarettes are combusted and is thus classed to the "Hoffmann analytes" [2]. More importantly, Chinese government attributes it to the toxic component in cigarette smoke of the flue-cured type cigarette. Therefore, the quantitative determination of HCN in cigarette smoke is integral to proper assessment due to its potential impact on public health. However, there are many challenges in accurately determining its amount in cigarette smoke; these include the need for developing an efficient and rapid smoke collecting method and the technique to analyze it in complex smoke mixture.

The methods used for trapping HCN in cigarette smoke are mainly solid adsorption [3,4] and solution absorption [5–7]. Although ideal concentrated samples can be produced, solid adsorption method has problems of uncompleted smoke trapping and desorption. Solution absorption method has the advantage of satisfactory trapping efficiency and has been widely used in tobacco industry. However, separately trapping HCN in the particulate and gas phase of cigarette mainstream smoke (MSS) is required. Furthermore, some difficulties have been experienced due to the reconstruction of smoking machine and thus result in some troubles when large numbers of cigarettes are needed to analysis. It is therefore of considerable importance to develop a trapping procedure for whole cigarette MSS.

Previously, a variety of methods, including coulometric titration [8], colorimetric analysis method [9] have been reported for determining HCN in cigarette MSS. Recently, gas chromatography (GC) [6], liquid chromatography–tandem mass spectrometry (LC/MS/MS) [7] methods have also been applied to analyze HCN in cigarette MSS. Unfortunately, these methods are technically complicated, time consuming or excessive analyzing procedures needed. Compared with those methods, ion chromatography (IC) exhibits advantages of simple operation, fast analysis, good selectivity, and nonuse of toxic solvents. More importantly, the development and application of electrochemical detection (especially pulsed amperometric detection) endow this kind of method with a high selectivity and improved accuracy, which eventually enable them to be widely applicable to the ion chromatography. Recently, extensive efforts have been done on determining cyanide by IC in matrices like food [10], surface water [11] and wastewater [12]. However, it is immature to apply this method to the determination of cyanide in complicated matrices (for example, cigarette smoke) for reasons that determining cyanide in such matrices may

* Corresponding author at: Research Center of Tobacco and Health, University of Science and Technology of China, Huizhou Road 1129, Hefei, Anhui Province 230052, China. Tel.: +86 551 3492147; fax: +86 551 3492065.
E-mail address: liusm@ustc.edu.cn (S.-M. Liu).

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be influenced by some factors. Therefore, our study focused on applying IC-PAD to the determination of cyanide in cigarette MSS by optimizing factors which include sample treatment, matrix interference, composition of eluents and so on. As result, an effective approach to directly determine cyanide in cigarette MSS by integrating IC with PAD has been developed and a novel way of totally trapping HCN in cigarette MSS by NaOH-treated Cambridge filter has been proposed. By comparison, method reported here possesses the advantages of high selectivity and great speediness, the NaOH-treated Cambridge filter is convenient and effective to collect HCN present in cigarette MSS, the possible interferent components in the contents range of cigarette smoke are not interference with cyanide determinations. The research is thus of significant importance to the determination and control of HCN yield in cigarette MSS.

2. Experimental

2.1. Reagents and materials

All chemicals used were analytical-reagent grade or better. The chemicals used for mobile phase were low carbonate, high purity 50% (w/w) sodium hydroxide (Acros Organics, USA) and sodium acetate (Acros Organics, USA). The cyanide standard solution was purchased from The National Institute of Metrology (Beijing, China) and diluted with sodium hydroxide (0.1 M). The eluents were installed on the chromatography system under an inert atmosphere (nitrogen) immediately after preparation. Cambridge filters (diameter 92 mm, 44 mm) and cigarettes were supplied by Technology Center of China Tobacco Anhui Industrial Corporation.

2.2. Instrumentation and chromatographic conditions

A 20 port channel Borg-waldt RM20H smoking machine (Borgwaldt KC GmbH, Hamburg, Germany) was used. A Dionex ICS3000 system that included a gradient pump GP40, an AS40 autosampler and an ED3000 electrochemical detector was used for chromatography. Ag, titanium and Ag/AgCl, KCl (sat) electrodes were used as working, counter and reference, respectively. The waveform used was previously optimized for a hydroxide eluent in Ref. [11]. Chromatographic separation was performed using the 250 mm × 4 mm i.d. IonPac AS7 (Dineox) analytical column and 50 mm × 4 mm i.d. IonPac AG7 guard column. The mobile phase was 0.6 M NaOH plus 0.3 M NaAC. The elution was carried out at a flow rate of 1.0 mL/min and column temperature was maintained at 30 °C. A sample loop of 25 μL was used for all the determinations. Instrument control and data handling were controlled by a Chromeleon 6.7 (Dionex) Data Management system. All CFA methods were performed on BRAN LUEBBE AutoAnalyzer3 (Hamburg, Germany). Freshly degassed, deionized water (18.2 MΩ cm resistivity) from Milli-Q (Millipore, France) water deionization system was used to prepare eluents.

2.3. Sample collections

2.3.1. Preparation of NaOH-treated Cambridge filter

Cambridge filter is a glass fiber filter which is fixed up by organic adhesives (polyacrylate). It is designed to collect particulate matter of MSS and has the feature of resistance to acid and alkali. Considering these properties of the Cambridge filter, we proposed a procedure for treating Cambridge filter in order to simultaneously trap HCN both in the particulate and gas phase in cigarette MSS. Initially, a 9 mL aliquot of 1.0 M sodium hydroxide ethanol solution was pipetted by a pipettor and then added evenly to the Cambridge filter (92 mm). After that, the filter was put in to the constant temperature and humidity equipment (60% relative humidity and 22 °C) for 2 h and then the NaOH-treated Cambridge filter could be used.

2.3.2. The collection of HCN in cigarette MSS

The procedures for collecting HCN in cigarette MSS only involve the use of the treated Cambridge filter. After conditioning for 48 h at a temperature of 22 ± 1 °C and 60 ± 2% relative humidity, randomly chosen five cigarettes of a particular brand were smoked for each analysis. The cigarette smoking conditions were one puff per minute, puff duration 2 s, puff volume 35 mL. A Cambridge filter pad holder with a 92 mm NaOH-treated plus a 44 mm untreated Cambridge filter were used to collect HCN in the whole cigarette MSS. When the smoking was finished, the filter holder was wiped with the standard weight degreased cotton. The cyanide trapped in the filter and the cotton was extracted with 100 mL 0.1 M sodium hydroxide in the triangular flask (150 mL) on a wrist action shaker for 10 min. A 5 mL aliquot of the extraction solution was diluted to 50 mL with 0.1 M sodium hydroxide. After filtered through 0.45 μm PTFE membrane, the diluted solution could be injected to the IC instrument for analysis.

3. Results and discussion

3.1. Optimization of NaOH-treated Cambridge filter method

HCN was present in both the particulate and gas phase of cigarette MSS. However, the common untreated Cambridge filters could only trap HCN in the particulate phase. To achieve the aim of fast analysis of HCN, this study demonstrated a whole cigarette smoke trapping method under the standard smoking conditions. Initially, we optimized the drying time of NaOH-treated Cambridge filter. The results show that the resistance of smoking as well as penetration of cigarette smoke increase and eventually influence the trapping efficiency of the filter when the balance time of NaOH-treated Cambridge filter is too short. A satisfactory result could be obtained when the drying time of the filter is chosen for 2 h. And then the number of treated filters was optimized. When one treated Cambridge filter (92 mm) was used, the content of HCN was 156.1 μg/cig and the trapping efficiency had arrived to 99.7%. However, penetration of cigarette smoke might be observed during the experiment. When one treated filter (92 mm) and one untreated filter (44 mm) was used, the content of HCN was 161.4 μg/cig and HCN was not found in the absorption tube. When two treated filters (92 mm) were used, the content of HCN was 158.8 μg/cig and the trapping efficiency was 99.2%. This might be caused by some characteristics of the cigarette smoke. Penetration factor of the smoke was strong and smoke flow rate was rapid, thus, one treated filter could not sufficiently trap all HCN. In contrast, when two treated filters were used, the resistance increased so as to reduce the yield of smoke, even to change the standard condition of smoking. A good compromise between these two factors was achieved when one treated filter (92 mm) and one common filter (44 mm) were used. Furthermore, we analyzed the same brand of cigarettes using the proposed method and solution absorption method (see Ref. [6] and Fig. 1). Mean content of HCN and RSD ($n = 5$) obtained by the proposed method was 161.0 μg/cig and 4.08% while that of solution absorption method was 168.0 μg/cig and 3.46%. So, a conclusion that the new proposed trapping method was in good agreement with solution absorption method could be drawn.

3.2. Optimization of eluent composition

The retention behavior of cyanide peak in the extract depended on NaOH plus NaAC concentration in the AS7 column. The results (see Fig. 2) show that when the concentration of NaOH was increased from 0.2 M to 0.6 M with the fixed concentration of NaAC

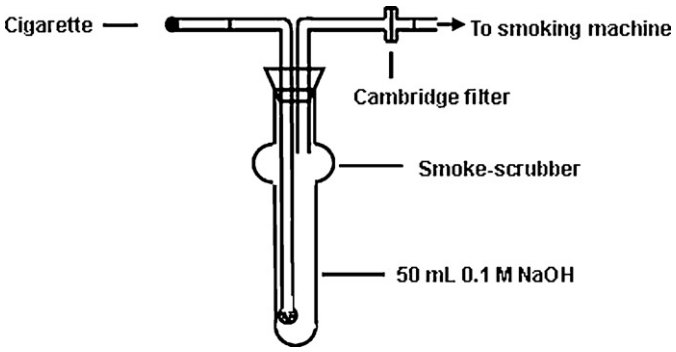

Fig. 1. Schematic diagram of solution absorption method.

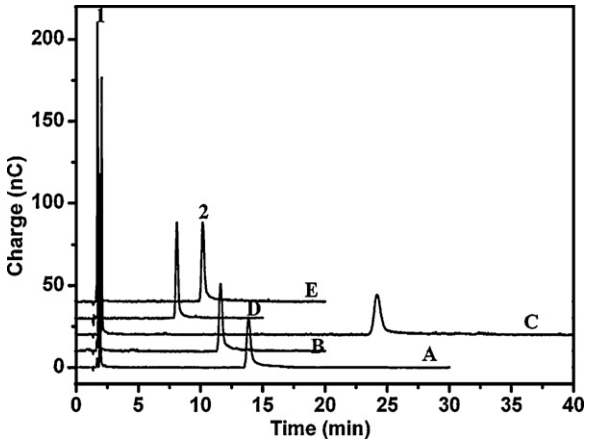

Fig. 2. Typical chromatograms obtained under the following eluent composition: A – 0.2 M NaOH, 0.2 M NaAC; B – 0.4 M NaOH, 0.2 M NaAC; C – 0.6 M NaOH; D – 0.6 M NaOH, 0.3 M NaAC; E – 0.6 M NaOH, 0.2 M NaAC. Flow rate: 1.0 mL/min, injection volume: 25 μL, column temperature 30 °C, detection waveform see Ref. [11]. Peak 1, unidentified; peak 2, cyanide.

(0.2 M), the retention time of cyanide peak decreased from 13.9 min to 10.2 min. In addition, the peak shape of cyanide became more and more symmetrical. Meanwhile, when the concentration of NaAC was increased from 0 M to 0.3 M with the fixed concentration of NaOH (0.6 M), the retention time of cyanide peak decreased from 28.9 min to 8.2 min. A comprise between the retention time and peak shape of cyanide was achieved, when the eluent composition of 0.6 M NaOH plus 0.3 M NaAC was used.

3.3. Evaluation of possible interferences

Interference experiment was done in order to validate IC to the practical use in the complex system of cigarette smoke and achieve the goal of direct determination of HCN in cigarette MSS. 18 types of components were chosen (see Table 1) and they were mainly divided into two groups. One was eight anions which might be eluted under the detection condition. The other was six cations as well as four volatile carbonyl compounds which probably reacted with cyanide. A series of synthetic samples containing both cyanide (0.34 mg/L) standards and the three gradient concentrations of interferents were measured. The added amount of the interferents covered or extended their average content in cigarette smoke [13]. The recovery of cyanide from these interferents was used to evaluate their effect of interference.

Table 1 shows good recovery of cyanide in the presence of all investigated interferents. It ranges from 99.0% to 102.6% for anions and from 99.4% to 101.7% for cations. The recovery of cyanide from four volatile carbonyl compounds is in the range 94.5–102.2%. However, it was observed that the recovery of cyanide showed slight tendency of decreasing with the extension of reaction time when formaldehyde existed (data not shown). To further examine interference by formaldehyde, we analyzed the mixture of 0.34 mg/L cyanide and 0.51 mg/L after 12 h for five replicates. The mean recovery of cyanide was 96.1% with RSD of 0.71%. However, when the real sampling and analyzing time was taken into consideration, a conclusion that the chosen carbonyl compounds have no influence

Table 1
Effect of possible interferents on cyanide recovery[b] (CN 0.34 mg/L).

Substance	Added concentration[a]	Recovery of cyanide (%)	Substance	Added concentration[a]	Recovery of cyanide (%)
Cl^-	0.41	99.1	Cu^{2+}	40	101.6
	2.1	100.6		200	101.1
	4.1	100.0		400	101.7
S^{2-}	0.04	101.0	Zn^{2+}	40	99.4
	0.21	101.2		200	99.8
	0.4	99.4		400	101.1
HSO_3^-	0.04	100.4	Pb^{2+}	4	100.8
	0.21	100.8		20	101.4
	0.4	100.9		40	101.0
SCN^-	0.04	100.4	Co^{2+}	0.04	100.7
	0.21	100.6		0.20	101.2
	0.4	100.9		0.40	101.3
Br^-	0.04	99.8	Hg^{2+}	0.04	100.2
	0.21	100.3		0.20	101.6
	0.4	100.4		0.40	99.7
I^-	0.04	100.8	HCHO	0.14	99.2
	0.21	100.2		0.29	99.4
	0.4	100.0		0.58	98.9
$S_2O_3^{2-}$	0.04	99.6	CH_3CHO	2.51	94.5
	0.21	101.1		5.02	97.1
	0.4	99.0		10.03	96.8
CO_3^{2-}	40	99.7	CH_3COCH_3	0.62	102.2
	200	100.0		1.23	99.6
	400	102.6		2.46	99.4
Fe^{3+}	40	100.0	$CH_2{=}CHCHO$	0.44	99.6
	200	99.9		0.88	99.4
	400	99.5		1.76	97.7

[a] The unit of concentration for each anion and carbonyl compound was mg/L; the unit of concentration for each cation was μg/L.
[b] The recovery was calculated by analyzing 0.34 mg/L cyanide standards without the interferent and with three gradient concentrations' substance. There were 2 injections of each sample set (spiked and unspiked) for all the samples. The recovery was average value of 2 injections ($n = 2$).

Table 2
Comparison of analytical performance of the proposed method with the reported methods.

Methods	LOD (ng/mL)	Recovery (%)	RSD (%)	Linear range (μg/mL)	Ref.
CFA method	0.04[a]	–	–	1.00–15.0	[5]
Coulometric titration	–	100.3	5.31	–	[8]
Colorimetric analysis	0.04[a]	95.0–105.0	2.70–3.50	0.04–0.80	[9]
GC	0.6	86.0–116.0	4.78	0.0250–15.0	[6]
LC/MS/MS	0.5	–	1.80–6.40	0.0024–0.331	[7]
IC-PAD	3	94.3–101.0	3.90–5.20	0.0147–2.45	This method

[a] The LOD of CFA method and Colorimetric analysis were 0.04 μg/mL.

Table 3
Determination of HCN in cigarette MSS.

Sample No.	HCN (μg/cig)		Relative deviation (%)
	IC	CFA	
1	125.9	122.2	3.03
2	110.3	107.8	2.32
3	178.2	171.0	4.21
4	119.1	113.9	4.56
5	102.8	101.1	1.68
6	115.0	110.0	4.54

on the measurement of cyanide can be drawn and thus the direct determination of cyanide in cigarette MSS can be achieved with IC-PAD.

3.4. Method performance

A six point calibration curve with a concentration range of 0.0147 °C 2.45 μg/mL was established. The mean slope, intercept and linear regression coefficient square were 0.0583, −0.037 and 0.9997. The limit of detection (LOD) of cyanide was 3 ng/mL at a signal-to-noise ratio (S/N) of 3. Intra- and inter-day variations were chosen to determine the precision of the developed method. For intra-day variability test, the same brand of commercial cigarettes were analyzed for five replicates within one day; while the inter-day precision of the method was determined by smoking the same commercial brand cigarettes for consecutive three days. Variations were expressed as relative standard deviations (RSDs). The types of blended and flue-cured cigarette were used to validate precision of the method. The overall intra- and inter-day RSD of blended cigarette were less than 3.90% and 3.63%, respectively; while the overall intra- and inter-day RSD of flue-cured cigarette were less than 5.20% and 3.93%, respectively. The recoveries were evaluated by adding cyanide (0.49, 0.98, 1.47 μg/mL) to each sample. The mean recovery and RSD ($n = 9$) for blended type cigarette were 96.87% and 2.88%, respectively; while the mean recovery and RSD ($n = 9$) for flue-cured type cigarette were 97.10% and 2.90%, respectively. Table 2 compares some analytical performance of methods reported for the determination of HCN in cigarette MSS. As can be seen, the proposed method has advantages over the CFA which has been recommended as the standard method for determining HCN in MSS, due to expanded linear range with lower LOD. Moreover, we analyzed the same commercial brand cigarettes with IC-PAD method as described previously and CFA method [5]. The results (see Table 3) show that they are in good agreement.

4. Conclusions

We have demonstrated a new method for the direct determination of hydrogen cyanide in cigarette mainstream smoke by efficiently integrating IC with PAD. The NaOH-treated Cambridge filter method of trapping hydrogen cyanide clearly has advantages over the solution absorption method. The optimization of composition of eluents and evaluation of possible interferents make this method selective and reliable. Compared with CFA method, the work demonstrated here proves to be advantageous, due to expanded detection range with greater accuracy and is thus highly anticipated to find wide applications in cigarette smoke analysis.

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