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Analytical Methods

Electrospun nanofibers prepared using polystyrene (PS) with polymeric additive for the determination of nicotine in cigarette mainstream smoke Zhifeng Guo*, Xiaoyang Wu, Jingjing Dong, Hiudan Su, Ru Cai Key Laboratory of Medical Chemistry and Molecular Diagnosis, College of Chemistry and Environmental Science, Hebei University, Baoding, 071002, China: Abstract: The objective of this paper is to use electrospun nanofibers as the adsorbent in solid phase extraction (SPE) to improve extraction efficiency. The electronspun nanofibers were prepared in lab using PS (what is PS) along with polymeric additives, poly-(methyl ethacrylate) (PMMA) and co-poly (melamine-urea-formaldehyde) (MUF) and put into a tip to form a SPE system. The polymeric additives can provide nanofibers more adsorption sites due to its chemically reactive hydroxyl groups, leading to a better adsorption rate during extraction. We used the nanofibers SPE system to extract nicotine from cigarette mainstream smoke. The isothermal adsorption and elution experiments showed that nicotine adsorption and organic solvent elution were good, and achieved high extraction efficiency. We also used the system to quantify nicotine content in mainstream smoke. The results showed a correlation between cigarette price and nicotine content. The higher price a cigarette is, the higher the nicotine content in that cigarette mainstream smoke is.

Keywords: electrospun; nanofibers; polymeric additive; solid phase extraction; nicotine; cigarette smoke.

1. Introduction

Electrospinning is a fiber spinning that disperses a fluid of polymers solution under a high electric field, which was first discovered by Cooley and Morton in 1902 [1,2]. In recent years, the electrospinning process has aroused great interest as an attractive technique for fabricating polymer fibers with small size diameters from micron to nanometer scales [3-6]. The micro/nanometer fibers have high surface-to-volume ratio and can be hence used as a solid-phase adsorbent for solid-phase extraction (SPE). An optimal SPE sorbent material should combine the following benefits: large specific surface area, slimmer, comparatively looser, modifiable, having an interconnected fibrous network, and simplified fabrication/synthesis. Fortunately, the electrospun fibers seem to have all of these characteristics and are desirable for several

applications [7-14]. In fact, some electrospun fibers as SPE sorbent are effective for the removal of organic molecules from liquid media and vapor phase [15-19], such as extraction of steroidal compounds [20, 21] and trazodone [22]from plasma, and the removal of phenanthrene and endocrine disruptors from aqueous solution [23,24].

Previous studies have reported that polystyrene (PS) and polystyrene copolymers can be electrospun to form nanofibrous sorbents for SPE applications. However, the comparative study of using these nanofibrous sorbents for the extraction of polar compounds showed that the extraction efficiency is not compatible with those polystyrene copolymers [8]. This trend was attributed to the fact that the polar model analytes favored the polar sorbent and the non-polar analytes favored the non-polar sorbent. To solve this problem, we add polymeric additives into nanofibrous sorbents to improve its polarity. It should be work since electrospinning can fabricate almost all polymeric material to form nanofibrous sorbents [25-29]. In particular, polymer along with polymeric additives patterned nanofibrous materials is more valuable in SPE sorbent.

Current studies are all focused on how to control the sizes and morphologies of the electrospun fibers by changing the experimental parameters during the electrospinning process. These parameters include the type of polymer, the polymer molecular weight, the type of solvent, the solution concentration, the applied voltage, the working distance and the flow rate [30-32]. Except all above, additives in polymers also play an important role on the size and morphology changes of the electrospun fibers. Components of electrospun fibers have been found to directly affect the characteristics of adsorption but few studies evaluate the influence of this effort on the extraction.

In this study, SPE sorbents were generated through electrospinning PS gel and PS gel with polymeric additive: poly (methyl methacrylate) (PMMA) and co-poly (melamine-urea-formaldehyde) (MUF) sol-gel. The polymeric additive PMMA and MUF can provide the nanofibers more adsorption sites due to its chemically reactive hydroxyl groups. The parameters for the optimization of electrospinning were investigated. The electrospun nonafibers were packed in a tip for the extraction of nicotine from cigarette mainstream smoke using four brands of commercial cigarette as samples. The adsorption and elution characteristics of the electrospun nanofibers tip for nicotine extraction were investigated under isothermal adsorption conditions.

Page 3 of 24

Analytical Methods

The quantification of nicotine content in cigarette mainstream smoke was conducted by GC / MS using double internal standard quantitative methods [33].

2. Experimental

2.1 Chemicals and instruments

All reagents were of analytical reagent grade. Doubly distilled water was used throughout. Tetrahydrofuran (THF), N,N-dimethylformamide (DMF), camphor, metacresol were obtained from the Kemiou Chemical company (Tianjin, China). Ethanol (95%) dichloromethane, methanol, ether and acetone were purchased from local chemical shop. Nicotine ethanol solution (V:V=1:1) was used as received from the local cigarette manufacturer. Polystyrene (158K) (PS) and poly (methyl methacrylate) (PMMA) presented as gift from the manufacture. Poly (melamine-urea-formaldehyde) sol-gel (MUF) was prepared in our laboratory and the synthesis methods described elsewhere [34].

Optical microscopy and scanning electron microscopy (SEM) (Hitachi S-3000N, Japan) were used to observe the size diameters of the fibers prepared in our experiment. The characteristics of packed tip for adsorption nicotine was determined by Gas chromatograph (Agilent, US) combine with Mass spectrometer (Micromass Corporation). Chromatographic column was HP-5 Crosslinking capillary column (32 $m \times 0.32 \text{ mm} \times 1.05 \text{ \mum}$).

2.2 Electrospun fibers

The electrospinning apparatus consisted of a 1 mL syringe connected to a high-voltage

power supply (Glassman Series EH) that was used to apply a potential of 10 kV to the syringe needle (Hamilton). The inner diameters of the needles used were 0.26 mm. A steady flow of sample solution to the tip of the needle was applied by using an artificial power. A grounded copper sheet was placed 25 cm from the needle tip to ensure that the fibers were dry upon collection. Polystyrene fibers were electrospun using a series of wt % concentration of PS in a mixture of tetrahydrofuran (THF) and N, N dimethyl formamide (DMF) (7:3, V/V) for all of the experiments reported here. Density of the PS sample was 1.05g/cm3. Nine of different concentrations of PS sample ranging from 6% to 14% were investigated to assess whether the viscosity of PS sample solution was available during electrospinning process. Electrospun fibers using PS with polymeric additive PMMA and MUF were in same condition as those of the PS fibers. 1.5 g PMMA was dissolved in 96 mL THF as PMMA solution and

MUF sol-gel was a hydro gel. All polymers were dissolved at room temperature.

2.3 Isothermal adsorption

PS or PS with polymeric additive electrospun fibers were packed in a glass column washing with methanol (10 mL \times 3) to ensure that the fibers were cleaned. After suction filtration to remove the remaining methanol, the dry fibers were immersed in different concentrations of nicotine aqueous solutions (3 mL) in dark brown vials. The vials were shaken for 10 min at room temperature in an ultrasonic oscillator and stored in dark place overnight to achieve equilibrium. The fibers parameters are shown in table 1. The amount of nicotine adsorbed per gram of fibers Q is defined as follow [35]:

$$Q = \frac{(C_0 - C)V}{M}$$
 I

Where C_0 and C represent respectively the concentration of nicotine solution at the initial and in the after point of adsorption equilibrium; V is the volume of the nicotine solution and M is the weight of the fibers.

Sample	PS	S: polymeric add	Filter	Adsorption		
number	PS (%)	SPMMA	GMFU	AM	Fiber	test
1	1 (6)				+	
2	1 (7)				+	++
3	1 (8)				+	++
4	1 (9)				+	++
5	1 (10)				+	
6	1 (11)				+	
7	1 (12)				+	
8	1 (13)				+	
9	1 (14)				+	++
10	1 (9)	0.025			+	++
11	1 (9)	0.05			+	++
12	1 (9)	0.1			+	++
13	1 (9)	0.15			+	++
14	1 (9)	0.2			+	++
45	1 (9)	0.3			+	
16	1 (9)	0.4			+	
17	1 (9)	0.5			-	
18	1 (9)	0.6			-	
19	1 (9)		0.1		-	
20	1 (14)		0.1		-	

Table 1 the ratio of PS and polymeric additive

21	1 (14)	0.1	+	++
22	1 (14)	0.3	+	++
23	1 (14)	0.5	+	++
24	1 (14)	0.6	-	
25	1 (14)	1	-	

PS: solution of PS dissolved in the mixture of THF and DMF (7:3, V:V);

SPM : solution of 1.6g PMMA dissolved in 96mL THF;

GMUF: hydro gel prepared in our laboratory;

AM: the mixture of PS(9%) and MUF, PS(9%): MUF = 1: 0.1 (V:V);

+ : fiber can be spun; - : fiber can not be spun; ++ : the fibers were used as sorbent to investigate its capacity of adsorption nicotine

2.4 Packed-fiber solid-phase column and elution

The packed-fiber solid-phase columns were prepared by packing an appropriate amount of fibers into a 500 μ L pipette tip. The end of the tip was connected to a vacuum pump. The packed fibers were made firm when the inner air of the tip was pumped out. Prior to an adsorption step, the packed fiber column was washed with methanol (10 mL×3). A 1 mL of the nicotine sample aqueous solution was added to the column. The sample liquid was flowed through the column under the unforced condition. Then the column was eluted with four different organic solvent (ether, acetone, methanol and chloroform, 3 mL for each) to select the optimum eluent. After the total nicotine was eluted out the fibers, the fibers were washed with water for the next extraction. The nicotine in the eluate was analyzed by GC/MS. The initial experiments were done by fiber-packed SPE column packed with 30 mg of PS fibers, and a water solution of nicotine (1000 μ LL⁻¹) was used as the model sample.

2.5 Mainstream smoke SPE procedure and GC/MS analysis

The Fig. 1 shows the homemade unit for the extraction of nicotine from cigarette mainstream smoke. The packed fiber column connected a gas collecting bottle to the vacuum pump. Tested cigarette was inserted on the top of the packed fiber column. Mainstream smoke was collected on individual. The collecting conditions were referred to US Federal Trade commission [36]. The adsorption process of mainstream smoke was done as follow: turn on the vacuum pump to make the gas collecting bottle at negative pressure and then the tested cigarette was lighted. The mainstream smoke started to flow through the fibers to the gas collecting bottle and then was pumped out. When the cigarette was smoked to a butt length 1cm or the length of the filter overwrap plus 1 cm, the vacuum pump was turn off. The tested cigarette was extinguished and removed out of the top of the column. The column underwent

elution procedure with methanol. The eluate (methanol) was divided into two aliquots. One was used as the sample to inject into GC/MS for the determination of nicotine in it and the other, being spiked nicotine solution ($300\mu LL^{-1}$), was used for recovery test. The experiments used four brands of cigarettes as samples. Each band cigarette was tested in two patterns filtered and unfiltered.

Fig.1

The amount of nicotine was conducted by GC / MS using double internal standard quantitative methods. Camphor and metacresol were used as the internal standard substance. They were dissolved in dichloromethane or ethanol (95%) as the internal standard solution. The mixture of nicotine standard solution with the internal standard solution was sampled for GC/MS analysis. The concentration of nicotine was on the (as) X axis, and the ratio of nicotine and camphor chromatographic peak area was on the (as) Y axis. A linear relationship with a good correlation coefficient was obtained (y = 34.2513 + 38.45528x, $R^2 = 0.99131$).

Gas chromatographic separations were performed on a crosslinking capillary column $(32m \times 0.32mm \times 1.05\mu m; HP-5)$. Helium at a constant flow-rate of 1.9 mL min⁻¹ was used as a gas carrier for the GC/CMS analysis. The column temperature program was 40°C, held for 1 min, then increased at 40°C min⁻¹ to 140°C, and further increased at 10°C min⁻¹ to 220°C, finally, held for 10 min. The injections (2µL each) were of the splitless mode with the injector temperature set at 220°C.

The mass spectrometer was operated in the electron impact ionisation (EI) positive-mode using automatic gain control. For MS experiments the instrumental parameters were set at the following values: electron energy 70 eV, the accelerated voltage of 6 kV, source temperature 200°C, collected current200 μ A, source vacuum 10⁻⁴Pa, analyzer vacuum 10⁻⁶Pa. Scan range was 33-600 m/z in whole scan mode.

Results and discussion

3.1 Fibers

25 samples are shown in table 1 for electrospinning fibers. They include 9 PS, 9 PS with PAAM additive and 7 PS with MUF additive in different concentrations. The

Analytical Methods

concentrations of PS solutions for this work were lower than those reported in the literatures [37]. The results show that the diameter of the fiber is related to the concentration of PS solution. When the concentration of PS solution was above 9%, the higher the concentration of PS solution used was, the larger diameter of the fiber was. But if the concentration of PS solution was below 7%, coarse diameter of the fiber would appear due to the drop of sample solution being formed in the collection board during the electrospinning process. When the concentrations of PS solution were from 7 - 9%, the diameters of eletrospun fiber were below 1 µm. Fig.2 is their SEM pictures. As shown in Fig. 2, the electrospun fibers are smooth, fine and steady and the diameter of fiber reached about 360 nm at 9% PS solution. Based on this condition, 9% PS solution was selected as parent solution to be added with PAAM and MUF. The result showed that the fibers became significant larger in the parent solution when added with PAAM; whereas the fibers were not electrospun in the parent solution when added with MUF. It is because the viscosity of the mix solution was changed when PS solution (9%) was mixed with PAAM or MUF polymeric additive and the diameter of electrospun fiber s is depended on the viscosity of the mix solution. The PAAM polymeric additive is THF solution, which can be mixed well with PS solution at any ratio for electrospun fibers, however the MUF additive cannot due to its hydrophilicity. The viscosity of the mixed solution decreased rapidly when MUF aqueous was added, leading to the failure of electrospinning. The viscosity of mixtures of PS with MUF gel is not thick enough for electrospinning fibers until the concentration of PS solution reaching 14%, indicating a critical viscosity needs to be achieved to form PS with MUF additives nanofibers, below this critical viscosity, the mixture of PS with MUF gel can not be electrospun fibers.

Fig.2

3.2 Adsorption of PS fibers

The effect of fiber diameter on the efficiency of the adsorption was investigated using PS fibers (PS solution concentration 7%, 8% and 9%) to extract aqueous nicotine solutions(1000, 1500 and $2000\mu LL^{-1}$) at room temperature. The result of adsorption is shown in Fig. 3. The adsorption capacity increased with increasing PS

solution concentration and nicotine concentration as well (e.g. adsorption capacity increased from 0.026 to 0.083 mgg⁻¹, 0.051 to 0.10 mgg⁻¹ and 0.073 to 0.11 mgg⁻¹ for 7% ,8% and 9% PS solution PS solution respectively when increasing the nicotine concentration from 1000 to 2000 μ LL⁻¹). It may be due to the increased surface-to-volume ratio and available adsorption sites with attenuation of the diameter of fibers. Hence, the fiber diameter spun by 9% PS should be the smallest, which was proved by measuring the average diameter of the abovementioned fibers using SEM view (Fig.2). The diameter of fiber with different PS solution concentration were 360 nm (9%), 440 nm (8%) and 490 nm (7%). As a result, the number of sites available for absorbing molecules increases.

Fig.3

3.3 Effect of additive on the adsorption capacity

The efficiency of the adsorption can not only be controlled by the surface-to-volume ratio of the electrospun fibers, but also by the component of fibers. By adding the poly- additive in PS solution, fibers with enhanced molecules adsorption sites can be made. In this experiment, two of poly-additives PAAM and MUF were added in PS solution for electrosuph fibers. PSP fibers represented using PAAM as additive in PS solution, and PSM fibers represented MUF as additive. The enhanced efficiency of the adsorption was expected due to the presence of a lot of chemically reactive hydroxyl in the PSP or PSM fibers. The adsorption experiment was carried out using PSP fibers with five different PS to PAAM ratios (V:V) to extract three different concentrations of nicotine solutions. The results are depicted in Fig. 4. The highest efficiency of nicotine adsorption is appeared when the PS to PAAM ratio (V:V) is 1: 0.2 with either 1500 or 2000 μ LL⁻¹ nicotine solution. The nicotine uptake efficiency, however, decreased in 1000 uLL⁻¹ of concentration nicotine solution with the same PSP fibers. The steadiest adsorption in the three concentrations of nicotine solutions appeared at those PSP fibers where the PS and PAAM volume ratio was 1: 0.1. Compared with 9% of PS fibers, the amount of adsorbed by PSP fibers was the same. But the diameter of 9% of PS was thinner than PSP fiber. In other wards, the surface-to-volume ratio of the PS fiber was bigger than

Page 9 of 24

Analytical Methods

that of PSP fiber. By assuming that the pores in porous materials are cylindrical in shape, the relative increment of the surface-to-volume ratio can be correlated with the radius of fibers according to the following equation [6, 38]:

$$\left(\frac{1}{R} - \frac{1}{R_0}\right)R_0 = \frac{-\Delta R}{R} \tag{II}$$

where R is radius of PSP fiber (1:0.2), R_0 is the radius of 9% PS fiber. The average diameter of PSP fiber (1:0.2) was 420 nm and PS fiber was 360 nm. By calculating using the above formulation, the surface-to-volume ratio of PSP fiber was reduced about to 15%. As a result, increasing adsorption sites in fibers can offset the surface-to-volume ratio lost due to the diameter of fiber growing thicker when additive was added. To prove this observation in details, the PSM fibers were used for adsorption nicotine experiment. Fig.5 shows that a little additive of MUF is added leading to great rising of the adsorption efficiency. As shown in Fig. 5, the amount adsorbed by PSM (1: 0.1) fibers is much higher than that of 14 % PS fibers. While the surface-to-volume ratio of PSM (1:0.1) was decreased about 24 % compare to the 14 % PS fibers using formulation *II* calculation. It illustrate that a little MUF added can improve the adsorption efficiency greatly. It is more likely because PSM fibers contain more available absorption sites for nicotine compared with PS fibers.

Fig.4

Fig.5

3.4 SPE nicotine from mainstream smoke

SPE experiment was carried out using a packed tip. The PSM fibers (PS (14%) : AM = 1: 0.1, V : V) were used as solid sorbent. Before solid phase extracting nicotine from mainstream smoke, the tip was underwent adsorption and elution procedure. Nicotine aqueous solution (1000 μ LL⁻¹,1mL) was used as analyte to flow through the tip for the adsorption of nicotine. After that the tip was eluted by four kinds of organic regents (ether, acetone, methanol and chloroform). The eluting result showed that methanol was the best among the four eluents because the other three organic regents partly dissolved fibers. Nicotine was not detected in the outflow after the pack column was eluted three times.

Analytical Methods Accepted Manuscript

Four brands of commercial cigarettes were used as samples for the extraction of nicotine from mainstream smoke. Each brand cigarette was divided two groups: the filtered and the unfiltered. The temperature of burnt cigarette is more than 400 °C, while the nicotine decomposed temperature is 247°C. Therefore, the nicotine in tobacco should be in two forms: free nicotine and non-free nicotine which was bound by plant cellulose or protein. When the cigarette was burnt some of free nicotine was decomposed and some bound nicotine was released at high temperature. The nicotine in smoke N_g should be the sum of the free nicotine and abovementioned two parts and described by the following equation.

$$N_g = (N_f + N_b \cdot R_r)(1 - B_r) \tag{III}$$

Where N_f represents free nicotine, N_b represents bound nicotine, B_r represents the rate of nicotine decomposition during burning process and R_r represents the rate of nicotine released in burnt process. The ratio of N_g / N_f is

$$\frac{N_g}{N_f} = (1 + \frac{N_{nf} \cdot R_r}{N_f})(1 - B_r)$$
(IV)

The analytical results are listed in Table 2. As shown in Table 2, the nicotine was not found in the outflow of fourth elution in the total eight tested samples except for diamond brand cigarette that nicotine is not found in the outflow of third elution whether filtered or unfiltered cigarette. The order of nicotine content in mainstream smoke of tested four brands cigarette samples is $S_1 < S_2 < S_3 < S_4$ as well as N_g/N_f . This order happens to be correlates with their selling price. The higher the price cigarette was, the more amount of nicotine inhaled is almost three times as that of smoking a cigarette of sample S_4 , the amount of nicotine inhaled is almost three times as that of smoking a cigarette of sample S_1 . The ratio of N_g/N_r (meaning nicotine transferring from burning per grams tobacco into mainstream smoke) of the sample S_4 is also the highest, which implies the picadura of sample S_4 is the best in the tested four brands cigarette. The rate of nicotine filtered is an another standard of assess cigarette, which can be defined as

$$\eta = \frac{\mathbf{M}_{uf} - \mathbf{M}_{f}}{\mathbf{M}_{uf}}$$

where M_{uf} is nicotine contained in mainstream smoke produced by burning unfiltered cigarette, and Mf is nicotine in mainstream smoke produced by burning filtered cigarette.

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In our test, the values of η for the four cigarette samples were 59.2%, 58.8%, 51.2% and 64.4%, respectively. These values of η were over 50 percent so it could be concluded that when one smoke a filtered cigarette, the amount of nicotine inhaled was less a half than that of in mainstream smoke. In spite of the η , the sample S4 was the highest; it does not mean the nicotine intake is low.

Table 2

Cigarette samples		Amount of nicotine eluted by elution times (nL)				$N_g (nL)$	$N_{f}(nL)$	N _g / N _f (%)
		1	2	3	4			
S ₁	filter	196±6	73.8±2	0	0	460.9±14		
	unfilter	465.4±14	135.9±4	60.7 ± 2	0	1130.9 ± 34	4892±147	23.1
S_2	filter	480±15	172 ± 5	0	0	1088.7 ± 33		
	unfilter	935.7±28	646.3±19	0	0	2641.5±79	5301 ± 147	49.8
S ₃	filter	980.9±29	0	0	0	1647.7±49		
	unfilter	1061.6 ± 32	844.1±25	104.2 ± 3	0	3376.3±101	5633±169	59.9
S_4	filter	873.7±26	$245.8\!\pm\!7$	0	0	1771.4±53		
	unfilter	1762 ± 53	1163 ± 35	239.9±7	0	5007.8 ± 150	6048±181	82.8

Ng: Amount of nicotine in main smoke which is produced by per grams tobacco cut.

 N_f : Amount of free nicotine per grams tobacco. S_1 : Xinshijiazhuang brand cigarette, S_2 : Diamond brand cigarette, S_3 : Hongta mountain brand cigarette, S_4 : Suyan brand cigarette.

Recovery runs were made on real cigarette samples spiked with 300 μ LL⁻¹ nicotine standards. Before spiking, the cigarette samples had been pre-tested. Satisfactory recoveries in the range of 89 – 110% were observed. The precision of the method was established by performing six consecutive runs of one brand cigarette samples spiked 300 μ LL⁻¹ of each of the nicotine standards. The R.S.D.s obtained

ranged from 3.6 to 5.3 %. The precision of the method was deemed acceptable for the analysis of nicotine in mainstream smoke.

4 Conclusions

This work has prepared nanometer electrospun fibers using the PS with polymertic additive solution. The results show that using PS with poly-additive for electrospinning fibers, the diameter of electrospun fibers are become little larger than those of using non-additive PS solution, but their adsorption efficiency for nicotine did not decreased notably. Therefore, these fibers can be used as sorbent assembling tip for separation of nicotine from cigarette mainstream smoke as well as other harmful substance i.e. polyaromatic hydrocarbons. Due to the PS with poly-additive electrosupn nanofibers being easy packed into column, they can be assembled as different tips for performance pre-enrichment analytes from different matrix. The nanofibers as sorbent for SPE have a number of advantages in simplifying sample preparation and reducing the cost and time of the analysis with less sorbent usage, acceptable reliability, and sensitivity. It is believed that the nanofibers will have more potential application in pretreatment areas.

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Fig.2 a

Fig.2 SEM pictures of electrospun fibers; a: 7% PS, b: 8% PS, c: 9% PS, d: 14% PS

169x147mm (96 x 96 DPI)



Fig.2 b

169x144mm (96 x 96 DPI)



Fig.2 c

169x144mm (96 x 96 DPI)



Fig.2d

168x144mm (96 x 96 DPI)







The adsorption capacity of PS electrospun fibers; X axis: percent concentrations of PS 110x67mm (96 x 96 DPI)



The adsorption capacity of PSP electrospun fibers; X axis: volume ratio of PS and PAAM solution 108x62mm (96 x 96 DPI)







The adsorption capacity of PSM electrospun fibers; X axis: volume ratio of PS solution and MUF hydro gel 107x65mm (96 x 96 DPI)