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Journal of Chromatography A, 689 (1995) 275–284

JOURNAL OF CHROMATOGRAPHY A

Applications of multiplex gas chromatography to the determination of organics in solid samples

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First received 7 June 1994; revised manuscript received 1 September 1994

Abstract

A multiplex gas chromatographic technique for determining nicotine in cigarettes is described and multiplex gas chromatograms of volatiles from other solid samples are also presented. Direct headspace sampling, which is carried out in a sampler modified from an injector, provides a continuous gas sample stream for multiplex gas chromatography. Volatiles evaporating from the sample are picked up and carried by a carrier gas to a thermal desorption modulator and column. Concentrations to be determined are modulated by the modulator. The thermal desorption modulator is a short section at the head of the capillary column. The modulator section is coated externally with a thin electrically conductive film. An electrical current pulse applied to the thin film heats the modulator section and the stationary phase within it. When the stationary phase is heated and cooled, it releases and adsorbs substances into and from the flowing carrier gas. The signal form resembles a derivative of a chromatographic injection. Large-volume, continuously flowing or headspace samples can be accepted directly. The modulator is simple and effective and is used as both a trap and desorption device. Multiple modulation pulse signals applied during an extended sample introduction period result in a multiplex detector output signal, from which the chromatograms are recovered and computed by applying some fairly simple computational techniques such as cross-correlation. It is possible to determine volatiles in solid samples where the solid material is neither volatile nor soluble in a solvent. No sample pretreatment, preconcentration, extraction or distillation are required. Both the accuracy and precision achieved are fairly good.

1. Introduction

There are many techniques for analysing liquid and solid samples, one of the most attractive being gas chromatographic headspace analysis [1]. By using this method, information on volatiles present in samples can be obtained. When the samples are liquids, it is easy to reach a thermodynamic equilibrium between the volatiles to be determined and the samples. Also, it is easy to obtain quantitative results. However, when solid samples are to be analysed, it is difficult to reach thermodynamic equilibrium between volatiles and solid samples, and quantitative analysis is more difficult. In this case, liquid solvents are often used to extract the volatiles from the matrix, followed by their determination. To achieve complete extraction,

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0021-9673/95/$09.50
SSDI 0021-9673(94)00858-2

sometimes multiple extractions are needed, which, however, results in very dilute extracts that cannot be concentrated by evaporation because the volatiles are to be determined. Kolb and co-workers [2–4] used a method called discontinuous gas extraction or multiple headspace extraction to solve this problem. However, some disadvantages still exist, e.g., often an incorrect linear relationship is obtained for log (analyte concentration) vs. analysis number for repeated analyses of the same sample, and the method is time consuming. A dynamic headspace technique or gas–solid extraction was proposed as a solution to these problems [5]. Its main advantage is that no equilibrium between the gas phase and sample is needed, but the problem is that the volatiles are split away from splitter vent, although all of them can be released from the sample.

Recently, we have developed a new technique, multiplex gas chromatography (MGC) with thermal desorption modulation of a fused-silica capillary column [6]. We have reported on the utilization of MGC with rapid concentration to determine trace organics in aqueous samples at below the ppb (v/v) level [7].

In this paper, we describe the use of MGC with direct headspace sampling (DHS) to determine organics in solid samples. As an example, we determined nicotine in cigarettes by this technique. Chromatograms for various other samples have also been obtained. Previously used methods to determine nicotine in smoke involved steam extraction [8], acid–methanol extraction, extraction and subsequent titration [9], steam distillation [10,11], gas chromatographic determination [12] and spectrophotometric determination [13]. Most of the steps in these methods are time consuming and cause some loss of components of interest. In MGC analysis, only a small amount of sample is needed. Prior to analysis, no extra procedure is needed. By using DHS, a continuous gas sample stream can be obtained, which is required in MGC. A concentration pulse generated from modulators which is equivalent to a small-volume injection is of appropriate volume for the column and no extra interfaces are needed. Hence the drawbacks that parts of volatiles are split away or some components of interest are lost can be circumvented. Also, in MGC a series of concentration signals are generated resulting in enhancement of the signal-to-noise ratio due to the multiplex and throughput advantages.

2. Experimental

2.1. Apparatus

The experimental system, is shown in Fig. 1. The experiments were performed on a Model 3920 gas chromatograph (Perkin-Elmer) equipped with a flame ionization detector. The chromatograph was modified as previously reported for MGC [7]. A make-up gas stream was added to sweep the sample emerging from the column to the detector. The laboratory computer system and data acquisition interface between the computer and the chromatograph and the electronic circuitry have been described elsewhere [6].

In these experiments, the injector was modified to be used as a direct headspace sampler for GC. The analytical columns were a Supelcowax 10 fused-silica open-tubular column (25.0 m × 0.250 mm I.D., stationary phase thickness 0.25 μm), an SE-52 fused-silica open-tubular column (6.0 m × 0.250 mm I.D., stationary phase thickness 0.20 μm) and OV-1701 fused-silica open-tubular column (1.0 m × 0.050 mm I.D., stationary phase thickness 0.20 μm). The modulator, which was coated with electrically conductive paint, was 8.0 cm long and its resistance was 2.0 Ω. Its design, shown in Fig. 1B, has been described previously [6]. The modulator was situated outside the oven and kept at room temperature. The computer was used to control the modulator current from a 40 V d.c. power supply using an OPTO 22 (Huntington Beach, CA, USA) Model ODC 5P optically coupled switch. The duration of the current pulse was 120 ms. A 10-Ω resistor was connected in series with the modulator to limit the magnitude of the current through the modulator. In order to

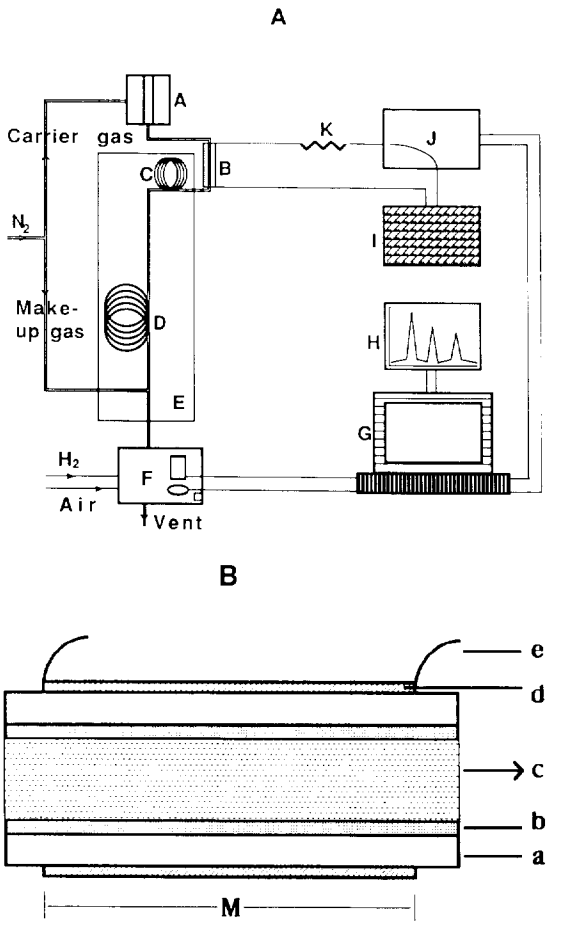

Fig. 1. (A) Schematic diagram of the main components of the multiplex gas chromatographic system. A = Sampler; B = modulator; C = retention gap; D = Supelcowax 10 analytical column; E = oven; F = detector; G = computer; H = plotter; I = power supply; J = electronic switch; K = resistor. (B) Design of thermal desorption modulator prepared on a fused silica open-tubular column. M = Modulator section; a = fused-silica column; b = stationary phase; c = gas stream flow; d = electrically conductive paint; e = electrical contacts.

eliminate peak broadening and peak distortion, a retention gap (an empty fused-silica column, 50 cm × 0.250 mm I.D.) was used ahead of the analytical column. On the other hand, there was no space between the oven and modulator port in order to eliminate peak broadening and to prevent larger molecules from being held in the insulation space.

2.2. Materials

Richland cigarettes (Brown and Williamson Tobacco) purchased from a supermarket were used as the main solid samples. Nicotine (reagent grade) was obtained from Fisher Scientific. The carrier gas was prepurified-grade nitrogen. Hydrogen was obtained from Air Products (Alltown, PA, USA). Soil was taken from the campus. Plastic wrappers for bread and plastic bags originated from a supermarket.

2.3. Procedures

The MGC conditions are given in the figure captions. HDS was carried out in the sampler modified from an injector as illustrated in Fig. 2. A glass tube (12 cm × 5.0 mm I.D.) was installed within the injector. Liquid samples could be placed in the bottom of capillary tubes, which were then inserted into the glass tube. Solid samples were placed in the middle of a smaller glass tube (open at both ends), which was then also inserted into the glass tube. A capped capillary tube or smaller tube containing a num-

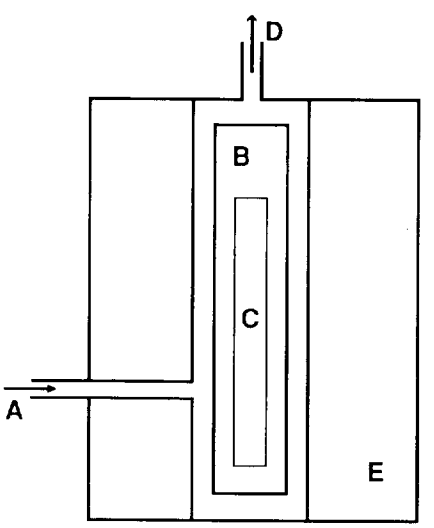

Fig. 2. Direct headspace sampler for MGC. A = Carrier gas inlet; B = glass tubing; C = capillary tube; D = to modulator; E = injector wall.

ber of samples was equilibrated in the sampler for about 5–10 min (it takes slightly longer for liquid samples), then its cap was removed, the capillary tube or the smaller glass tube was inserted and the whole sampler was quickly installed. Generally, the time depends on the state, the properties and the quality of the samples.

By varying the capillary diameter and length or sampler temperature, the sample evaporation rate was adjusted.

We employed the equation $S = x\rho\pi r^2/2L$ [14] to measure S, the diffusion rate of liquids (g/s). Of course, we should obtain x (a constant for the liquid at temperature T, cm/s) before S. In order to obtain x, a plot of L^2 vs. time was made, so a series of L values (depth of the liquid meniscus below the capillary mouth, cm) were measured in an oven with the same temperature as in the MGC sampler at different times. The results are given in Table 1. A plot of L^2 vs. time is shown in Fig. 3.

By MGC, a series of multiplex gas chromatograms of nicotine external standard were obtained. The peak area counts could be plotted against the corresponding concentrations of nicotine calculated from the above equation.

Cigarette samples were placed in the sampler, MGC was run and different chromatograms were obtained as different parts of the cigarettes were tested. The tests on unsmoked cigarettes were repeated at least five times.

After adding a series of nicotine standards to unsmoked cigarettes, MGC was run, giving chromatograms to identify and recover the nicotine.

Multiplex gas chromatograms of other solid samples were also obtained.

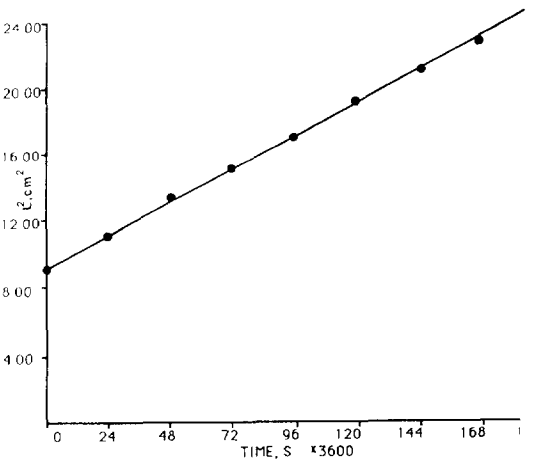

Fig. 3. Plot of L^2 versus time. L = Depth of the liquid meniscus below the capillary mouth; time = corresponding diffusion time of the liquid.

3. Results and discussion

3.1. Multiplex gas chromatograms, calibration, nicotine contents and accuracy

Fig. 4 shows a typical multiplex gas chromatograms obtained at various nicotine concentrations for capillary C in Table 2. The whole concentration series and corresponding peak areas are given in Table 2. In the chromatogram of a nicotine sample, only a single peak is present, although the average time between pulses, equivalent to repeated new injections, is 26 s (1792/69 + 0.120 = 26.09). A series of nicotine peaks would be expected with a distance of about 26 s. For conventional GC, the above conclusion can be drawn without question. However, in the MGC technique, chromatographic peaks from the modulation pulses are severely

Table 1
Diffusion time and corresponding depth of the nicotine meniscus below the capillary mouth (L)

Depth	Time (s × 3600)								
	0	24	49	72	96	120	144	168	192
L (cm)	2.99	3.38	3.69	3.95	4.18	4.42	4.62	4.79	4.95
L^2 (cm^2)	9.00	11.42	13.62	15.60	17.44	19.53	21.34	22.94	24.50

Temperature, 110°C; capillary I.D., 0.150 cm.

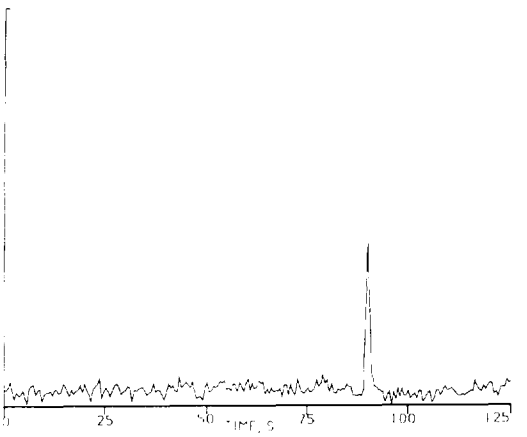

Fig. 4. Typical multiplex gas chromatogram for various nicotine concentrations using capillary C in Table 2. (C) $1.56 \cdot 10^{-6}$ g/ml from capillary of 5.33 cm × 0.150 cm I.D. Supelcowax 10 fused-silica column (25.0 m · 0.250 mm I.D.); stationary phase film thickness, 0.25 μm; modulator length, 8.0 cm; modulator resistance, 2.0 Ω; data acquisition rate, 2 Hz; modulator pulse duration, 0.120 s; modulation signal duration, 1792 data points (30.0 min); average time between pulses, (C) 1792/69 = 26.0 s; others (not shown), (A) 1792/63 = 28.4 s, (B) 1792/83 = 21.6 s, (D) 1792/70 = 25.6 s and (E) 1792/85 = 21.1 s (including a dead time of 4 s); carrier gas flow-rate, 6 ml/min; make-up gas flow-rate, 27 ml/min; sampler temperature, 110°C; column temperature, 220°C; detector temperature, 250°C.

overlapped at the detector, resulting in an output that is not directly interpretable, but a greater information content can be recovered with computer and presented in the form of a chromatogram by a computational technique such as cross-correlation or deconvolution. The computation required to recover the chromatogram is a very effective signal-averaging procedure that compensates for the decrease in sensitivity and dynamic range due to the small volume of each concentration pulse.

Fig. 5 shows multiplex gas chromatograms of different parts of cigarettes. Their nicotine contents are given in Table 3. From these, several attributes of nicotine contents in cigarettes are clear. First, by comparing the retention times of samples with that of the nicotine standard and by adding nicotine as an internal standard, one can identify the nicotine in the cigarettes (see Figs. 5E and 4C). Second, before smoking, the cigarette filter tip contains no nicotine, but after smoking, it contains a fairly high concentration of nicotine, i.e., ca. $4.5 \cdot 10^{-7}$ g/ml in a 0.0204-g cigarette filter tip. It can be concluded that cigarette filter tips play a good role of adsorbing nicotine. Third, in the part of a cigarette remaining after smoking, there is a high concentration of nicotine, showing that it also plays a role in adsorbing nicotine in cigarettes. Concerning the nicotine content, as the total mass of one cigarette is 0.7297 g (0.760 g of smoke and 0.1694 g of filter tip), the total amount of nicotine in an unsmoked cigarette is $2.57 \cdot 10^{-5}$ g/ml [$(0.7603/0.0204 \cdot 6.90 \cdot 10^{-7}$ g/ml] and the total amount of nicotine in a filter tip is $3.74 \cdot 10^{-6}$ g/ml [$(0.1694/0.0204 \cdot 4.50 \cdot 10^{-7}$ g/ml)]. It is more convenient to use this kind of concentration for monitoring the volatiles from solid samples and to prevent workers from being exposed to harmful chemicals. We have already used MGC and related techniques to determine trace organics in aqueous samples, using the quantitative concentration in ppb (v/v) [7].

Table 2
Peak areas obtained for various nicotine concentrations from different capillaries

Capillary I.D. (cm)	Length (cm)	Nicotine concentration		Peak area (cm^2)
		g/s	g/ml[a]	
(A) 0.053	2.00	$5.18 \cdot 10^{-8}$	$5.18 \cdot 10^{-7}$	44.7
(B) 0.150	8.00	$1.04 \cdot 10^{-7}$	$1.04 \cdot 10^{-6}$	75.0
(C) 0.150	5.33	$1.56 \cdot 10^{-7}$	$1.56 \cdot 10^{-6}$	111.2
(D) 0.150	4.00	$2.08 \cdot 10^{-7}$	$2.08 \cdot 10^{-6}$	149.5
(E) 0.150	3.20	$2.60 \cdot 10^{-7}$	$2.60 \cdot 10^{-6}$	203.2

[a] Carrier gas flow-rate 6.0 ml/min.

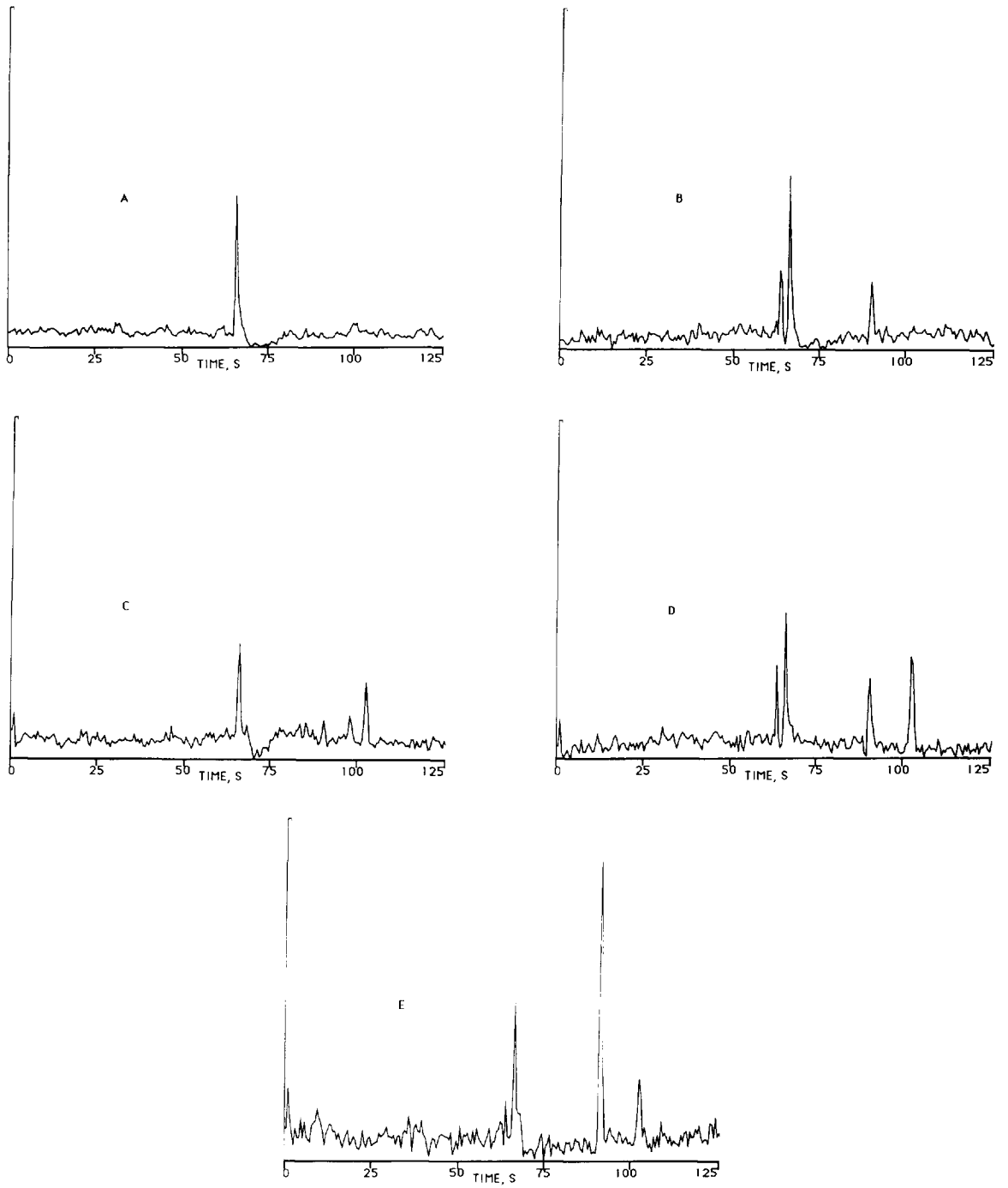

Fig. 5. Multiplex gas chromatograms of different parts of cigarettes. (A) Cigarette filter tip before smoking; (B) cigarette filter tip after smoking; (C) cigarette remaining after smoking; (D) unsmoked cigarette; (E) unsmoked cigarette with nicotine added. Average time between pulses; (A) 1792/80 = 22.4 s; (B) 1792/60 = 29.9 s; (C) 1792/67 = 26.7 s; (D) 1792/91 = 19.7 s; (E) 1792/78 = 23.0 s. Analytical conditions as those in Fig. 4.

Table 3
Nicotine contents of different parts of cigarettes

Part of cigarette	Mass (g)	Peak area (cm^2)	Nicotine concentration (g/ml)
Cigarette filter tip before smoking	0.0204	0	0
Cigarette filter tip after smoking	0.0204	32.3	$4.50 \cdot 10^{-7}$
Cigarette remainder after smoking	0.0204	14.1	$2.00 \cdot 10^{-7}$
Unsmoked cigarette	0.0204	50.3	$6.90 \cdot 10^{-7}$

The recovery of added nicotine was constant to within ±3%, indicating good accuracy (Table 4).

3.2. Reproducibility of nicotine determination by MGC

Table 5 shows that the relative standard deviation among five samples of the same cigarette was less than 3%. This indicates that the precision is comparable to that of other GC techniques.

3.3. Detection limit and sensitivity

By varying the I.D. and the length of capillaries and measuring the peak height, we obtained the detection limit, which is about $1.44 \cdot 10^{-13}$ g/ml (it was obtained using an 8.0 cm × 0.005 mm I.D. column as a capillary tube) and the sensitivity is $3.3 \cdot 10^{-2}$ A s/pulse/g). The detection limit is about two orders of magnitude below the concentration detection limit for a conventional single-injection determination using the same detector and column. This is a direct result of the long modulation signal.

Table 4
Recovery of nicotine added to unsmoked cigarettes

Parameter	First time		Second time		Third time		Fourth time	
	Peak area (mm^2)	Concentration (g/ml)	Peak area (mm^2)	Concentration (g/ml)	Peak area (mm^2)	Concentration (g/ml)	Peak area (mm^2)	Concentration (g/ml)
Unsmoked cigarette	50.3	$6.90 \cdot 10^{-7}$		$6.90 \cdot 10^{-7}$		$6.90 \cdot 10^{-7}$		$6.90 \cdot 10^{-7}$
Nicotine added		$2.08 \cdot 10^{-6}$		$1.04 \cdot 10^{-6}$		$5.18 \cdot 10^{-7}$		$2.59 \cdot 10^{-7}$
Total nicotine found	211.0	$27.1 \cdot 10^{-7}$	134	$17.2 \cdot 10^{-7}$	75.2	$12.2 \cdot 10^{-7}$	70.4	$9.57 \cdot 10^{-7}$
Nicotine recovered		$20.2 \cdot 10^{-7}$		$10.3 \cdot 10^{-7}$		$5.30 \cdot 10^{-7}$		$2.67 \cdot 10^{-7}$
Recovery (%)[a]		97		99		102		103

[a] Range ±3%.

Table 5
Reproducibility of nicotine determination by MGC

Mass of unsmoked cigarette (g)	Peak area (mm^2)	Nicotine concentration (g/ml)	Mean	S.D.	R.S.D. (%)
0.0204	50.3	$6.90 \cdot 10^{-7}$	$6.90 \cdot 10^{-7}$	$0.172 \cdot 10^{-7}$	2.5
0.0204	52.0	$7.11 \cdot 10^{-7}$			
0.0204	49.8	$6.77 \cdot 10^{-7}$			
0.0204	48.8	$6.70 \cdot 10^{-7}$			
0.0204	51.3	$7.04 \cdot 10^{-7}$			

The desorption modulator is a major component of the chromatographic instrumentation on a par with the detector and column. The modulation acts like an automatic and highly reproducible small-volume injection for a continuously flowing sample stream. A thermal desorption modulator has been used in high-speed GC analysis for sample preconcentration and introduction to monitor process streams [15] and in capillary GC for direct headspace sampling to determine the activity coefficients of binary liquids [16]. The multiplex and throughout advantages which have been exploited so successfully in the various Fourier and Hadamard transform spectroscopic methods apply also to MGC. A multiplex advantage exists because each output signal data point contains information encoded from the entire chromatogram; a throughout advantage exists because more sample is passed through the column to the detector per unit time than for batch separation chromatography. The output signal amplitude is directly proportional to the rate of sample flow through the chromatographic system while the amplitude of many noise sources remains constant.

The MGC peaks are very sharp because this modulation technique generates a very sharp injection and is limited by band broadening in the column usually caused by the dead volume, which is often large when a conventional sampling device is used.

The baseline noise is mainly correlation noise caused by approximations in the calculation, and could be eliminated by using a more sophisticated computational procedure. However, the "noise" does not limit detection because it is not random, while a modulation signal is a random signal which is generated by using a pseudo-random number algorithm [17].

3.4. Applications of MGC

The use of MGC in the analysis of real solid samples is reported here for the first time. Previously, we have reported the use of MGC to determine methane in ambient air [18] and trace organics in aqueous samples [7]. MGC with DHS is applicable to the analysis of soil, plastic wrappers for bread, plastic bags, etc. Typical multiplex gas chromatograms are shown in Fig. 6.

4. Conclusions

The use of MGC with DHS to determine nicotine in cigarettes was reported and some chromatograms of solid samples were presented. This technique has the following advantages: simple apparatus and sample introduction, no need for sample pretreatment, preconcentration, extraction or distillation, fairly good accuracy and precision, low detection limit and high sensitivity. It should be easy to carry out automatic analysis if the further modifications of the sampler are made, because the multiple pulses and data acquisition have already been computerized. Further work will be devoted to the

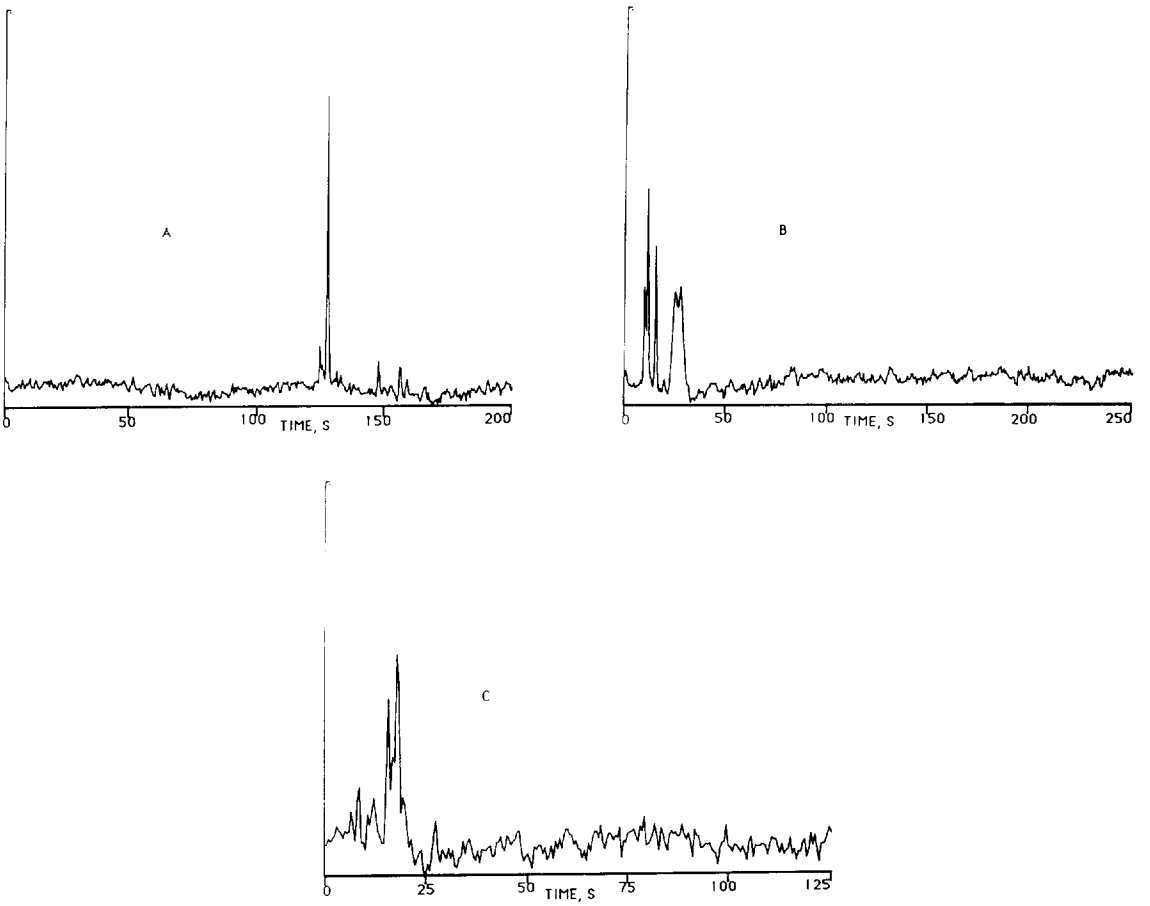

Fig. 6. Multiplex gas chromatograms of other solid samples. (A) Soil. Analytical column as in Fig. 4. Modulation signal duration, 7168 data points; average time between pulses, 7168/267 = 26.8 s; sampler temperature, 120°C; column temperature, 220°C; other conditions as in Fig. 4. (B) Plastic bag. SE-52 fused-silica column (6.0 m × 0.250 mm I.D.); stationary phase film thickness, 0.20 μm; modulator length, 8.0 cm; modulator resistance, 1.8 Ω; average time between pulses, 1792/66 = 27.2 s; carrier gas flow-rate, 3.0 ml/min; make-up gas flow-rate, 20.0 ml/min; sampler temperature, 100°C; column temperature, 120°C; other conditions as in Fig. 4. (C) Plastic wrapper for bread. OV-1701 fused-silica column (1.0 m × 0.050 mm I.D.); stationary phase film thickness, 0.20 μm; modulator length, 5.0 cm; modulator resistance, 1.5 Ω; modulation signal duration, 7168 data points; average time between pulses, 7168/253 = 28.3 s; carrier gas flow-rate, 0.14 ml/min; make-up gas flow-rate, 18.0 ml/min; data acquisition rate, 4 Hz; sampler temperature, 100°C; column temperature, 120°C; other conditions as in Fig. 4.

analysis of other solid samples and real environmental samples, with emphasis on quantitative analysis.

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