Determination of Airborne Nicotine by Automatic Two-Stage Thermal Desorption Gas Chromatography

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An automated two-stage thermal desorption technique has been developed for the determination of airborne nicotine. Pumped samples are collected on adsorbent tubes and analysed by capillary gas chromatography using flame ionisation detection. The preconcentration effect of the adsorbent compared to solvent trapping or solvent desorption methods permits shorter sampling times and precludes the need for a selective detector.

By use of a basic program all exposure volumes and component details are entered into a method run table and after analysis exposure levels are automatically calculated and printed in report form by the data handling system. Consequently a large throughput of samples may be analysed automatically and efficiently with minimal analyst involvement or sample preparation.

The technique described was originally developed to sample airborne nicotine in workplace environments where tobacco is processed. Comparison between this technique and the standard NIOSH method for airborne nicotine is discussed.

KEY WORDS: Airborne nicotine, automated two-stage thermal desorption technique, capillary gas chromatography, flame ionisation detection, nicotine.

INTRODUCTION

In recent years interest in the quality of indoor air we breathe has grown, with a subsequent increased commitment to monitoring a wide range of chemical species at work.

During the processing of tobacco the application of heat and moisture are necessary to control the quality of the finished product and may release volatiles such as nicotine, which is a major constituent virtually unique to tobacco, into the workplace environment.

The Health and Safety Executive (HSE) publish a series of guidelines[1] which list occupational exposure levels for a range of substances in an attempt to control emissions into the workplace. Two types of exposure limits are listed, i.e., a long-term exposure level (LTEL) and a short term exposure level (STEL). Both exposure levels are expressed as time weighted average (TWA) concentrations which are simply airborne concentrations over a specified period of time (i.e., LTEL = 8 hrs TWA; STEL = 10 mins TWA).

The occupational exposure levels recommended by the HSE[1] for nicotine are: an LTEL of $0.5\,mg\,m^{-3}$ and an STEL of $1.5\,mg\,m^{-3}$.

The collection and quantification of airborne nicotine has involved a wide range of analytical techniques including trapping in various media such as acid, solvent, water, impregnated filters and adsorption techniques with subsequent gas chromatography.

Adsorption techniques evaluated included the method adopted by the National Institute for Occupational Safety and Health (NIOSH)[2] which requires solvent desorption and specific detection, and several thermal desorption methods similar to that described by Muramatsu.[3]

However, all of the methods evaluated require a high degree of analyst involvement both in terms of sampling and sample preparation and consequently are difficult to automate.

A commercially available automated thermal desorption system was purchased and all further development carried out using the Perkin Elmer ATD 50 Automated Thermal Desorption System. This system, by its design incorporating 2-stage thermal desorption, overcame most of the problems found with other methods and allows the use of short term sampling times and portable sampling equipment.

Preconcentration of the sample on the adsorbent eliminated the need for a nitrogen/phosphorus detector, all analyses were conseq-

uently performed using flame ionisation detection with an external standard.

This paper describes a reliable and efficient method for airborne nicotine which involves readily portable sampling equipment.

EXPERIMENTAL

A Perkin Elmer Sigma 115 Gas Chromatography System incorporating a Sigma 1 Analyser fitted with a flame ionisation detector and a Sigma 15 Data Station with integral tape drive and basic programming facilities was used. This system was interfaced to a Perkin Elmer ATD50, configured for capillary chromatography and incorporating BCD readout of sample tube identity and communication commands, i.e., Level 3 Communications and Control. The complete system was controlled by means of an "ATD" Program (on tape cassette kindly supplied by Perkin Elmer Ltd.).

As an alternative to the chromatography system described, this technique was also applicable using an ATD50 interfaced to a Perkin Elmer 8320 Gas Chromatograph equipped with Re-integration, BCD and Automation Control Boards. By means of the Automation Control facility and suitable quantification scaling factors, this system will express tube identity and results in the form required. The ATD50 pneumatics are illustrated in Figure 1.

A modification was made to the transfer line interfacing the ATD50 to the capillary column in an attempt to minimise leaks and enhance resolution. The fused silica transfer line from the ATD50 cold trap connected to the column end by means of a zero dead volume (ZDV) union was removed from the heated transfer line (Figure 1), and the analytical column fed directly into the cold trap. The ATD50 cold trap was packed with 10/12 mg Tenax TA (60–80 mesh), retained by silanised glass wool plugs, and the analytical column used was SE54 fused silica (25 m × 0.22 mm ID, film thickness 0.25 micron) or equivalent.

An outlet splitter kit (Perkin Elmer No. L407-0042) was fitted to the ATD50 enabling sample splitting prior to the capillary column. This was later replaced with a Multiple Splitter accessory (L407-0043).

Standard ATD50 tubes were packed with 200 mg Tenax TA (60–
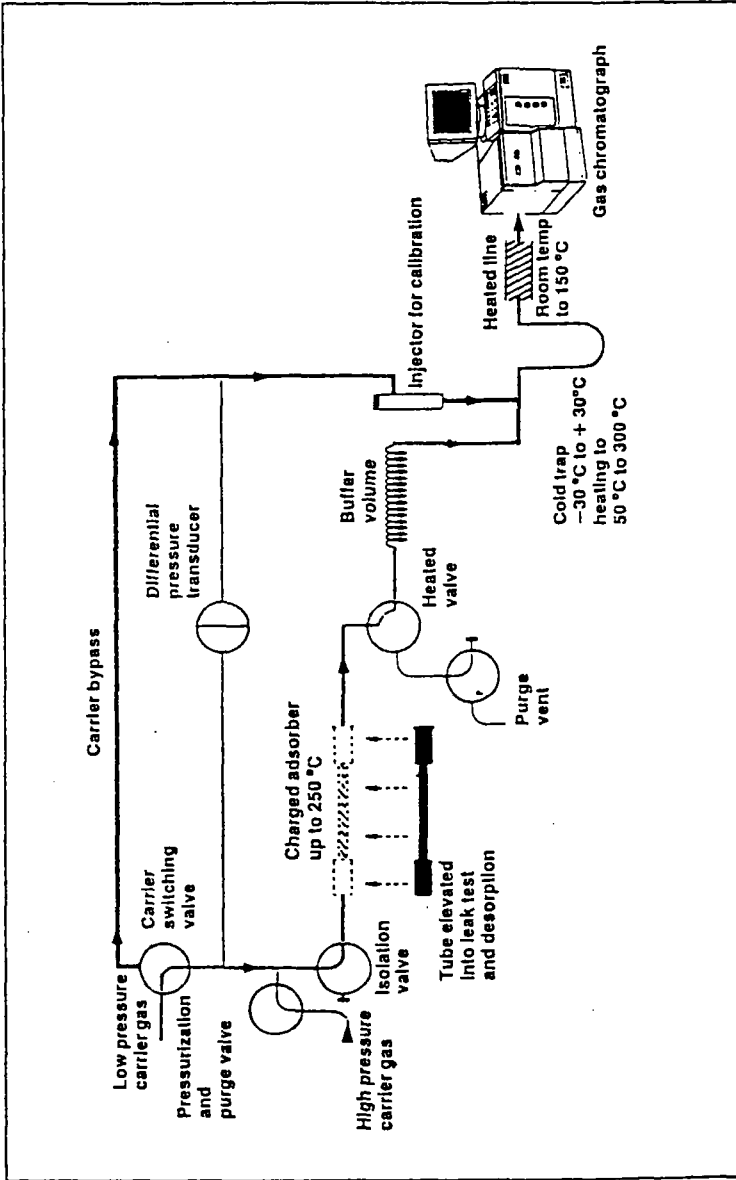
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Figure 1 ATD 50 pneumatics system.

80 mesh) to a travel of 40 mm on the tube loading rig. Tenax was conditioned for 24 hours at 300 °C in a stream of helium and stored in a sealed vessel in a dessicator. Sample tubes are schematically illustrated (Figure 2).

Only two of the six principal modes of ATD50 operation are relevant to this method:

Mode 2

Sample tubes undergo an automatic two-stage desorption which includes pressure and leak tests on the complete ATD50 system. If a sample tube fails either of these tests it is returned to the turntable for analysis later. The sample is desorbed from the tube for a preset time into the cold trap where it is retained. Upon completion of this primary desorption stage the cold trap is flash heated to a predetermined cold trap high temperature, the vaporised sample entering the analytical column, i.e., secondary desorption.

Mode 6

In this mode calibration standards may be injected directly into the cold trap by means of the ATD50 injection port. The injected standard undergoes a single stage desorption from the cold trap onto the analytical column.

ATD50 Conditions

Desorption time	15 minutes
Desorption temperature	250 °C
Split ratio (single splitter)	25:1
Box temperature	150 °C
Cold trap low temperature	−30 °C
Cold trap high temperature	300 °C

GC Conditions

Oven temperature	150 °C
Detector temperature	250 °C
Column flow rate	$1 \, cm^3 \, min^{-1}$
Carrier gas	Helium
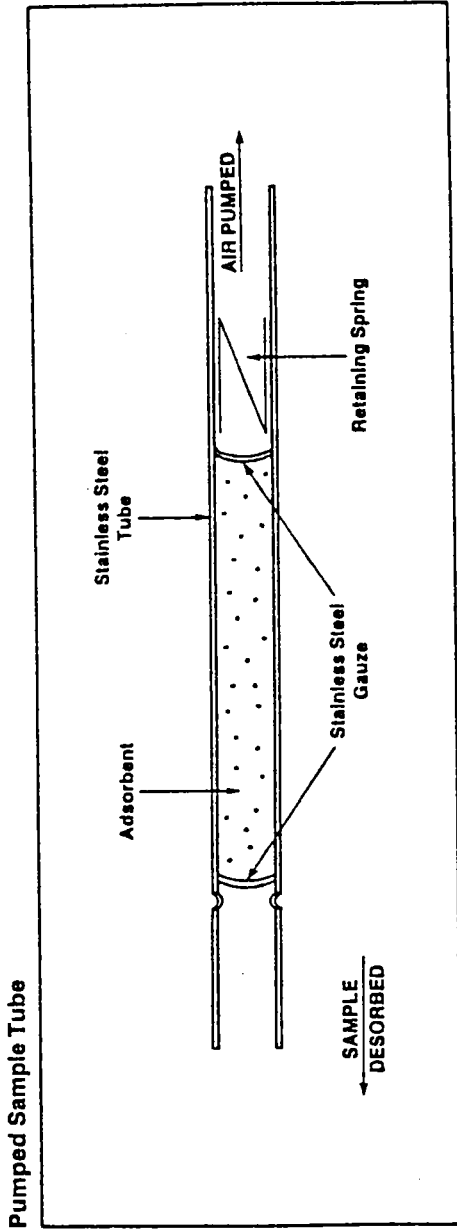
Pumped Sample Tube

Figure 2 Pumped sample tube.

All standards were injected using a plunger in needle type syringe—
1 ul SGE 1B7.

Reagents

Tenax TA (60–80 mesh) supplied by Chrompack (UK) Ltd.

Nicotine supplied by Sigma Chemical Co. ($>98\%$ pure). Dichloro-
methane of distilled grade.

Calibration

1 ul of 0.1% w/v nicotine in dichloromethane was injected, giving a
standard equivalent to the LTEL ($500\,\text{ug m}^{-3}$) for nicotine assuming
2 litres of air were sampled.

The linearity of the technique was established by injecting a range
of standard nicotine solutions equivalent to 5–$500\,\text{ug m}^{-3}$ into the
injection port of the ATD50 and analysing using Mode 6 desorption.

Sampling

Initially MDA Accuhaler 808 Sampling Pumps were used for
sampling in workplace environments. These were later superseded by
Dupont Alpha Air Samplers (programmable) and Dupont S200
pumps. All Dupont pumps were supplied by Shaw City. For the
purposes of sampling workplace environments requiring static
samples the Alpha Air Samplers allowed a rapid and controllable
means of collecting nicotine on the sample tubes. Samples were
collected at a flow rate of $100\,\text{cm}^3\,\text{min}^{-1}$ for 20 minutes. Immediately
upon completion of sampling, the tubes were sealed with the end
caps provided and returned to the laboratory for analysis.

Analysis

The ATD50/Chromatography system under the control of the basic
program allows the operator to enter all relevant component details
including Component Name, Molecular Weight, Action Level (i.e.,
50% of LTEL), format of results (ppm or mg m^{-3}) and form of
report.

Tube identity and exposure volumes are entered for each sample

tube. All calculations and reporting of results in tabular form is performed automatically by the Data Station.

Consequently Level 3 Communications and Control combined with Sigma BASIC allows routine analyses to be run automatically and unattended.

Validation

A validation study was completed before this method was accepted as routine. The trapping efficiency and breakthrough volume of Tenax TA sample tubes was determined by collecting simulated atmospheres of nicotine on sample tubes and back-up sample tubes connected in series using flow rates up to 10 times the rate recommended for field trials (i.e., $100 \, cm^3 \, min^{-1}$). Less than 1% of the total nicotine introduced was found in the back-up tube. Application of methods discussed by Brown and Purnell,[5] Clark et al.[6] indicated that the retention volume for nicotine was well in excess of 100 litres of sampled air at levels greater than LTEL.

An optimum desorption time of 15 minutes, using Tenax TA was established, which also ensured conditioned tubes prior to re-use. A desorption efficiency of 99% for nicotine was obtained by repeat desorptions of tubes ($n = 15$) containing a mean of 1600 ng nicotine per tube. Repeat desorption of those tubes indicated a mean of 19.5 ng nicotine remaining on the tubes after one desorption.

Sample tubes containing adsorbed nicotine at levels corresponding to LTEL/STEL were stored and monitored at intervals over a 2 week period. No significant change in the nicotine level was observed and artefact formation was not apparent. Zlatkis et al.,[7] discuss similar findings.

A reproducibility study of the ATD50 technique was performed in conjunction with a similar exercise using the NIOSH method. Levels equivalent to the LTEL and STEL for nicotine, down to the relevant detection limits for each method were studied. Results are shown in Table 1. The reproducibility of the ATD50 technique was superior to that obtained from the NIOSH method.

A detection limit of $2.5 \, ug \, m^{-3}$ using flame ionisation detection operating in the split mode was obtained for the thermal desorption method compared to a detection limit of $20 \, ug \, m^{-3}$ for the NIOSH method using nitrogen/phosphorus detection operating in the split

Table 1 Reproducibility of NIOSH method versus thermal desorption method

Method	NIOSH		Thermal desorption		
Equivalent volume of sample					
(litres)	65	65	2	2	2
Level on tube	89 ug	28.5 ug	1707 ng	1007 ng	220.3 ng
SD	20.33	22.5	97.21	100.77	32.58
CL	14.53	5.90	45.64	47.01	15.29
95% CL	16.32	13.02	2.67	4.67	6.94
Equivalent air conc" ug m^{-3}	1369	347	854	503	110

(Mean of 20 results for both methods).

mode. Jenkins et al.[8] claim a detection limit of 0.1 ug m^{-3} from a thermal desorption technique using nitrogen/phosphorus detection, however, an internal standard is required. The increased sensitivity of the ATD50 technique is attributable to the preconcentration effect of the adsorbent tube, the contents of which are injected into the GC system. A solvent volume of 1 cm^3 is required for desorption of NIOSH tubes thus greatly diluting the sample. Nominally 1 ul is injected, an effective dilution of 1000.

To complete the validation study, a reproducible means of introducing a controlled atmosphere of nicotine onto sample tubes was required and a Dynamic Standards Generator, built in-house, was developed. The flow diagram is shown in Figure 3. A diffusive cell system, based on a theory formulated by Altschuller and Cohen,[4] was adopted. Large volumes with lower surface losses than static systems are produced in this form of dynamic system. Consequently, where higher boiling species such as nicotine are involved, surface adsorption is minimised as an equilibrium between the walls of the system and the flowing gas stream is achieved.

RESULTS AND DISCUSSION

The method described has been used extensively for several years in tobacco factory locations to monitor employee exposure to airborne nicotine which may be released from tobacco processing into the workplace environment.

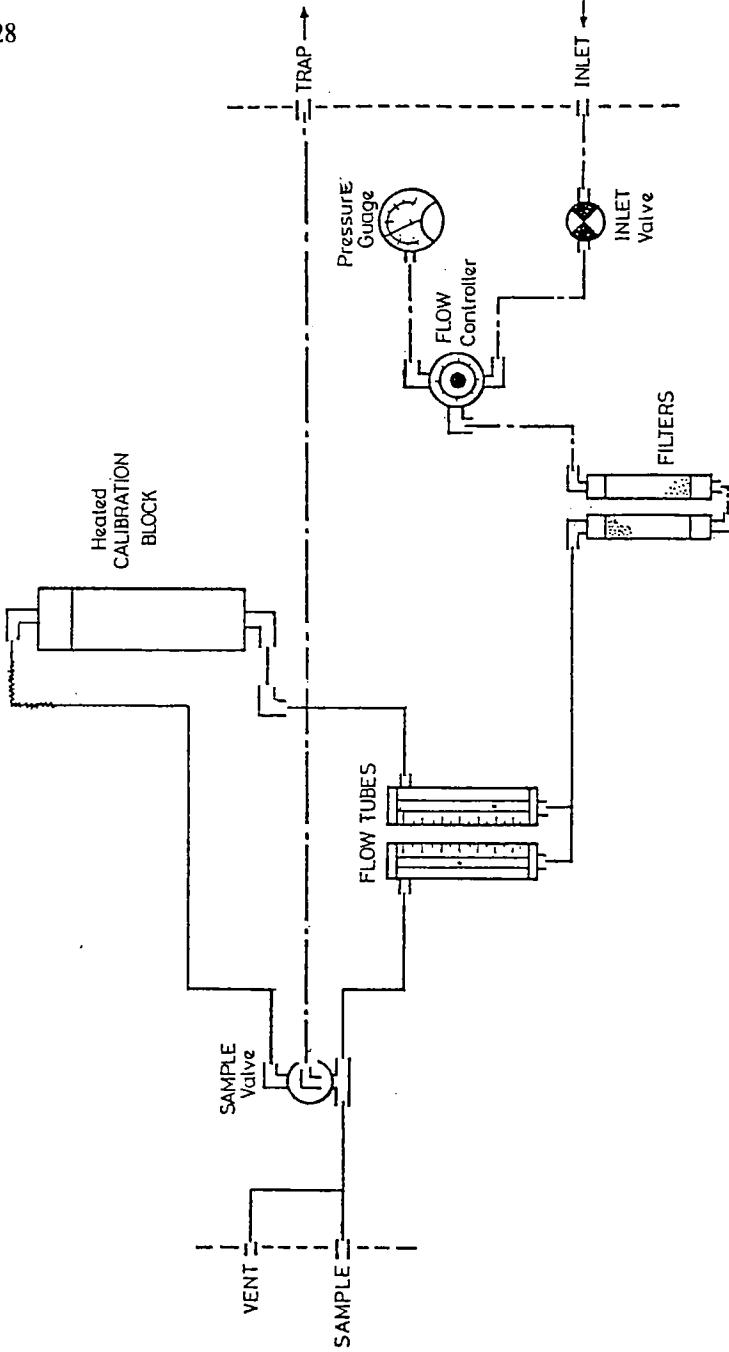A typical ambient air chromatogram showing nicotine present in a

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Figure 3 Dynamic standards generation system.

sample collected in an area where tobacco is continually being processed is shown in Figure 4(b). A standard injection equivalent to the LTEL of nicotine is shown in Figure 4(a) (assuming an exposure volume of 2 litres).

Nicotine levels in a tobacco processing room are shown in Table 2. The levels obtained (mean $= 39\,ug\,m^{-3}$) are considerably less than the occupational exposure levels recommended by the Health and Safety Executive[1] (LTEL $= 500\,ug\,m^{-3}$). One problem encountered with this technique in the early stages of method development was that low recoveries were obtained for nicotine desorbed from tubes compared to nicotine injected directly into the cold trap.

Initially these low recoveries were attributed to two possible effects, i.e., adsorption of nicotine on the $1/16''$ stainless steel tubing between the desorption oven (i.e., tube) and the cold trap (Figure 1); or the transfer line and box pneumatics temperature (i.e., heated valve, buffer volume etc.) being insufficiently high (150 °C max).

Similar effects have been discussed previously by Alder et al.[9] who encountered memory effects caused by the temperature of the injection port, buffer volume and transfer line.

In our instance it was felt that nicotine was adsorbing on the pneumatics of the ATD50 prior to the cold trap during primary desorption, and that the buffer volume, required for single stage desorption of tubes, was responsible. Alder et al.[9] suggested that before this technique could be applied to the analysis of relatively involatile compounds, some modification of the equipment was required.

Our system was modified by replacing the outlet splitter with a Multiple Splitter accessory (Perkin Elmer L407-0043) which was required for ATD50 applications other than nicotine monitoring.

Installation of this accessory completely eliminates the buffer volume, consequently reducing the problems of adsorption within the ATD50 pneumatics to an acceptable level, and at the same time allowing a more flexible ATD50 system.

Potentially this method may be applied to the determination of nicotine levels in air containing environmental tobacco smoke (ETS).

As a flame ionisation detector rather than a selective detector is used for analysis potential interferences from other organic species which may co-elute with nicotine were studied by combination of thermal desorption with mass spectrometry. No obvious inter-
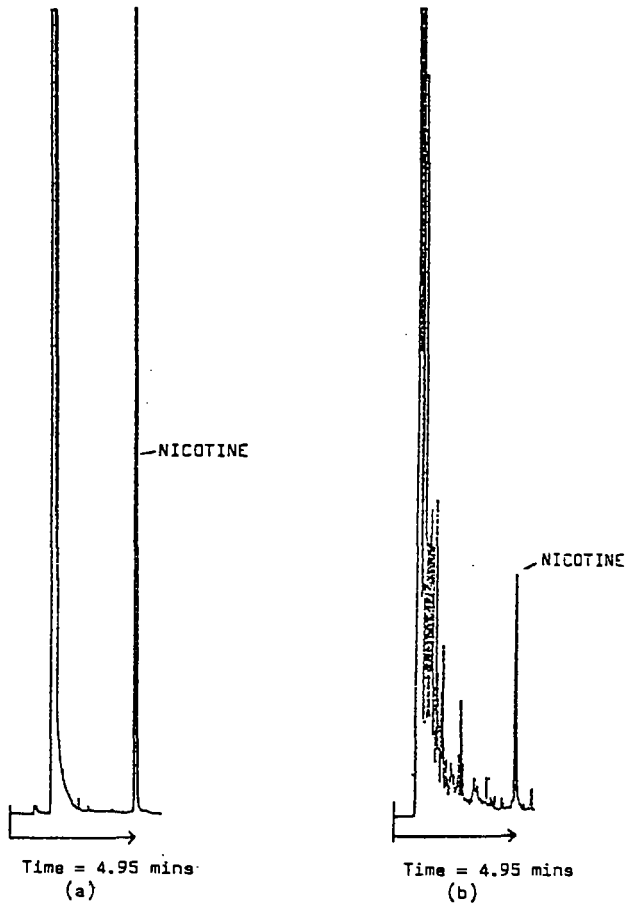
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Time = 4.95 mins
(a)

Time = 4.95 mins
(b)

Figure 4 (a) Standard nicotine injection; (b) Airborne nicotine from tobacco processing plant.

ferences were apparent in samples collected in factory atmospheres and the presence of nicotine was confirmed.

CONCLUSION

A rapid routine method for the determination of airborne nicotine in the workplace has been developed. The method is applicable to the

Table 2 Levels of airborne nicotine in tobacco processing room

Location site	$ug\,m^{-3}$ of airborne nicotine
1	31
2	38
3	30
4	31
5	50
6	48
7	41
8	41
9	26
10	31
11	40
12	51
13	47
14	40
15	11
16	81
17	50
18	15
19	33

Mean = 39

estimation of nicotine in other environments and should lend itself by the introduction of nitrogen selective or mass selective detectors to use in the diffused or passive mode of sampling. This mode of sampling should increase sample throughput further and eliminate the need for expensive sampling pumps.

Samples collected in tobacco factory atmospheres indicate the low level of nicotine, relative to the recommended occupational exposure levels, to which factory workers are exposed.

Acknowledgements

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