

# Instrumentation

## Development of a Curie-Point Headspace Sampler for Capillary Gas Chromatography

Naoki Oguri' and Akira Onishi

Japan Analytical Industry Co. Ltd, Musashi, Mizuho, Nishitama, Tokyo 190-12, Japan

Toshihiko Hanai

Int. Inst. Technol Anal., Health Res. Fond Inst Pasteur de Kyoto 5F, Sakyo-ku, Kyoto 606, Japan

### 1 Introduction

Because of Its Separating Power. Capillary gas Chromatography has been used in many different fields; to a large extent. However, the success of the technique is dependent on the method used for sample introduction. Examples of on-line sampling methods include purge and trap sampling for the analysis of volatile compounds in water [1-3], headspace sampling for volatile compounds in solids [4-6], and pyrolyzers for polymer analysis, etc [7-10]. The disadvantage of such techniques is either the requirement to exchange the sample introduction system whenever the type of sample changes, or the need to dedicate gas Chromatographs to specific applications: if a gas Chromatographic system is to be used for multipurpose analysis, several sample introduction techniques need to be integrated into one system

### 2 Experimental

The Model JHS-100 injection system from

Japan Analytical Industry Co Ltd (Tokyo,

Key Words:

Capillary gas chromatography

Multipurpose sample injector

Curie-point desorption

Curie-point pyrolyzer

Summary

A Curie-point headspace sampler (CPHS) equipped with a purge and trap sampler has been developed for use with capillary gas chromatography. The new system can handle a variety of samples, including gases, liquids, and solids, and can also be used as a pyrolyzer.

Japan), shown schematically in Figure 1, comprises, essentially, a Sample vessel, a valve, and an adsorption tube. The sample vessels employed for analysis of different types of sample (e.g. gas, liquid, paste and solid) are illustrated in Figure 2. Following introduction of the sample into a suitable vessel the analytes are extracted by purging with helium at an appropriate temperature and pass through an 8-port

valve (Figure 3A) into the adsorption tube which is cryogenically cooled with liquid nitrogen. Here they become adsorbed on the glass wool, Tenax or other material used to pack the tube. The 8-port valve is then switched to the defrost position (Figure 3B) and the adsorption tube warmed to 30°C (in order to obtain symmetrical gas chromatographic peaks after desorption). When the adsorption tube has reached room temperature the 8-port valve is automatically switched to the analytes position (Figure 3C) and the analytes desorbed by Curie-point heating and transferred on to the capillary column. The sample vessel can be heated as high as 350 °C for the analysis of samples such as heat resistant polymers.

### 3 Results and Discussion

#### 3.1 Analysis of Polycarbonate Resin

111 mg of polycarbonate resin were measured into the sampling vessel used for solids and heated to 250 °C. After passage through the valve the extracted analytes were adsorbed on glass wool cooled to -40 °C with liquid nitrogen. Following Curie-point heating the compounds desorbed were analyzed by capillary GC-MS, the chromatograms obtained is illustrated in Figure 4. The volatile components of the resin were identified as trichloromethane, Phenol, dichlorobenzene, -capro-

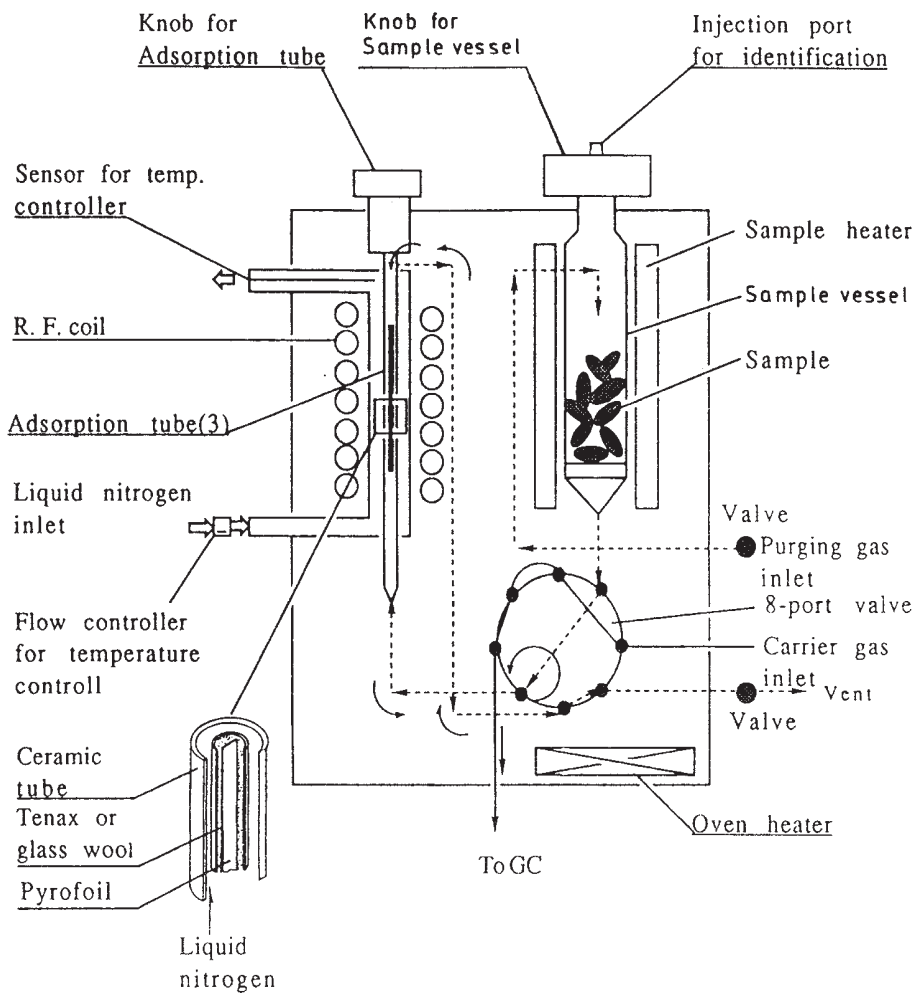


Figure 1

Schematic diagram of Curie-point headspace sampler. The sample vessel volume can be 1 or 10 ml. The 8-port valve is switched automatically to the purge and trap, defrost, or analysis positions. Maximum oven temperature is 200 °C. 20 Kinds of Pyrofoil® can be obtained, providing desorption temperatures between 160 and 1040 °C. The adsorption tube may be cooled cryogenically with liquid nitrogen down to -160 °C.

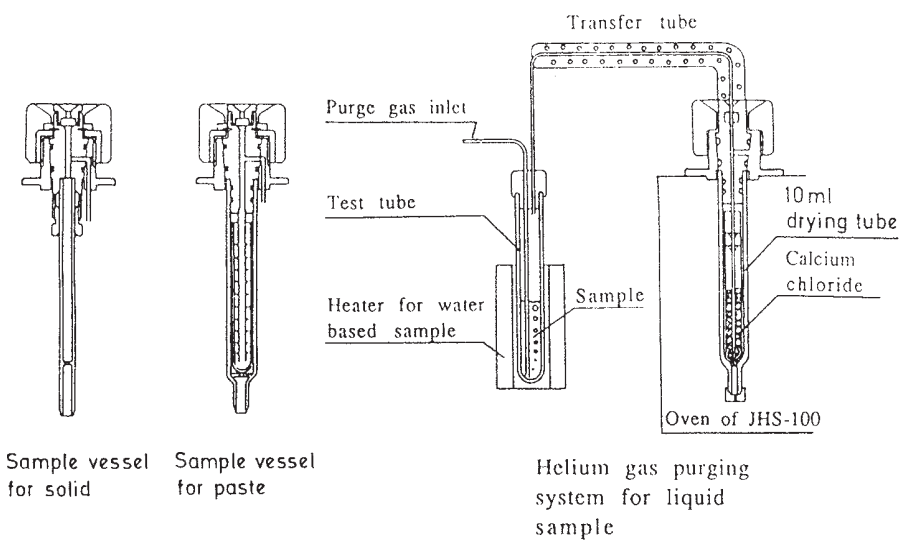
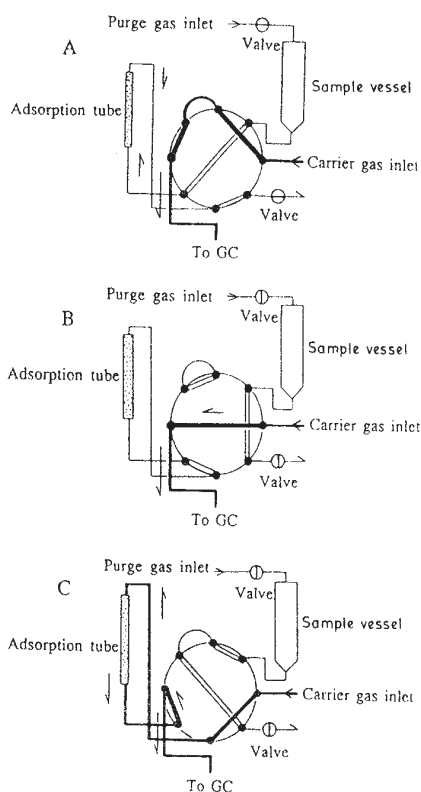


Figure 2

Vessels used for different types of sample.



**Figure 3**  
Operational positions of the 8-port valve:  
A) purge and trap; B) defrost; C) analysis

lactam, lindane, dimethylhexanol, and dioctyl phthalate.

### 3.2 Analysis of Fermented Soy Bean Paste

50 mg of paste were measured into the sampling vessel used for paste and heated to 80 °C. The compounds extracted were adsorbed on Tenax® at -40 °C and again desorbed by Curie-point heating before analysis by capillary GC-MS. The chromatogram obtained is illustrated in **Figure 5**: the flavor components identified were 2-propanol, cumene, diphenylhydroquinone, and N-ethyl-N-phenylbenzenemethanamine.

### 3.3 Analysis of Musty Substances in Water

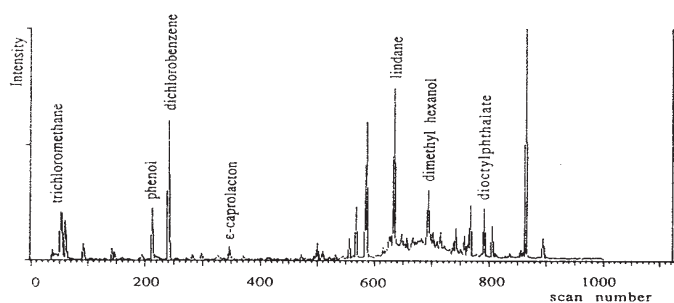
A glass bottle with helium gas purging system was connected to a sample vessel packed with calcium chloride as in Figure 2: in this arrangement the vessel is being used to trap moisture. Compounds purged from the water were adsorbed on cryogenically cooled Tenax®, desorbed by Curie-point heating, and analyzed by capillary GC-MS. A typical chromatogram is illustrated in **Figure 6**. The substances responsible for the musty odor of the water were identified as 2-methylisoborneol and geosmin, both present at the 1 ppb level. The mass spectra of the compounds are also presented in Figure 6

### 3.4 Analysis of ABS Resin by Curie-Point Headspace GC and Pyrolysis GC

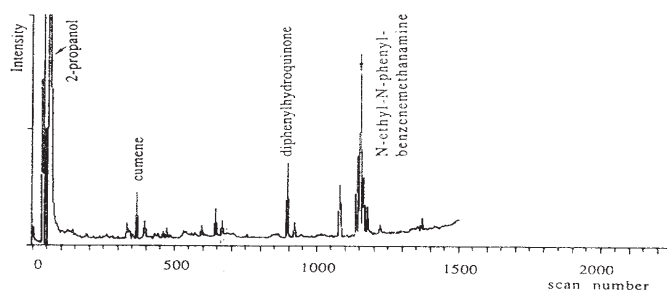
When a pyrolysis tube is installed in place of the adsorption tube the system may be operated as a Curie-point pyrolyzer. The chromatogram obtained from 250 mg of ABS resin by Curie-point headspace GC is shown in **Figure 7A**; that obtained from 0.3 mg of the same resin by Pyrolysis GC is shown in **Figure 7B**. Acrylonitrile, toluene, styrene, and other volatile compounds were identified following Curie-point headspace GC-MS (Figure 7A) and the trimmers acrylonitrile-acrylonitrile-styrene (AAS), acrylonitrile-styrene-acrylonitrile (ASA), and styrene-styrene-styrene (SSS) following pyrolysis (Figure 7B). Many of the peaks shown in Figure 7A were identified as monomers of the compounds in Figure 7B, and a trimer, SSS, was also observed amongst the compounds obtained following.

CPHS. Whether polymer additives or polymer degradation products, found using the solid sample injection system, can be identified by comparison of the chromatogram with that obtained from pyrolysis GC.

In conclusion, this multipurpose injection system, CPHS, can be applied to the analysis of environmental, food, petrochemical, and biological samples.



**Figure 4**  
Total ion current (TIC) chromatogram from headspace GC-MS analysis of polycarbonate resin. Sample extraction temperature, 250 °C for 10 min; helium flow, 30 ml/min; glass wool desorption tube temperature, 358 °C for 10 s. GC conditions: column, 30 m × 0.25 mm i.d. DB-1; oven temperature, 50 °C for 3 min then programmed to 300 °C at 10°/min; split ratio, 1:100; MS detector, Shimadzu QP-2000.



**Figure 5**  
TIC chromatogram from headspace GC-MS analysis of fermented soy bean paste. Sample extraction temperature, 80 °C for 15 min; helium flow, 35 ml/min; Tenax™ desorption tube temperature, -40 °C for adsorption, 358 °C for 10 s for desorption. GC conditions: column, 30 m × 0.25 mm i.d. DB-1; oven temperature, 50 °C for 5 min then programmed to 300 °C at 5°/min; split ratio, 1:100; MS detector, Shimadzu QP-2000.

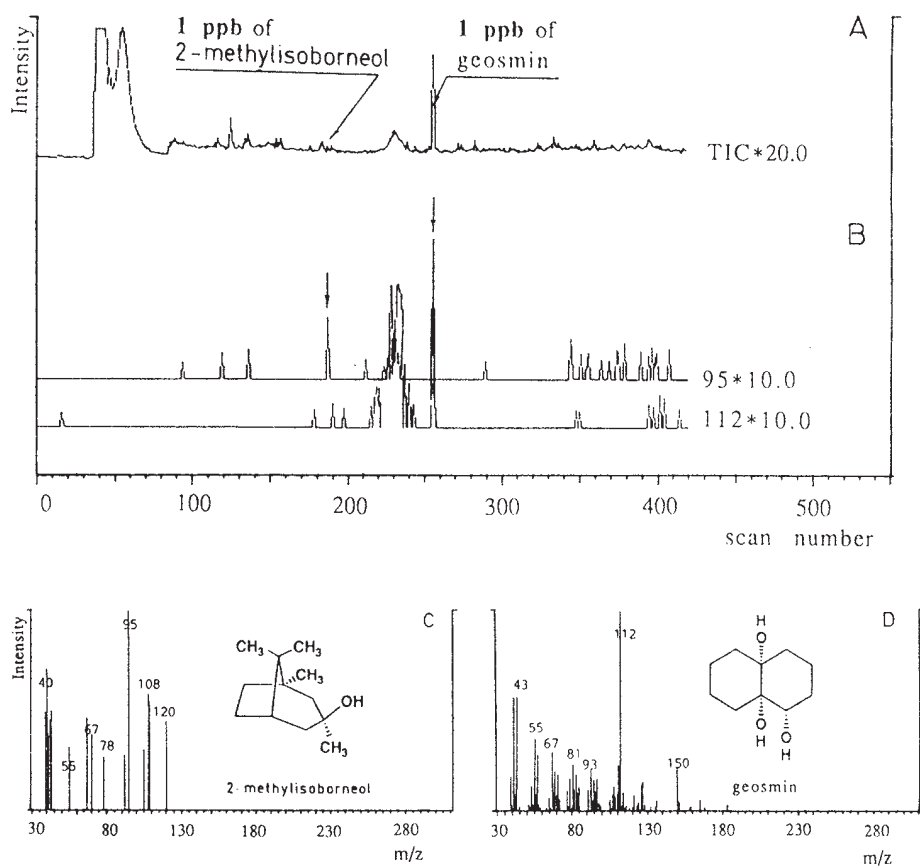


Figure 6

A) TIC and B) single ion ( $m/z$  95 and 112) chromatograms from headspace GC-MS identification of musty substances in water. Sample extraction temperature, 80 °C for 30 min; helium flow, 60 ml/min; Tenax<sup>®</sup> desorption tube temperature, -40 °C for adsorption, 220 °C for 10 s for desorption. GC conditions: column, 25 m × 0.25 mm i.d. DB-1; oven temperature, 50 °C for 3 min then programmed to 270 °C at 15°/min; split ratio, 1:100; MS detector, Shimadzu QP-2000. C) Mass spectrum of 2-methylisoborneol. D) Mass spectrum of geosmin.

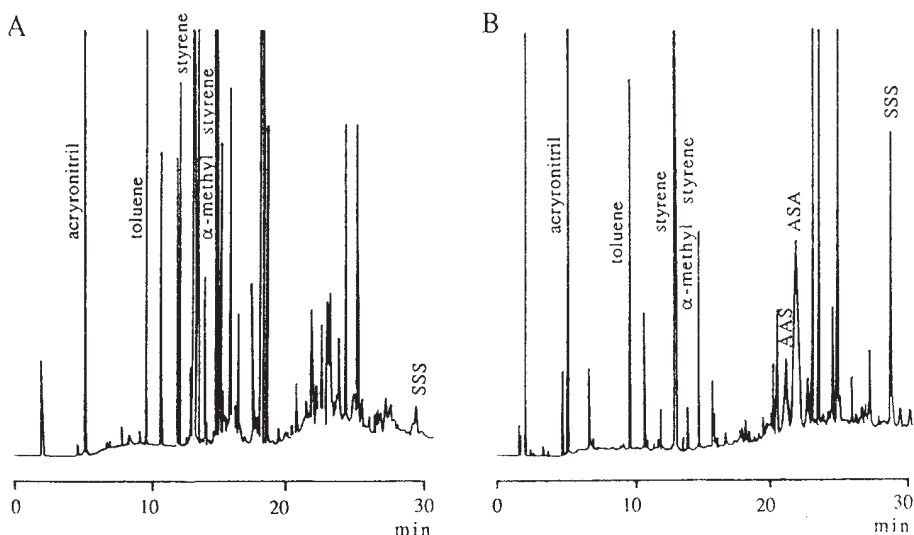


Figure 7

GC chromatograms from analysis of ABS resin. A) Curie-point headspace GC: sample extraction temperature, 200 °C for 10 min; helium flow, 30 ml/min; Tenax<sup>®</sup> desorption tube temperature, -40 °C for adsorption, 358 °C for 10 s for desorption. GC conditions: column, 25 m × 0.25 mm i.d. OV-1701; oven temperature, 50 °C for 3 min then programmed to 250 °C at 10°/min; split ratio, 1:100; chromatograph, Hewlett-Packard HP 5890. B) Pyrolysis GC: pyrolysis temperature 590 °C for 5 s; GC conditions as for A.

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