Rapid Characterization of Spices and Herbs by Direct Heating Sample Introduction Using a Curie-Point Pyrolyzer

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Key Words:

1 Introduction

Analysis of the components of spices and herbs is very important for research into their composition and for quality evaluation. and also for their identification. A promising method for this purpose is capillary gas chromatography. However, gas chromatographic analysis of the volatile components of spices and herbs usually requires appropriate sample preparation procedures. such as solvent extraction, steam distillation. *efc*. These procedures are tedious and difficult with small amounts of sample. On the other hand. pyrolysis GC is one of the most useful auxiliary techniques in polymer characterization [1 -3], and has been used for examination of complicated biological materials [4-6]. It is well known that these techniques can be applied directly to solid materials and we have already discussed their application to crude drugs [7]. The pyrolysis temperature has a great effect on the product distribution. At relatively low temperature. thermal desorption can be achieved in the pyrolyzer. but no pyrolysis occurs. The chromatograms may then be fairly similar to patterns obtained from solvent extracts or steam distilled fractions by conventional injection. A similar technique has been used for the thermal desorption of volatile compounds from insects [8-9]. At higher. temperature. the evaporated volatile components together with the pyrolysis products of volatile and non-volatile components give a characteristic pattern as an analytical fingerprint for a given a characteristic pattern as an analytical fingerprint for a given spice or herb. A suitable pyrolyzer for this purpose is of the high frequency induction heating type (Curie-point pyrolyzer), because of a highly repeatable pyrolysis temperature ad rapid temperature rise time. This paper describes the analysis of spices and herbs by direct heating using a Curie-point pyrolyser and comparision of the conventional method.

2 Experimental

A laboratory-made Curie -point pyrolyzer was directly coupled with a Hewlett Packard 9880A gas chromatograph (or Shimadzu GC-7A) equipped with a name ionization detector(FlD). Two FSCC were used which were coated with immobilized methylpolysiloxane (0.25 mm x 25 m) and PEG-20M (0.25 mm X 25m). Nitrogen carrier gas flow rate (40 ml/min) at the pyrolyzer was reduced to 0.8 ml/mn at the capillary column through a splitter. The other analytical conditions were described in the figure captions. A given ground (or chopped) spice or herb was placed h rolled ferry magnetic foils. and direct heating was performed in various ferromagnetic foils. each having a different Curie-point temperature by high frequency induction. These ferromagnetic foils with Curie point of 349°C 358°C. 385°C. 423°C. 500°C. 650°C, 747°C, and 920°C were purchased from Japan Analytical Industry Co Ltd. (Tokyo Japan). The vaporized gases from the pyrolyzer were introduced into the injector at 270°C through a heated 5 cm length 0.5 mm i.d. glass-lined stainless tube. The samples of spices and herbs (commercial origin in Japan) were ground (or cut) and 1-10 mg aliquots were analyzed respectively.

Table 1

Quantitative determinations of anethol in various spices and their reproducibilities by direct heating method

Spices	Sampling weight (mg)	Anethol [a] absolute peak area	Peak area/ sample (mg)	C V %	Anethol content w/w %	Conventional [b] method w/w %
Fennel (Kyoto)	1 7	36022	21189		3 25	3.11
	6 1	132378	21700	1 21	3 33	
	9 1	194221	21343		3 27	
Fennel (China)	2 5	25092	10037		1 54	1 46
	4 6	46574	10125	0 88	1 55	
	7 1	70637	9949		1 53	
Star anise (pericarp)	3 5	128524	36721		5 63	5.40
	4 2	153434	36532	0 52	5 60	
	5 3	192612	36342		5 57	
Star anise (seed)	5 4	26259	4863		0 75	0.67
	6 2	29744	4797	0 68	0 74	
	7 8	37674	4830		0 74	
Anise	6 6	6639	1006		0 15	0 15
	8.2	9086	1108	4.85	0 17	
	8.4	8979	1069		0.16	

a) Measured by a Hitachi 834 Chromato-Processor
b) The steam distillates were determined by gas chromatography

3 Results and Discussion

Direct heating of the spices is achieveed on ferromagnetic foils in the pyrolyzer. Typical chromatograms of sage obtained by direct heating at 358°C and 650°C for 3 s are illustrated in Figures 1 and 2. The reproducibility of the retention times obtained by this method is very good. also at other temperatures [7]. The reproducibility of quantitation by this method was evaluated by measurements of absolute peak area of anethol in fennel. star anise. and aniseed (see Table 1 and Figure 5). and was found to be highly reliable.

At relatively low temperature (349°C. 358°C. and 385°C). the chromatograms resemble the GC pattern obtained for the solvent extracts introduced by conventional injection, although some slight pyrolysis seems to occur. The chromatograms of cloves obtained by both methods are illustrated in Figures 3 and 4. After heating at 349°C for 3 s in the pyrolyzer. the residual simple is analyzed again and again. The area of the major peak(eugenol) of the second run chromatogram is just one fifteenth of that of the first run. and in the third run it is negligible. For vaporization of all the volatile components. Such as the essential oil. a temperature of 349°C proves to be adequate with a heating time of 7s,while at 385°C heating for 3 s is sufficient. It thus becomes possible evaluate the volatile components in a small sample of a spice without tedious sample preparation procedures. This is especially valid with aromatic spices and herbs which contain much essential oil.

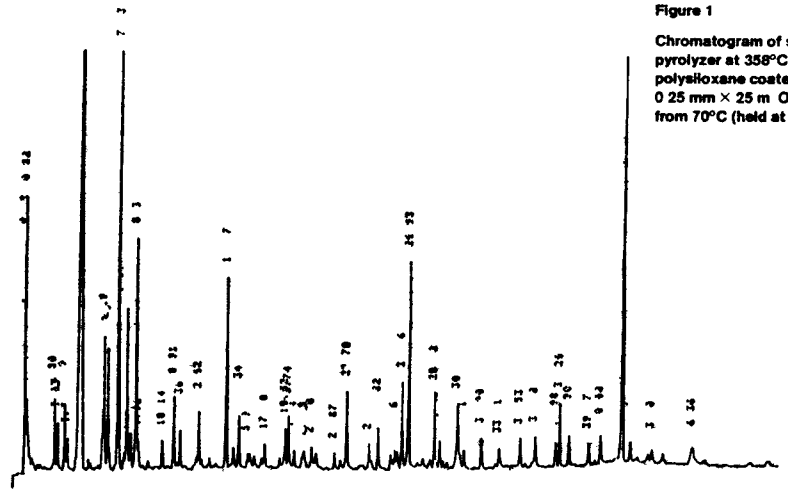

Figure 1

Chromatogram of sage by direct heating using a Curie-point pyrolyzer at 358°C for 3 s Column immobilized methyl polysiloxane coated fused silica capillary column 0 25 mm × 25 m Oven temp programmed at 5°/min from 70°C (held at 2 min) to 270° C.

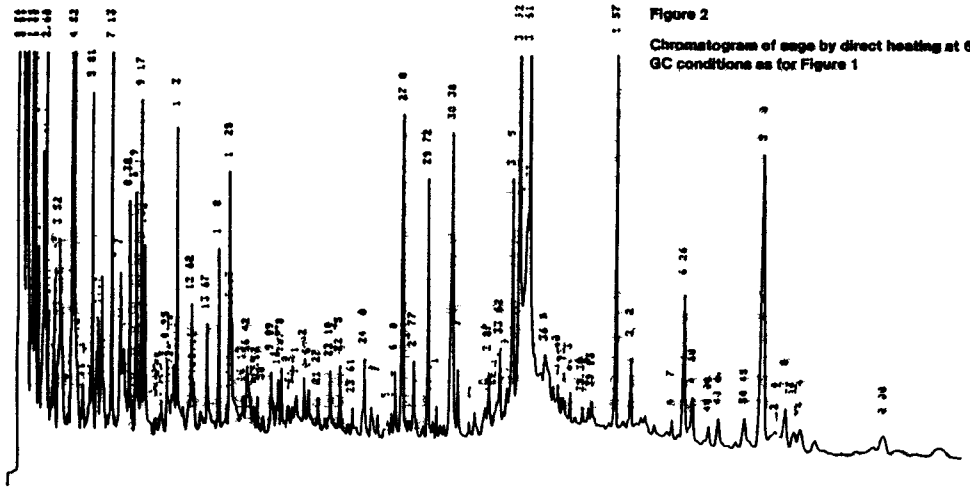

Figure 2

Chromatogram of sage by direct heating at 650°C for 3 s. GC conditions as for Figure 1

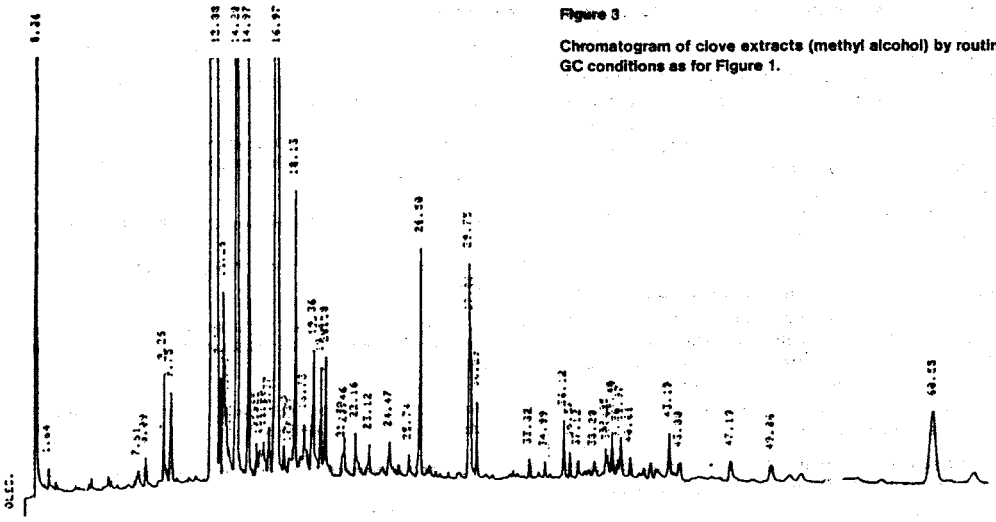

Figure 3

Chromatogram of clove extracts (methyl alcohol) by routine injection. GC conditions as for Figure 1.

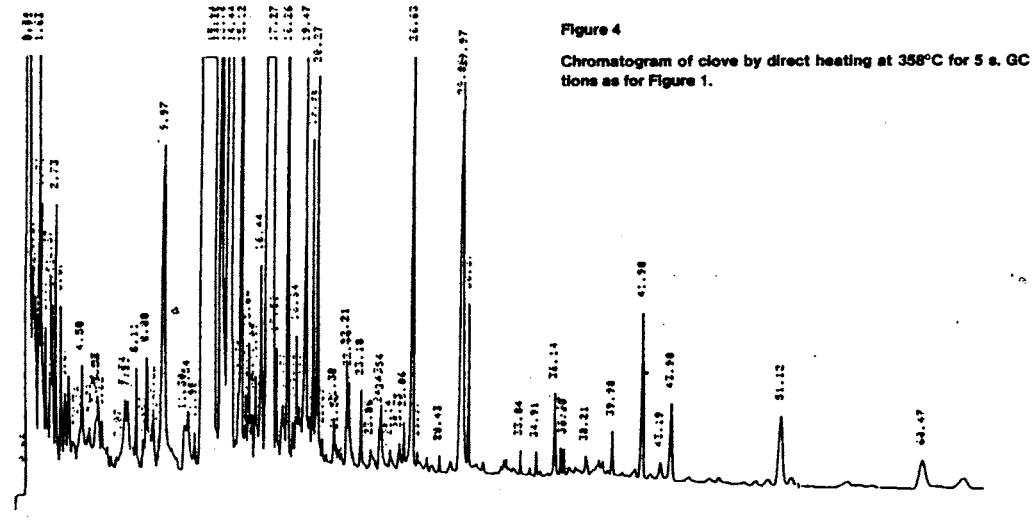

Figure 4

Chromatogram of clove by direct heating at 358°C for 5 s. GC conditions as for Figure 1.

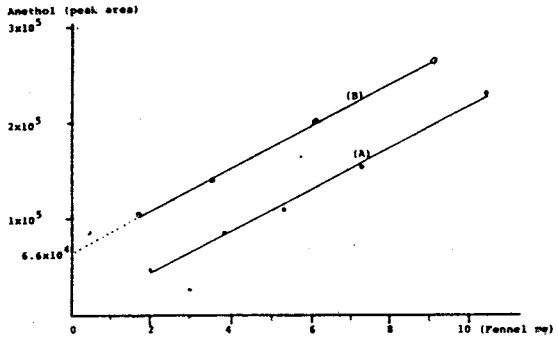

Figure 5

Calibration curves of fennel (A) and after addition of a weighed amount of anethol (B). Anethol 0.01012 mg gives the peak area 6.6 × 10^4 arb. units.

When used at relatively low temperature this method is applicable to determination of anethol in fennel, star anise. and aniseed. Quantitative determination of anethol in various spices is perfomed by the method of standard addition (addition of a weighed amount of anethol) to avoid discrimination at the sample inlet system. A plot of the peak area of anethol vs. sample weight gives a straight line. also after addition of anethol (0.01012 mg) to the samples containing anethol. The calibration curves for fennel are shown in Figure 5. The anethol contents (%) of various spices determined by this method are summarized in Table 1. The results compare favorably with those obtained by the conventional method..

The chromatograms obtained at higher temperature (650. 757. and 920°C for 3 s) show numerous peaks differing from those of the solvent extracts. The evaporated volatile components together with the pyrolysis products of the volatile and non-volatile components give a characteristic pattern. or analytical fingerprint. for a given spice or herb. However. the identification of each peak becomes increasingly difficult.

Consequently. this simple. rapid method using small sample size and giving good reproducibilities. is applicable to the evaluation and identification of spices and herbs.

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