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Studies on Rice Volatiles Using Direct Thermal Analysis Gas Chromatography

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Abstract: The Direct Thermal Analysis (DTA) chromatograms of different rice varieties/mutant revealed 17 components for Basmati-370, Basrnati-198, Kashmir Basmati and DM-25 and 16 components for NIAB-IRRI-9 on SE-30 packed column. The genetic relationship between Basmati -198, Kashmir Basmati and DM-25 and their parent Basmati-370 appeared to be reflected in the composition of their volatiles. A peak of rice aroma, found at retention time 10.84 min. in Basmati-370, Basmati-198, Kashmir Basmati and DM-25 (aromatic varieties/mutant) was absent in NIAB-IRRI-9 (nonaromatic variety) which was supposed by sensory evaluation of the column effluent.

Key words: Rice volatiles, direct thermal analysis, gas chromatography

Introduction

A variety of techniques are available for the analysis of volatile and semi-volatile organics in food materials. In previous studies of flavour and aromas in food and food products headspace gas chromatography (GC) have been the method of choice (Gregoire, 1984). However, the headspace techniques are limited in their level of detection and identification of many organic volatiles, especially the serni-volatiles (Kernik *et al*., 1984). Higher boiling volatiles and semi-volatiles are not detectable with these techniques due to their low partition in the gas headspace volume. In addition sensitivity of the technique is limited, typically to concentrations in the ppm to ppt range.

More sensitive analytical techniques are needed to profile and identify flavours, fragrances, off-flavours, off-odours and potential contaminants that may be present as flavour and fragrance additives at lower concentrations. The purge and trap (P&T) technique permits the analysis of wider range of both volatile and semi-volatile organic compounds and is more sensitive as compared to static headspace technique (Manura and Overton, 1994). By purging samples at higher temperatures, higher molecular weight compounds can be detected. However this technique require more time for sample preparation. In addition very light volatiles and gases will not be trapped on the adsorbent resin and therefore will be missed in the analysis.

A new technique entitled Direct Thermal Analysis (Manura *et al*., 1990) is unique for the analysis of wide range of volatiles and semi-volatiles in different kinds of materials with high sensitivity. In this technique, volatiles and semi-volatiles can be thermally extracted directly from solid matrix sample without the use of solvent or any other sample preparations. The samples are ballistically heated and together with the carrier gas flow through the samples the volatiles are outgassed into the injection port and on to the front of the GC column for subsequent analysis via the GC and/or GC/MS. The technique is quick and no solvent extraction is required, which eliminates the exposure of laboratory staff to these solvents and also eliminates the disposal of these solvents. In addition the thermal extraction of the volatiles and semi-volatiles from the solid sample is thorough and complete and no trace of foreign contaminants from the extraction technique or solvents contribute to the chromatograms. By selecting the proper extraction temperature, the user can control the complexity of the chromatogram. The technique has been used for the determination of off-odours and other volatile organics in food packaging films (Hartman, 1990) for quantification of Naphthalene in contaminated pharmaceutical products (Hartman, 1992), on-site detection of Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCB) in contaminated soils (Robbat *et al.,* 1992a, b). In the present study, this technique has been used to analyze rice samples with a possibility of developing a method to distinguish aromatic and nonaromatic varieties by utilising very small sample size, which may be helpful for rice breeders, as they can not spare large number of seeds for destructive analytical techniques in their early breeding period.

Materials and Methods

Rice varieties/mutants Basmati-370, Basmati-198, Kashmir Basmati, DM-25 and NIAB-IRRI-9 were grown at NIAB experimental farm during the year 1998. The paddy samples from each variety/mutant were collected, after dehusking and polishing the paddy samples, the rice grains were ground to fine powder (0.25 micron) with Grinding Mill (Retsch KG 5657 HAAN, Type ZM1 Nr. 23728, West-Germany). For the analysis of volatiles and semivolatiles in these rice powders the direct thermal analysis technique, developed by Manura *et al*. (1990) was used after making following modifications. Glass liner (Fig. 1) was made in the glass blowing workshop of NIAB which could be inserted into preheated injection port (Fig. 2) of gas chromatograph PERKIN-ELMER model 3920 for thermal desorption of volatiles and semivolatiles.

Analytical Procedure: Rice powder (0.5 g) was added directly into the glass liner between two glass wool plugs. The liner enclosed with the sample was then inserted into the GC injection port (Fig.2) at preheated set temperature, 150°C. The injection port was opened and immediately closed after the insertion of the liner. The volatiles and semivolatiles evolved from the sample were flushed directly onto the GC column and were analyzed qualitatively by the gas chromatograph equipped with flame ionization detector (FID) and Shimadzu CR-4A Chromatopac. The column was 2 m x 2 mm i.d. glass, packed with 10% SE-30 On 80-100 mesh Chromosorb W AW. Flow rates; nitrogen, 25 ml/min., hydrogen, 40 ml/min., air, 500 ml/min. Injector temperature, 150°C. Temperature programming: 50°C for 2 min., 50-62°C at 2°C/min., 62-135°C at 16°C/min. and isothermal at 135°C for 11 min. Four determinations were made for each sample.

Sensory Evaluation of the Chromatographic Effluents: The odour characteristics of volatiles and semi-volatiles from the rice powder samples were studied by sniffing the gas chromatographic effluents. The analysis were carried out by a panel of 4 judges and a free descriptive method was used. The column effluent was splited between the FID and odour port and the split ratio was 1:2 (FID: odour port).

Results and discussion

The chromatograms of volatiles and semivolatiles of Basmati-370, Basmati-198, Kashmir Basmati, DM-25 and NIAB-IRRI-9 by direct thermal extraction (Fig. 3) revealed 17 components for Basmati varieties/mutant and 16 components for the nonaromatic variety NIAB-IRR1-9. the genetic relationship between Basmati-198,

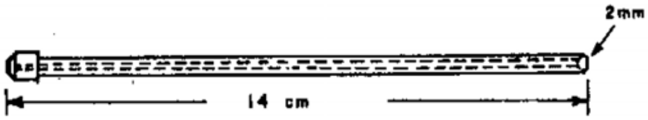

Fig. 1: Glass liner used for thermal extraction of rice volatiles

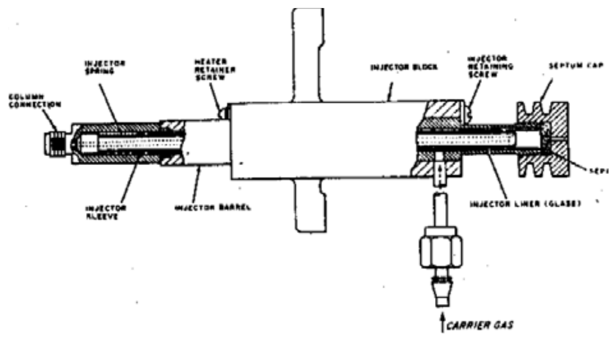

Fig. 2: Injector of perkin-elmer gas chromatograph model 3920

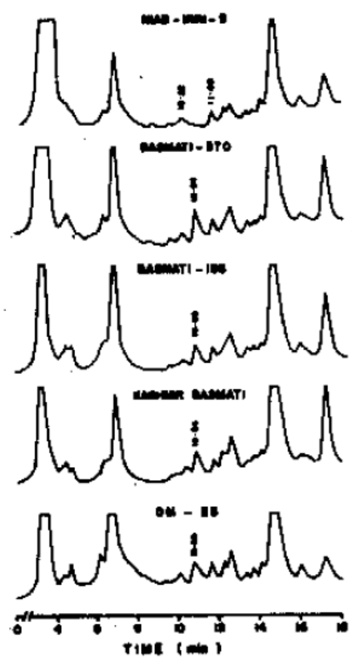

Fig. 3: Chromatograms of Different rice varieties mutant by direct thermal analysis

Kashmir Basmati, DM-25 and their parent Basmati-370 appeared to be reflected in the composition of their volatiles. In the variety NIAB-IRRI-9 a peak at the retention time 10.84 minutes was found missing where as it was found in all the Basmati varieties/mutant under test (Fig. 3). Aroma of Basmati rice may be due to the compound/compounds, detected at retention time 10.84 minutes. Odour profiling and the location of sensorially significant compounds by GC/peak sniffing analysis with the aid of column outlet splitter is a long established strategy in flavour research (Cronin and Caplan,1987). Sensory evaluation of the volatiles of the studied samples of rice revealed the presence of an important ricy region between retention time 9 to 12 minutes. In Basmati varieties/mutant the ricy region has a strong odour note characteristic to scented Basmati rices whereas it was found very weak in NIAB-IRRI-9, which has supported our findings that aroma in Basmati varieties/mutant was mainly due to the presence of a compound/compouneds detected at retention time 10.84 minutes. As NIAB-IRRI-9 is nonaromatic variety and the absence of peak in its chromatogram at retention time 10.84 minutes has shown a clear difference between nonaromatic and aromatic rice.

This present method developed by using the Direct Thermal Analysis technique, requiring a sample amount of only 0.5 g of rice for gas chromatographic analysis to distinguish aromatic and nonaromatic rice, may be helpful to rice breeders. The sensitivity of the method is significant, since accumulation of the number of .grains at an early stage of breeding is most difficult and several seasons of cultivation time may be saved before an analysis can be performed to verify the aromatic trait.

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