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A gas chromatographic procedure for measuring the isostatic permeation of volatile aroma components of food through packaging films

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Introduction

The application of synthetic foils in the packaging industry as well as in separation processes has stimulated research on mass transport through plastics. Although the mechanism of permeation is still not clearly understood, several methods for the determination of the permeation of permanent gases and water vapour have been published. Data obtained by these studies can be of help for the selection of films for proper food packaging.

Harris (1962) reported on the permeation of food odours and single volatiles by organoleptic tests. *Hanousek* (1963) reviewed earlier studies on permeation and described an interferometric method for measuring the permeation of single

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compounds. *Hadorn* and *Zürcher* (1964) used a gravimetric method in permeation studies at fixed relative humidity. *Heiss* and *Robinson* (1964) indicated the possible alteration of the original aroma by selective permeation. They compared the «organoleptic test time» for organic compounds and natural concentrates penetrating through different films, as did *Samuels* and *Seidler* (1965) for coffee. These methods also permit the study of permeation at fixed relative humidities, which is of interest in handling hydrophilic films. *Hoffmann* et al. (1965) reported on a sensitive radiometric method for labeled volatile compounds and on organoleptic tests for the same non-labeled components.

The use of interferometric, gravimetric and radiometric methods is restricted to the quantitative estimation of the permeation of single compounds. They cannot be applied for the study of qualitative and quantitative changes which take place in the composition of a complex aroma during permeation. *Varsányi* (1965) emphasized the importance of high sensitivity gas chromatographic methods for permeation studies. The application of gas chromatography in permeation studies of permanent gases had been reported earlier by *Fricke* (1962), *Karel* et al. (1963), *Taylor* (1964), *Lockart* (1965) and *Lyssy* and *Mohler* (1965), while *Eustache* (1963) used mass spectrometry.

At this laboratory gas chromatographic research on the permeation of organic food volatiles was started in 1963. *Maarse* and *De Nie* (1965) studied the permeation of single compounds and their mutual influence during the permeation of mixtures. In the present report a gas chromatographic method is described for the study of the composition of food odours relative to their permeate through a film. Since the concentrations of the volatiles in the permeate were found too low for detection when normal vapour analysis techniques are employed, the volatiles had to be cumulated preceding analysis. Our experiences during the independent development of a pre-column cumulation arrangement for this purpose support the results recently published by *Morgan* and *Day* (1965), *Williams* (1965) and *Gottauf* (1966). Any selective permeation of individual components in a mixture is demonstrated by ratio changes of the peak areas on the chromatogram. The method is designed to compare the barrier properties of different foils to food odours and is considered of interest for the control of odour quality in packed food products. The practical use of the arrangement is demonstrated by a study of the permeation of the vapours over ground roasted coffee through low density polyethene (l. d. p. e.) foil.

Materials and methods

Gaschromatograph. A Carlo Erba Analytical Unit Model C Fractovap, equipped with a hydrogen flame ionization detector, was used. A 4 metre × 4 mm i. d. Al column packed with 25 % of Lac I-R-296 on Chromosorb W, 60—80 mesh was operated at 65 ° C. N_2, H_2 and air flow rates of 35, 30 and 300 ml per minute respectively were used throughout. The injection port temperature was 100 ° C. A gas-tight stainless steel B & D syringe was used for direct injection of 6,25 ml vapour samples.

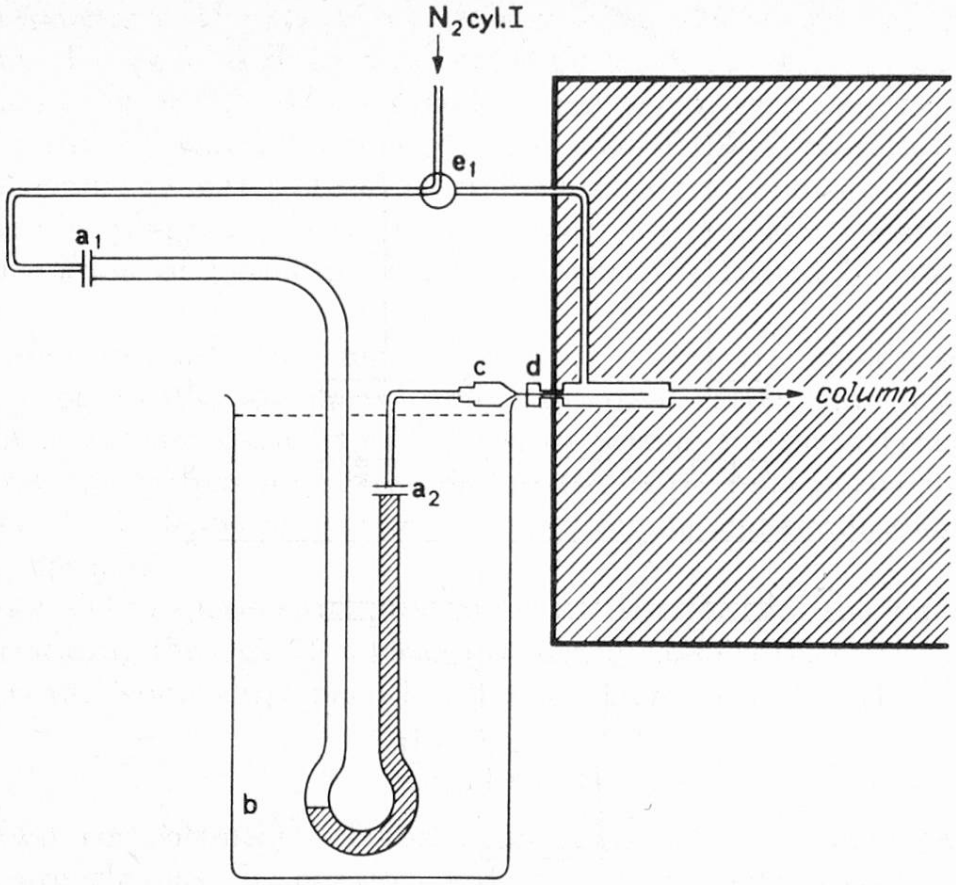

Fig. 1. Arrangement for sample introduction by pre-column

Pre-column (fig. 1). A 34 cm × 4 mm i. d. stainless steel tube with silver soldered Edwards fittings a_1 and a_2, was packed over a length of 14 cm (from b to a_2) with 0,5 g of the same filling as was used for the main column. The non-packed section probably facilitates the condensation of water vapour to the wall, avoiding the freezing up of the packed section of the pre-column (*Gottauf*, 1966). Dry-ice without organic solvent was used as a coolant to avoid contamination of the sample with solvent vapour (*Williams*, 1965). For the transfer of the condensed volatiles to the main column, the pre-column is heated by means of a water bath, as shown in fig. 1. Viton O-rings which produce no contaminations when heated, were used in all Edwards fittings. A 0,8 mm B & D G 21 needle c is soldered to the Edwards fitting a_2.

The pre-column is adjusted to the injection port by piercing a silicon rubber septum d. The carrier gas (cylinder I) is either introduced by way of the pre-column or directly to the main column without interrupting the flow by manipulating the gas-tight 3-way valve e_1. (*Sprecher* and *Strackenbrock* (1963), *Libbey* et al. (1963) and *Novák* et al. (1965).

Permeation cell (fig. 2). The permeation cell is arranged by clamping two Quickfit flat flange vessels f_1 and f_2 to a 127 mm i. d. stainless steel ring g mounted with rubber O-rings. The film k is placed between g and f_2, dividing the cell into two compartments.

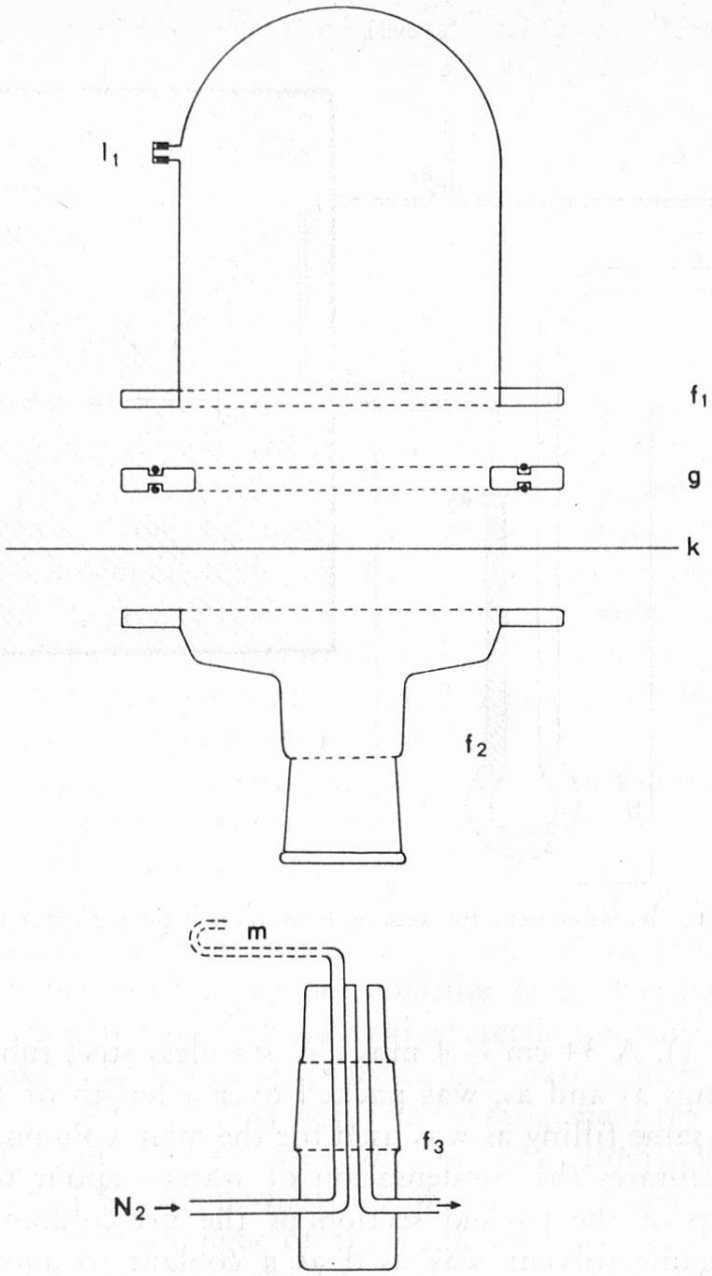

Fig. 2. Permeation cell

In the upper 900 ml compartment f_1 a food product is placed directly upon the film. Through the serum cap l_1 a vapour sample over the product can be taken for analysis. The lower 140 ml compartment is closed with a double perforated conical joint f_3. A stream of nitrogen, introduced tangentially below the membrane by means of a flexible teflon tube m, entrains the permeate and carries it outside the cell.

Flow arrangement (fig. 3). During the experiment the permeation cel f is kept in an oven at 30 ° C. The pre-column can be connected to the outside of the oven by means of a T-piece z with a screw fitting. A gas-tight Becker (Delft, The Netherlands) 4-way pressure valve e_2, fitted to the inside of the oven wall, can be manipulated from the outside of the oven. By way of f and e_2 the N_2 stream from cylinder II reaches either the pre-column or the water resistance

q and manometer t. The N_2 stream from cylinder III can be lead directly to the pre-column. The two N_2 flows are cleaned by molecular sieves s_2 and s_3 and carefully adjusted by needle valves r_2 and r_3. The resistance h_1 of the pre-column is measured with the water manometer t. The compensation resistance q is adjusted to the same value by means of the injection or with-drawal of water through cap l_2. Normally z_2 is plugged. Flows are measured with the flow meter u. To prevent any condensation of permeate in z, the T-piece is heated by an I. R. heating element v.

Cleaning. Since all trace impurities in the system are equally cumulated during the experiments, all parts, teflon tubings, valves, and connections are cleaned in a vacuum oven at 65 ° C before setting up the arrangement. Molecular sieves and pre-columns are conditioned with a nitrogen flow of 30 ml/min at 140 ° C. In between experiments the cleaning and conditioning of the pre-column is repeated.

Materials. The experimental procedures are described for the vapour of roasted coffee permeating through 25 micron low density polyethylene (l. d. p. e.), manufactured by the Koninklijke/Shell Plastics aboratorium, Delft, The Netherlands.

Experimental

The two compartments of the permeation cell, separated by a sheet of l. d. p. e., are clamped in position and the upper compartment is rinsed with nitrogen. About 20 g of roasted coffee beans are ground quickly, and 15 g of the ground coffee is put in the upper compartment through l_1. A 2 g sample of the ground coffee is brought under nitrogen into a 125 ml serum flask, which is then closed by a pierceable screw cap. The serum flask and the permeation cell are then placed in the oven and the permeation cell is connected to the flow system.

By means of a flexible piece of teflon tubing (shown by a single dotted line) with a needle attached to one side piercing the rubber cap l_1 and an Edwards fitting to the other side, f_1 and f_2 are temporarily connected through w_2. The adjustable water resistance q is filled to the height h_2 (approximately 10 cm water), which had been determined before. With e_2 in the position drawn in fig. 3, flow II is introduced and adjusted at 30 ml per minute with r_2. In this way the pressure on both side of the membrane is equalized and permeation is isostatic.

After taking away the teflon connection, w_2 is connected to cock e_3 and the permeation cell is left overnight in the oven. While flow II keeps the lower compartment at zero concentration by entraining all permeated volatiles through the compensation resistance, the vapours over the coffee are equilibrating the membrane material to saturation.

The next day 6,25 ml vapour samples are taken through holes in the oven door from the reference flask and from the upper compartment through l_1, followed by re-injection of 6,25 ml nitrogen. Previous to the collection of permeate samples, the pre-column is inserted between z_1 and serum cap l_3. Cock e_3 is connected to z_2 and flow III is adjusted at 30 ml per minute. Cock e_2 is now in the position drawn in fig. 3. The heating element v is alighted and the pre-column is

cleaned by the N_2 stream while immersed in boiling water for 15 minutes. The water bath is removed and the pre-column is cooled at —80 ° C for 40 minutes. A $CaCl_2$ tube s_4 excludes water vapour from the atmosphere. During this period the pressure at the top of the pre-column is measured and when necessary the compensating resistance is readjusted.

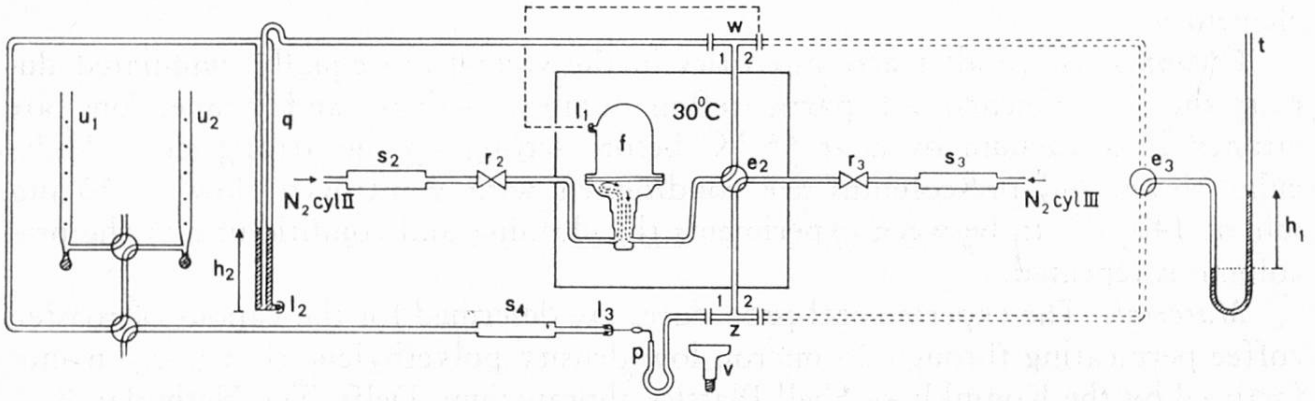

Fig. 3. Arrangement for concentrating food volatiles permeated through packaging foils

Since both flows and resistances are equal, the turning of e_2 after the cooling period causes no disturbances in the permeation cell and the cumulation of the permeate on the pre-column is started. After 10 minutes 300 ± 5 ml of nitrogen, measured for volume by successive employment of u_1 and u_2 and carrying the volatiles which have permeated, have passed through the pre-column and e_2 is switched to the original position.

The pre-column is then disconnected from the system. Temporarily the needle c as well as a_1 (fig. 1) are plugged with a piece of silicon rubber and a closed Edwards fitting respectively and the dry-ice is removed. The plugging prevents any condensation of vapours from the atmosphere into the column. The pre-column is coupled to the gas chromatograph by first connecting fitting a_1 and then inserting the needle into the injection port. It is quickly immersed in boiling water, e_1 is turned and the evaporating volatiles moving through the pre-column, are introduced to the main gas chromatographic column.

When the experiment is finished the foil is removed and examined for possible pinholes by clamping the foil to one of the open sides of a piece of glass tubing with the same diameter as the permeation cell. It is then studied as a separating layer between water and an aqueous solution of Congo red. Both liquids are stirred. The presence of pinholes in the foil is evident when the water is coloured red within 24 hours.

Previous to the permeation experiments, a blank experiment is carried out without coffee resulting in blank values for the whole system including the foil to be examined. At intervals the detector response is checked by injecting vapour samples of an aqueous standard solution of acetone equilibrated for 45 minutes at 30 ° C.

Results and discussion

All blank experiments with l. d. p. e. foils, performed at maximum sensitivity of the detection system, showed values for peak heights which could be neglected when compared to those resulting from the tests with permeating coffee vapours.

The reproducibility of the method was tested by carrying out 4 replicate experiments. A single experiment consisted of the analysis of:

— a 6,25 ml vapour sample (R) from the reference flask (19 hrs after starting the experiment), resulting in peak areas X_R
— 6,25 ml vapour samples (A) from the upper compartment of the permeation cell in duplo (after 16 and 20,5 hrs; $\Delta t = 4{,}5$ hrs), resulting in peak areas X_A
— the volatiles permeated through the foil in 10 minutes and cumulated on the pre-column (B) also in duplo (after 17 and 21,5 hrs; $\Delta t = 4{,}5$ hrs), resulting in peak areas X_B.

All components appearing in the chromatograms of the coffee vapours from the reference flask and from the upper compartment are also found in the chromatograms of the cumulated permeates.

Peak areas X_{Ri}, X_{Ai} and X_{Bi} for 9 of the main peaks ($i = 1$—9) were calculated. Since the acetone peak areas for detector response checks varied less than 4 %, no corrections were made for detector response variations. The averages for each one of the 9 peaks ($\overline{X}_{Ri}$, $\overline{X}_{Ai}$, and $\overline{X}_{Bi}$) are given in table I.

Table I Peak averages

peak i	1	2	3	4	5	6	7	8	9
$\overline{X}_{Ri}$	2235	0844	0596	1345	3436	1836	1930	0997	1049
$\overline{X}_{Ai}$	1354	0450	0351	1042	1974	1173	1562	0598	0619
$\overline{X}_{Bi}$	0728	0760	0579	1220	3024	2085	3324	1734	3850

The coefficients of variation of the 4 replicates for each peak i separately, calculated from the averages $\overline{X}_{Ri}$, $\overline{X}_{Ai}$ and $\overline{X}_{Bi}$ and the corresponding standard deviations are presented in table II.

Table II Coefficients of variation

i	1	2	3	4	5	6	7	8	9
R	16,8	14,8	15,2	14,2	12,9	17,0	10,4	13,4	10,2
A	11,6	10,4	8,5	7,1	11,4	15,7	7,7	11,9	14,6
B	12,6	11,8	12,2	11,0	11,5	11,6	9,7	11,0	11,4

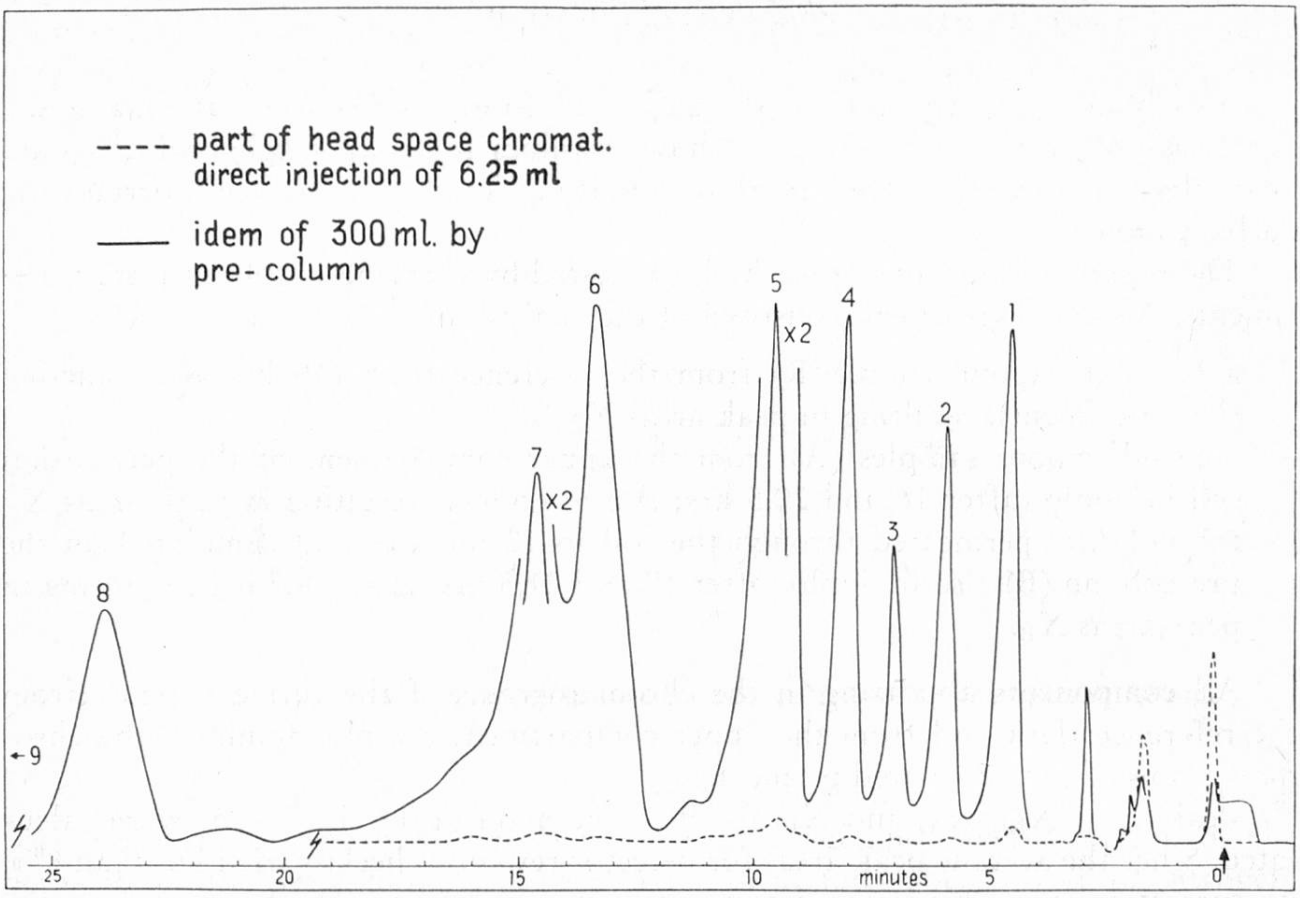

Fig. 4. Coffee vapours permeated through membrane

The enrichment effect of the pre-column is seen in fig. 4. The foils that had been used were found to be free of pinholes.

From the figures of Table II it is seen that the reproducibility of the described methods is adequate when compared to the much larger differences known to be caused by using various types of foils (*Maarse* and *De Nie*, 1965).

In order to examine any change in the ratio of peak areas of the coffee in the upper compartment of the permeation cell, the values of the peak areas X_{Ai} were related to the values of the peak areas X_{Ri}. By means of analysis of variance*, it was found from these relative values that significant ratio changes had occurred in the mixture of volatiles over the stored product. Consequently the odour of the product over the foil must have been altered.

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Summary

The permeation of food odour volatiles through packaging foils is studied in a permeation cell. The permeating vapours are entrained with a nitrogen flow and cumulated on a cooled pre-column. They are subsequently brought to the injection port of a gas chromatograph and analysed. A special flow arrangement compensates for the resistance of the pre-column and allows for isostatic permeation. The method is described for the vapours of ground roasted coffee permeating through low density polyethylene foil. All components are found to be present in the permeate, but quantitative ratios of the components are different from those over fresh coffee. The odour of the coffee as a consequence will be altered by packing in this type of foil.

Zusammenfassung

Arbeit über die Diffusion flüchtiger aromatischer Substanzen von geröstetem und gemahlenem Kaffee durch Polyaethylenfolien geringer Dicke. Alle aromatischen, flüchtigen Bestandteile finden sich im Diffundierten, aber in Proportionen die vom Kaffee abweichen. Daraus ergibt sich, daß der Geruch des Kaffees sich ändert sobald er in Polyaethylenfolie verpackt wird.

Die Prüfung der flüchtigen Substanzen geschieht mittels Gaschromatographie.

Résumé

Etude de la diffusion des substances aromatiques volatiles du café rôti et moulu à travers des feuilles de polyéthylène de faible densité. Tous les composants aromatiques volatils du café se rencontrent dans ce qui a diffusé, mais en proportions différentes de celles présentes dans le café. Il en résulte que l'odeur du café se trouve modifiée lorsqu'il est emballé dans ces feuilles de polyéthylène.

L'examen des substances volatiles est fait par chromatographie en phase gazeuse.

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