A C T A A L I M E N T A R I A P O L O N I C A

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EDWARD KAMIŃSKI
ERWIN WĄSOWICZ
ROMAN PRZYBYLSKI
ANDRZEJ SZEBIOTKO
RENATA ZAWIRSKA

ISOLATION OF VOLATILES FROM PACKAGING MATERIALS AND THEIR SEPARATION WITH GAS CHROMATOGRAPHY

Department of Food Technology of Plant Origin, Agricultural University, Poznań

Key words: packaging materials, head space method, gas chromatography distillation-extraction methods.

Isolation of volatiles from packaging materials was carried out with the head space and distillation-extraction methods. Separation of the volatile components was performed in a gas chromatograph.

INTRODUCTION

Many divers materials are presently used in packaging of food products. Most of them are characterized by their own individual, often very exiguous odour, which, however, can induce off flavor in stored food products. The literature provides very little data on volatiles in packaging materials. This is related to unavailability of appropriate and precise methods of isolation of such components for further analysis with gas chromatography.

The present study was aimed at selecting effective methods for isolation of these volatile compounds from packaging and subsequent gas chromatography analysis.

MATERIALS AND METHODS

MATERIALS AND REAGENTS

Packagings

1. Domestic paperboard with printing, coated on one side
2. Sulphate packing paper (70/g/sq.m.)
3. Cellophane (Tomofan) coated with polyamid and printed over

4. Cellophane (Tomofan), plastified, unprinted (plasticizer: glycerine + propylene glykol)
5. Printed polyethylene
6. Laminate, unprinted, (paper-polypropylene)
7. Laminate, printed, (paper-polypropylene)

The packaging were provided by the R and D Center for Packaging in Warsaw.

Additionally, polyamid-polyethylene laminate and cellulose polyacetate Wipak (Findland) were used in the study.

Reagents

The following standards of volatiles were used in the model analyses:
1. acetone (boiling temp. −56°C)
2. ethyl acetate (77°C)
3. methylo-propyl ketone (102°C)
4. amyl alcohol (137°C)
5. benzyl alcohol (205°C)

The above compounds were used as 0.02% water solution of each component.

Adsorbents

Chromosorb 106, 80-100 mesh (Johns Manville, Denver)
Porapak Q, 80-100 mesh (Hewlett-Packard)
Tenax, 60-80 mesh (Enka IV, Holland)

PREPARATION OF SAMPLES FOR THE "HEAD SPACE" ANALYSIS

Any given tested packaging material was cut into strips 1,5 cm wide and 10 g of it was put into a 500 cc sample bottle. After stoppering a microsyringe was used to put throught the stopper 0,2 µl ethyl caprylate used as an inner standard. The sample was heated in a drier for 1.5 hr at 120°C. After removal from the drier immediately 3 cc vapors were collected with a syringe and injected into the gas chromatograph's column.

CONDENSATION OF THE VOLATILES FROM PACKAGINGS WITH ADSORBENTS

The apparatus for condensation of the volatiles with adsorbents included a cylinder with high-pressure nitrogen, a 15 cm long copper pipe filled with heated Chromosorb and kept at −80°C, and a filter filled with molecular sieves for purification of nitrogen. Attached to the filter was a glass pipe (4 cm in dia, 40 cm long), which contained the material being tested. Another attachment was a trap with adsorbent which consisted

of a 24 cm long (4 mm in dia) glass pipe filled over 18 cm of its length with adsorbent. The elements of the apparatus were connected with teflon tubes. Prior to their use adsorbents were purified by extraction in a Soxhlet apparatus with the following solvents: ethyl ether, methylene chloride and carbon disulphide. Extraction was continued for 6 hrs with each solvent. After extraction adsorbents were conditioned for 48 hrs at 180°C with nitrogen flow of 60 cc/min.

For condensation of the volatiles 1 sq.m. of packaging was cut into pieces of 2-3 sq. cm. The sample was placed in the glass pipe and attached to the apparatus. Isolation of the volatiles was continued for 4 hrs passing nitrogen through the sample (60 cc/min.; 90°C). The trap with adsorbent was kept throughout this time at room temperature.

Desorption of the volatiles was performed after detaching the trap from the apparatus by passing nitrogen through the adsorbent at 30 cc/ /min. in opposite direction. Desorption continued for 0.5 hr and the adsorbent tube was kept at 180°C. The eluated volatiles were condensed in a glass capillary cooled with dry ice.

The model analyses were conducted with water solutions of the standards. For condensation, 200 ml solutions were collected. Parameters of desorption and condensation were the same as given above.

ISOLATION OF THE VOLATILES IN PACKAGINGS BY DISTILLATION AND EXTRACTION

This procedure involved steam distillation and simultaneous extraction of the distillate with a mixture of ethyl ether and pentane. Isolation was conducted in a glass apparatus constructed after Linkens and Nickerson [4]. For distillation, the material was cut into pieces 1 × 2 cm and 50 g was dispersed in 2 l bidistilled water. Extraction was performed with a mixture of 15 cc pentane and 15 cc ethyl ether. Distillation continued for 90 min. The resultant extract of the volatiles was dried up with anhydrous sodium sulphate and condensed to the final volume of 100 µl in the apparatus described by Kamiński et al. [2]. Purity of the applied solvents and of bidistilled water was checked with the so-called blank test'. Chromatographic analysis of extract obtained from this sample did not show any peaks deriving from impurities.

CHROMATOGRAPHIC ANALYSIS

Finnigan 9610 gas chromatograph with a flame ionization detector was used. Separation was performed in a 2 m long glass column (1.8 mm in dia) filled with Carbowax 20 M on Chromosorb P, 100-120 mesh [1]. Temperature of the column during the "head space" and the adsorbent tests was kept at 40°C for 3 min. after injection. Then it was heated up to 175°C at a rate of 6°C/min. During the distillation and extraction pro-

cedures the column temperature was kept at 70°C for 3 min. after injection and subsequently heated up to 200°C at a rate of 6°C/min. Nitrogen flow — 20 cc/min. Olfactory assessment of the eluate from the column was carried out according to the method described by Kamiński et al. [3].

DISCUSSION OF RESULTS

ANALYSIS OF THE VOLATILES IN PACKAGINGS WITH THE "HEAD SPACE" METHOD

Fig. 1 presents examples of chromatograms of the "head space" tests for three kinds of packagings: printed cellophane coated with polyamid (*A*), unprinted laminate, paper-polypropylene (*B*) and printed paperboard (*C*).

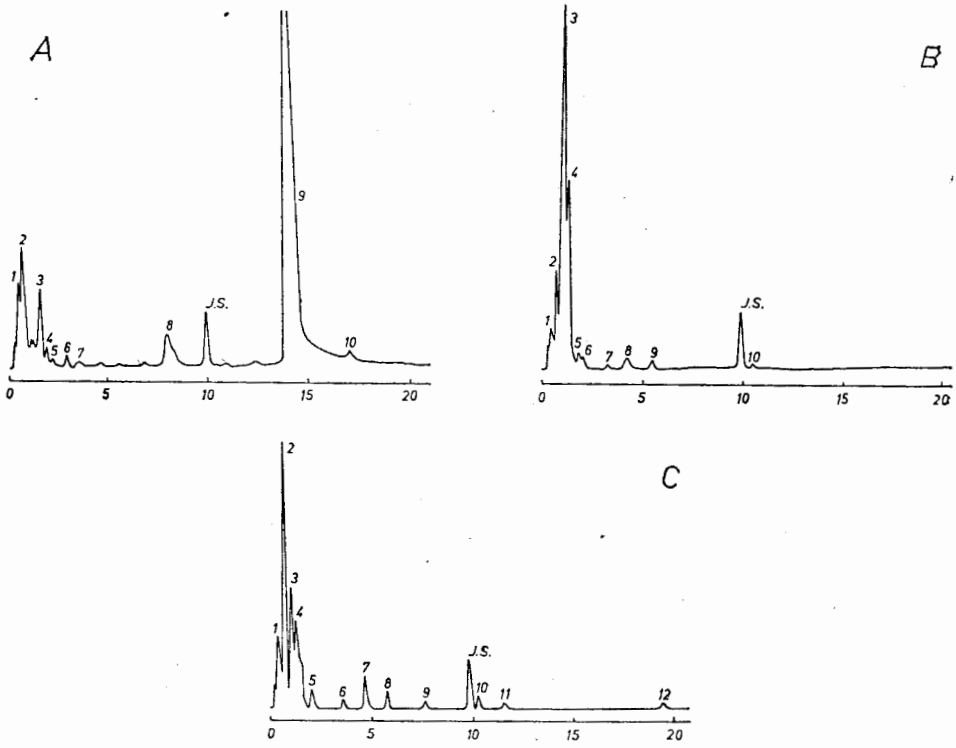

Fig. 1. The "head space" chromatograms; A. Printed cellophane coated with polyamid, B. Unprinted laminate — paper/polypropylene, C. Printed paperboard coated on one side I. S. — Internal standard

In order to check repeatability of the applied method and the scattering of results, an average height of peaks and a relative standard deviation after 6 analyses of the "head space" tests of printed paperboard. Examples: Peak 5 — average height 1.8 mm, and standard deviation 1.7; Peak

7-37.4 mm, and 3.8, respectively. These examples indicate sufficient repeatability of the "head space" method for quantitative determinations of volatile components of packagings in concentrations permitting their direct detection with gas chromatography. The method's error due to the technique of collecting and injection of samples can be eliminated by the inner standard.

PACKAGING VOLATILES CONDENSED WITH ADSORBENTS

Degree of condensation of the volatile compound standards was determined with the use of adsorbents Chromosorb 106, Poropak Q and Tenax (Table). Data obtained in this way indicate different degrees of condensation being dependent on the kind of polymer used. The highest level of condensation for nearly all of the investigated compounds was reached with Chromosorb 106.

Table. Degree of condensation of standards from solution at 90°C, adsorbed with different porous polymers. Thermal desorption time — 30 min.

Standards	Adsorbent		
	Chromosorb 106	Poropak Q	Tenax
Acetone	121±3.7*)	21±1.4	44±0.3
Ethyl acetate	532±4.1	238±4.4	74±3.4
Methyl-propyl ketone	832±5.3	236±5.1	69±6.7
Amyl alcohol	867±4.9	223±3.4	51±13.2
Benzyl alcohol	49±2.3	71±1.0	44±3.6

*) Data from six repetitions; arthmetical average; ± standard deviation.

The degree of condensation of the analyzed compounds with the same adsorbent varied. The analyses were performed at 20°C, 50°C, 90°C and over different time periods — 15, 30 and 60 min. — of desorption. It proved that we cannot control the selection of parameters in such a way that all compounds get condensed at a degree common to all of them.

Fig. 2 shows chromatograms from separation of the volatiles in packagings after condensation in Chromosorb 106: the polyamidcoated printed cellophane (*A*) and the paper-polypropylene unprinted laminate (*B*). These chromatograms, compared with the ones from the "head space" technique, reveal strong condensations of some components, particularly those eluated in the first minutes of the separation process. It points out a possibility of using this method of isolation for analyses of very volatile

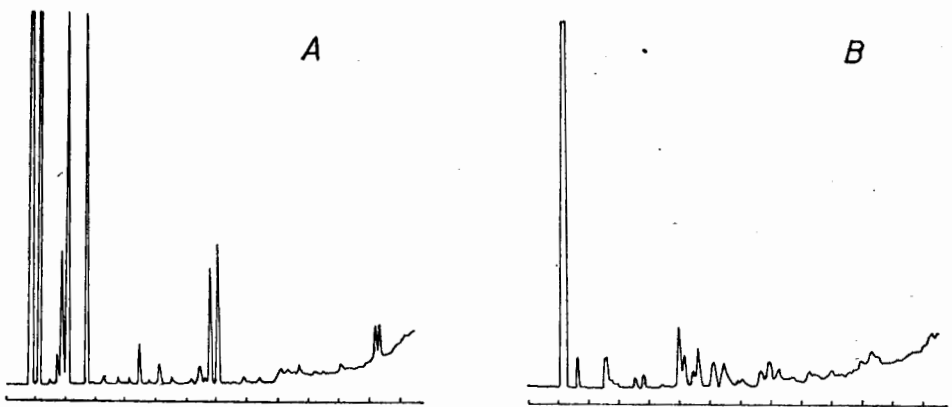

Fig. 2. Gas chromatograms of the volatile components in packagings condensed with Chromosorb 106; A. Cellophane, printed and coated with polyamid, B. Unprinted laminate — paper/polypropylene

components in packaging, particularly those which have their vapor condensation over the tested material too low to be tested by the "head space" technique.

Quantity of the volatiles in the capillary after desorption is high enough to permit several repetitions of the chromatographic analysis which is important in a situation when identification by MS — method is necessary.

PACKAGING VOLATILES CONDENSED BY DISTILLATION AND EXTRACTION

The method of condensation of volatiles from packagings by steam distillation and extraction with a mixture of ethyl ether-pentane allowed to obtain 100 µl concentrate of volatiles with a condensed flavour of the initial material.

Fig. 3 gives a chromatogram of the paper-propylene, unprinted laminate. The two previously mentioned methods are less effective in comparison with the distillation-extraction technique, which provides for isolation and analyses of the largest number of volatiles. The chromatogram presents 53 peaks. The number of peaks from the other types of packagings reached the same level.

The studies by Schultz et al [5] showed that recovery of most compounds, except for the extremely volatile ones, came to about 90% and the method can be used for quantitative determinations.

A very positive aspect of the distillation-extraction technique is that relatively big quantities of extract can be obtain, and this is important from the point of view of further identification and organoleptic evaluation of the compounds. Concentrations of particular components in con-

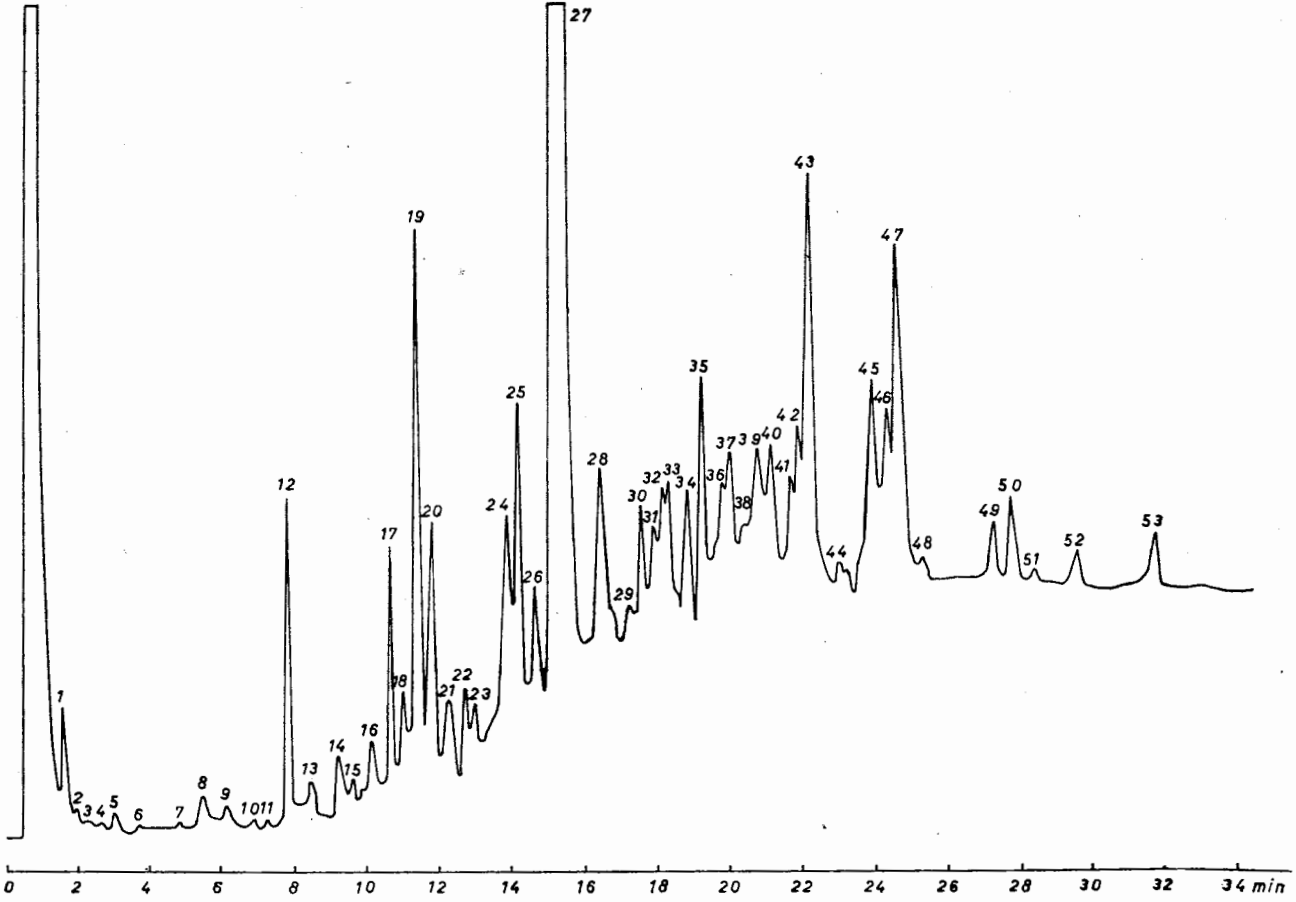

Fig 3. Gas chromatogram of the volatiles isolated by distillation and extraction from the unprinted laminate paper/polypropylene

densates obtained in this mode of operation were also sufficient to evaluate their (odour) smell after the chromatografic separation. For example, the odour of the volatiles from the paper-polypropylene laminate was described as "a plastic-paper" note.

The chromatografic separation (Fig. 3) was followed by an olfactory test confirming the characteristic odours: Peak 12 — rancid fat; Peak 17 — paraffin; Peak 20 — rubber, and Peaks 26 ann 30 — the smell of printer's ink.

The chemical characteristics of these compounds and their effects upon odour of packaged products call for further study. It follows from the analyses carried out in the project that every of the methods presented here provides different possibilities for examining the packaging volatile compounds and choice of one of them should depend on the researcher's objective. The most effective procedure is that of the distillation-extraction technique, which can give the highest level of concentration of the volatiles.

The most exiguous volatile compounds are best analyzed with the "head space" and the adsorbent condensation methods. The "head space method" is simpler but it calls for a considerable level of experience on the part of the entire procedure. On the other hand, when concentration of the compounds in vapors from a sample is too low to obtain interpretable chromatograms, it is reasonable to use the technique of condensation volatiles on the adsorbent. This permits condensation by several hundred times. Using this method, however, it is necessary to apply various correcting factors because of diverse degrees of adsorption showed by particular compounds.

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Authors address: 60-624 Poznań, Wojska Polskiego 31

E. Kamiński, E. Wąsowicz, R. Przybylski, A. Szebiotko, R. Zawirska

WYODRĘBNIANIE LOTNYCH SKŁADNIKÓW MATERIAŁÓW OPAKOWANIOWYCH I ICH ROZDZIAŁ ZA POMOCĄ CHROMATOGRAFII GAZOWEJ

Instytut Technologii Żywności Pochodzenia Roślinnego, Akademia Rolnicza, Poznań

Streszczenie

W pracy sprawdzono przydatność stosowania metody „head space", zagęszczania na adsorbentach oraz metody destylacyjno-ekstrakcyjnej do wyodrębniania lotnych składników opakowań w celu ich analizy metodą chromatografii gazowej.

Metoda „head space" pozwala na analizę bardzo lotnych składników opakowań występujących w dużych stężeniach. Koncentracja związków lotnych na polimerze Chromosorb 106 pozwala na zagęszczanie niektórych składników kilkaset razy w stosunku do próby wyjściowej. Metoda destylacyjno-ekstrakcyjna daje możność wyodrębniania z opakowań największej ilości lotnych składników. Stężenie wyodrębnionych składników metodą destylacyjno-ekstrakcyjną jest wystarczające do oceny węchowej eluowanych składników z kolumny chromatograficznej oraz do ich identyfikacji metodami spektroskopowymi.