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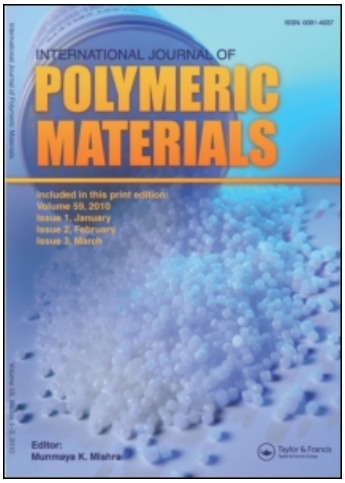


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# DETERMINATION OF SILICONE COMPONENTS CONTAINED IN PAPER MATERIALS WITH RELEASE PROPERTIES

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*Silicone components are commonly added to paper in order to reduce the sticking on the surface to favor the separation of commodities with fat matrix from the paper wrapping.*

*In this work infrared spectroscopy (in the HATR version) was evaluated for performing the quantitative determination of the silicone components content present on the surface of the aforesaid packages.*

*The proposed method is demonstrated to distinguish papers that are differentiable for a content of at least 0,1–0,2 g/m$^2$, furnishing results in rapid and predictable way and not necessitating any preliminary sample preparation.*

*Its application has allowed, for example, to determine the different level of silicone components that could be found in a paper used for oven-cooking of foods or in paper-packages for minicakes found on the market.*

*Keywords*: infrared, horizontal attenuated total reflection, silicone, paper

## INTRODUCTION

One of the characteristics required in some types of paper packages is to avoid sticking to the commodities that are in contact with the package. In this sense papers that wrap food products characterized by a rather fat matrix are typical.

The ''release property'' on the paper is obtained thanks to the addition in bulk (or as a coating) of polymeric compounds, chiefly methyl-silicone based. In fact, these polymers are already in the rubbery state at refrigeration temperatures and so they are the appropriate temperature to confer to the paper the desired release characteristics with respect to the commodities in contact with the surface. They also have the advantage of being biologically inert [1].

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The normal quantity of silicone compounds employed is in between 0,5 and 1 g/m$^2$, moreover bigger amounts would involve only an increase of cost without the benefits of measurable improvement of the release properties.

In some cases the paper factories also use other compounds (for example paraffin, *etc.*) to bestow on the material further increase of release character, although silicones remain the components most frequently employed.

Precisely, a GC-MS analysis of the headspace of papers used for food contact has demonstrated the real and marked presence of added molecules having infrared active C—Si bonds.

The existence of methods is known then in literature [2] that describe the extraction with solvents followed by measurements in infrared spectroscopy for determining silicone polymers.

Always remaining in the field of the infrared spectroscopy, in this study a more immediate method is purposed, based on the direct analysis of the paper material surface by means of HATR (the horizontal version of the Attenuated Total Reflectance) technique.

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## EXPERIMENTAL PART

### Materials and Instruments Employed

- FTIR Spectrophotometer: Philips PV9800 equipped with HATR device
- Software: Omnic 4.1a – Nicolet
- Detector: DTGS-KBr
- Window material: ZnSe
- GC-MS: Fisons Mega HRGC 5300 with capillary column Chrompack CP-WAX 52 CB 50 × 0,32 mm
- Paper samples with different content of silicone components
- Minicakes packages and paper for oven-cooking, commonly found in the market.

## PROCEDURE

Initially it has been verified by means of Headspace GC-MS Analysis, that the paper materials having "easy-release" properties show above all the volatilization of small molecules derived from di-methyl-silanol (Fig. 1).

In fact, gas chromatographic-mass spectrometry techniques are frequently used for measuring volatile silicones and other silicone by-products [3].

After this preliminary investigation, it has been then decided that the quantitative determination of the present silicone could have been performed by means of infrared spectroscopy, trying to identify some characteristic bands associated with the absorption of the terminal bonds (indicated in Fig. 1).

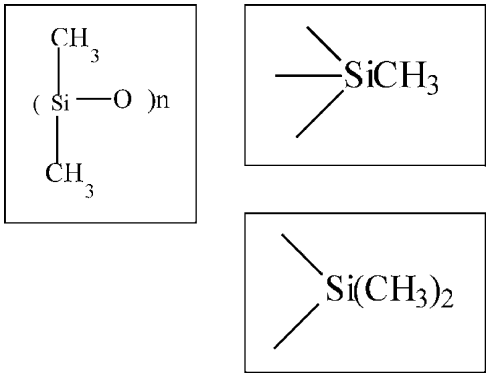


**FIGURE 1** Typical chemical structures produced by paper containing silicone compounds, heated during GC-MS headspace analysis.

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It has been elected to use the infrared technique called HATR, which is based on the following operation procedure: focusing the radiation in a crystal of IR transparent material and with elevated refraction index, results in internal reflection of the IR radiation. Setting a sample in contact with the crystal surface, the evanescent wave of each reflection is then attenuated by the same sample. The penetration of the evanescent wave in the sample for each reflection is in the order of a few microns or fractions of micron.

Among the factors that determine the real penetration of the ray in the sample there are: the incident angle, the refraction index of the crystal and the number of reflections. Additionally, the sample-crystal contact also influences the absorbance intensity of the recorded peaks: to exclude this aspect of variability, HATR is therefore equipped with a "little press" with a micrometric regulation of the applied pressure on the sample.

The optimal dimensions of a test sample for the analysis in this experimentation, compatible with those of the crystal employed in the spectrophotometer, coincide to a rectangle with a length of at least 100 mm and a width of 30 mm.

Therefore the test sample of paper is set under the crystal and pressed on it with an applied appropriate pressure (regulated through the spring of the little press previously said) which is maintained constant for all the analyzed standard samples and for the respective unknown samples.

The press reliability is very important: in fact if it isn't adequate it will require to create each time a new calibration curve using the same available paper samples with known content of silicone components.

Infrared spectra has been recorded with a scan-speed of 1,58 scans\second and a total of 64 scans for every samples.

The resolution used was equal to $4\,cm^{-1}$ and the infrared zone detected was in between 1400 and $700\,cm^{-1}$.

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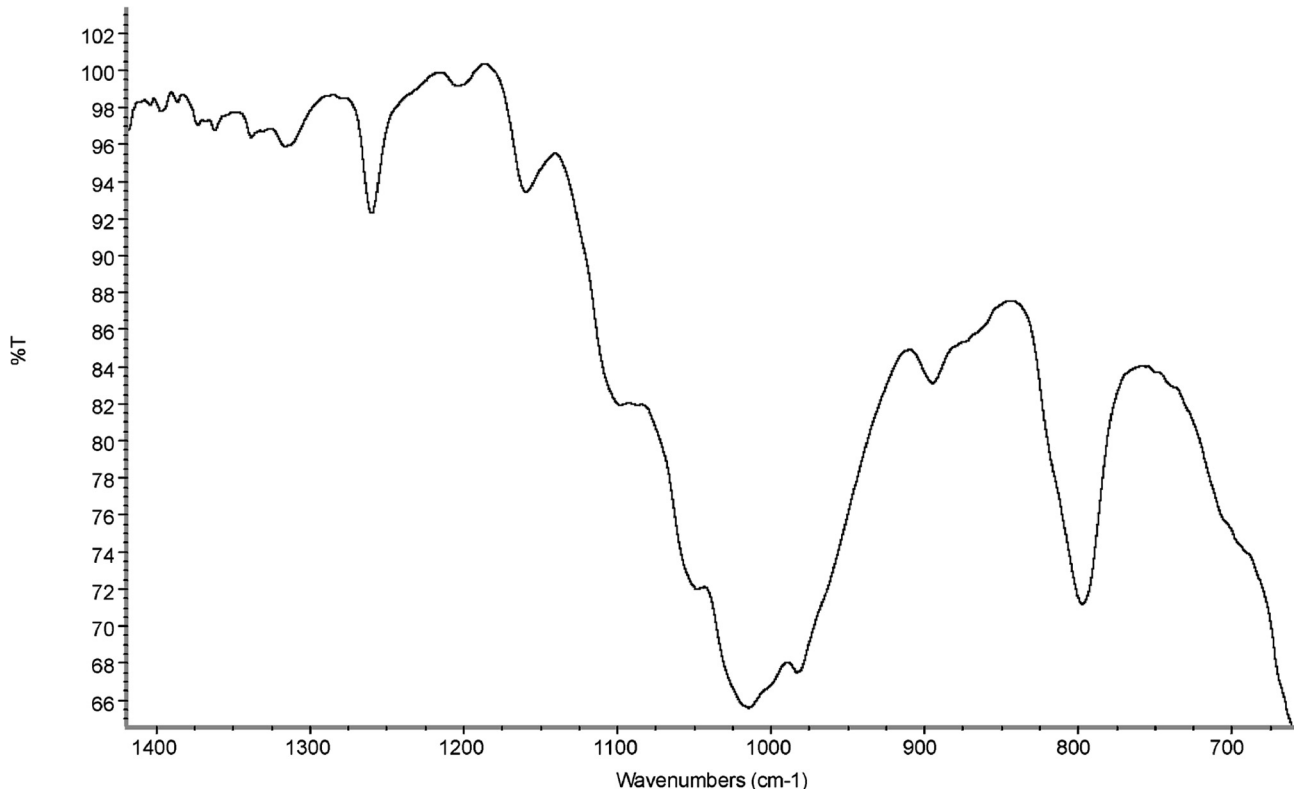


**FIGURE 2** Infrared spectra of a paper sample, which contains silicone compounds distributed on its surface.

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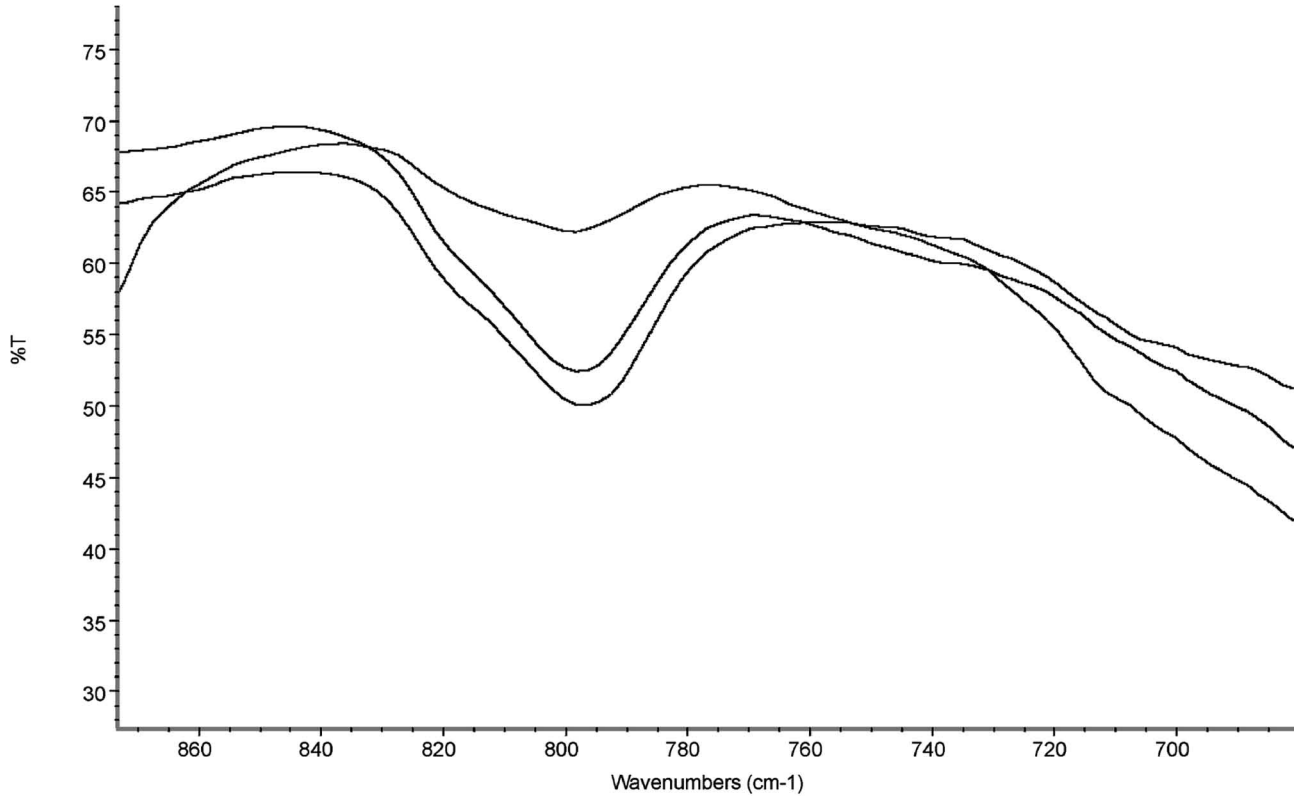


**FIGURE 3** Peaks area increase due to the presence of silicone compounds from 0,3 to 0,7 g/m$^2$.

## RESULTS

As may be noticed from the Figure 2, a characteristic peak of the IR paper samples spectra exists at a wavenumber of around 795 $cm^{-1}$. It has been verified that its area is proportional to the amount of silicone components present and, considering that it is located in a zone fairly free from interference, it has been selected as the "measure-peak".

At the same time, a "reference-peak" (invariant with respect to the level of silicone components) has been selected, *i.e.*, the wide peak centred at 1000 $cm^{-1}$ and included between the extremes of 840 and 1140 $cm^{-1}$.

In Figure 3, the increase of the measure-peak area could be observed in correspondence to the rise of the silicone content passing respectively from 0,3 to 0,5 and 0,7 $g/m^2$.

Finally the method has been applied to the control of the silicone content in a paper used for oven-cooking and in a paper material for the packaging of minicakes commonly present on the market.

Then, a calibration curve (Fig. 4) was constructed, using the measure-peak area and the reference-peak area, reporting the area-ratio as a function of the amount of silicone components added to the paper and expressed in units of $g/m^2$.

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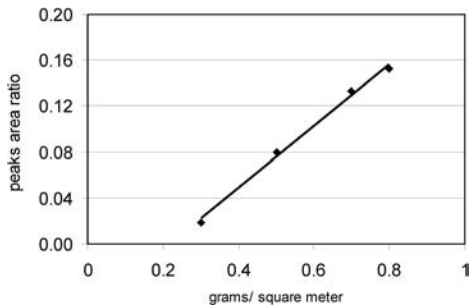


**FIGURE 4** Calibration curve – FTIR silicone compounds determination on paper materials.

**TABLE 1** IR data for calibration curve

| *Level of silicone compounds on paper surface* ($g/m^2$) | *Peak area at* 795 $cm^{-1}$ | *Peak area at* 1000 $cm^{-1}$ | *Peaks area ratio* |
|---|---|---|---|
| 0,3 | 132 | 7019 | 0,019 |
| 0,5 | 438 | 5476 | 0,080 |
| 0,7 | 504 | 3803 | 0,133 |
| 0,8 | 250 | 1636 | 0,153 |

**TABLE 2** Approximated silicone levels in test samples

| *Samples analyzed* | *Peak area at* $795\,cm^{-1}$ | *Peak area at* $1000\,cm^{-1}$ | *Peaks area ratio* | *Level of silicone compounds* ($g/m^2$) |
|---|---|---|---|---|
| Oven-cooking paper | 130 | 1045 | 0,100 | $\sim$0,7 |
| Minicakes-package | 80 | 950 | 0,084 | $\sim$0,5 |

The obtained results are shown in Table 2: a typical value to allow an easy removal of food cooked in a oven (placing it over the paper) is around $0{,}7\,gr/m^2$; in the case of a fluted paper cups for containing minicakes the measured value is around $0{,}5\,gr/m^2$.

## CONCLUSIONS

It has been demonstrated that the HATR infrared spectroscopy is a reasonably reliable technique and, above all, very convenient for discriminating different levels of silicone additives on paper materials added to enhance the release properties.

Moreover, the proposed method doesn't necessitate any preliminary sample preparation.

Samples with a known silicone content are directly obtainable from paper mills: with these standards a calibration curve could be quickly built based on a characteristic zone of absorption of the C—Si bonds.

Therefore, it become possible to determine the silicone content in unknown samples such as paper for oven-cooking or for the packaging of bakery products, sweets, *etc*.

In the future, an improvement to the obtained results will be necessary for a better validation of the method, extending the linearity range by means of other samples (always obtained from certified paper mills) with a silicone content higher than the levels tested here.

By the way, having focused only on the surface layers of the material, the HATR technique allows a rapid execution of the analysis; also, the results are particularly suitable for characterizing the effective silicone content present at the interface between the package and the commodity: the part that is directly responsible of the release properties.

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