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Studies on the usability of recycled PET for food packaging applications

Abstract The need of and opportunities for recycling of plastics for food packaging have been recognized, and a lot of work to find meaningful and cost-effective solutions to this issue is in progress. The safety of recycled plastics for food contact use is largely dictated by the ability of post-consumer contaminants to absorb into recycled materials and later diffuse from recycled plastics into the food. The objective of the present study was to establish a suitable analytical approach to identifying and quantifying any chemical substances that derive from the earlier use and remain in the polyethylene terephthalate (PET). A simple gas chromatographic technique using flame ionization detection was developed to allow quantification of solvent extractable compounds in a series of recycled PET samples. Identification of the nature and extent of contaminants in the PET samples was also attempted using GC/MS analysis.

Keywords Recycled polyethylene terephthalate · Food packaging materials · Gas chromatography analysis · Contaminants

Introduction

Under the influence of environmental considerations, plastics' recycling is a growing economic activity. The need to open up new channels for discarded packages has stimulated the recycling of plastics to produce new packaging materials. Such technical processes are being developed for the most widely used polymers: polyolefins, polystyrene, polyvinyl chloride and polyethylene terephthalate (PET) [1].

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Plastic food packaging materials manufactured from waste food packaging raise concerns about safety and organoleptic quality. The contamination problems for recycled plastics from contact with non-food products affect plastic containers [2, 3].

Considerable progress has been made from a scientific point of view in the understanding and physicomathematical modeling of diffusion processes of adventitious hazardous compounds from a recycled plastic in direct contact with food. The central question concerning the reuse of recycled plastics for food packaging is the lack of knowledge about the components present in the recycled materials such as pesticides or household products, which could migrate from the package into the food [2, 4, 5, 6].

There exist neither in the US nor in Europe any regulations or directives for the use of recycled plastic materials for food packaging. In the last few years the FDA has developed an informal guidance document entitled "Points to consider for the use of recycled plastics in food packaging: chemistry considerations". The guideline separates post-consumer contaminants into four broad groups based on volatility and polarity. By this guideline polymers should not impart more than 0.5 ppb of any contaminant to the food supply. This critical cutoff has come to be known as the "threshold of regulation" [5, 7]. In the EU, only article 2 of the framework directive 89/109/EEC can be applied which requires very generally that the consumer's health must not be endangered.

PET is widely used for packaging of beverages, as it is more resistant than other types of plastics to CO_2 permeation losses. It is a low diffusivity plastic (i.e. it doesn't allow severe penetration of organic compounds into the plastic) and is the most promising polymer for reuse as a food packaging material. In 1993, 450 million pounds of post-consumer PET bottles including 40% of all carbonated soft-drink bottles were recycled in the USA. The 1993 recycling rate of plastic packaging was 6.9% with PET at 28% [8, 9].

Concerning PET recycling two main processes are currently applied:

a. Conventional PET recycling, involving the following steps: sorting, grinding, washing and drying. The use of the resulting material for direct food contact should be avoided or it should be used in connection with an appropriate food contact barrier layer. Risk from contaminant migration into food would be expected to be negligible, provided that the recycled resin was separated from the food by an effective barrier constructed of regular virgin resin or other appropriate material [1, 10, 11, 12]

b. "Super clean" PET recycling, that is, conventional PET recycling with an additional deep cleansing process, for example, solid state post-condensation. The resulting material can be expected to be suitable for direct food contact applications.

In any case, the cleaning efficiency of the recycling process should be evaluated by a challenge test. Another necessary requirement for food contact applications is the quality assurance of the recycled product. Therefore, there is a need for the development of a quick quality assurance method to determine any unwanted concentrations of chemical substances, which can migrate from the recycled material to the foodstuff.

Since it is a well-established fact that food constituents and other compounds can be sorbed by packaging polymers [13], the aim of the present work was: (a) to develop a rapid and simple method for extracting and analyzing sorbed compounds from recycled PET materials, and (b) to draw up a statistical overview of the nature and extent of contaminants in PET recovered from the food packaging market.

Materials and methods

Materials

Five PET samples were used for method development. Table 1 summarizes the PET samples. For further validation of the analytical method, 17 recycled PET samples (flakes and pellets) were used. Sources of the samples were taken from as many EU countries as possible. These materials were treated by either a conventional or a super clean recycling process. All chemicals and solvents used were of analytical grade (i.e. purity>99%) purchased from Merck (Darmstadt, Germany).

Analytical method

Establishment of the most appropriate method to extract contaminants from PET samples. In the present work, four different extraction procedures (a, b, c, and d) using all five samples of Table 1 (V, G, R1, R2, and B) were applied.

a. Solvent extraction using $CHCl_3$: 0.5 g of PET material was extracted with 5 ml $CHCl_3$ at 60 °C for 48 h.

b. Solvent extraction using CH_2Cl_2: 0.5 g of PET material was extracted with 5 ml CH_2Cl_2 at 60 °C for 48 h.

c. Solvent extraction using 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)/2-propanol combination: 0.5 g of PET material was swollen with 1 ml HFIP at 40 °C for 24 h. The swollen material was further extracted with 4 ml 2-propanol at 60 °C for 24 h.

Table 1 PET samples used for method development

Sample	Description
R1	Post-consumer PET flakes from Texplast, Germany, washed and ground soft drink-bottles, colorless
R2	Post-consumer PET flakes from PlastConsult, Spain, washed and ground water-bottles, blue
G	Post-consumer PET flakes from PolyRecycling, Switzerland, washed and ground soft drink-bottles, colorless, regranulated with a twin-screw extruder with vacuum degassing
V	Virgin PET material from Hoechst, Polyclear T 86
B	Single-use Coca-Cola bottle, rinsed with water, purchased from a local supermarket

d. Solvent extraction using a $CHCl_3$ /CH_2Cl_2 combination: 0.5 g of PET material was extracted with 5 ml of a $CHCl_3$/CH_2Cl_2 (1/4 v/v) mixture at 60 °C for 48 h. The extracts were GC-analyzed with the internal standard method. Ethyl myristate was used as the internal standard.

A typical chromatogram of sample B extracts using the HFIP/2-propanol extraction method is shown in Fig. 1. Similar chromatograms were also obtained for the extracts of the other PET samples.

GC analysis. The GC unit used was a Fisons 9000 series gas chromatograph equipped with an auto injector and a flame ionization detector. The separation column was a 30 m×0.32 mm internal diameter fused silica capillary DB-1 with a film thickness of 0.25 µm. The following GC parameters were kept constant: detector temperature, 315 °C; injector temperature, 220 °C; injection mode, split ratio ca. 10 ml/min; injection volume, 1 µl. The column temperature program was as follows: 50 °C (4 min), from 50 °C at a rate of 10 °C/min to 310 °C (10 min). The carrier gas was He, at a flow rate of 1.45 ml/min.

Identification of the contaminants in the PET samples was performed using a GC/MS system consisting of an HP 6890 series gas chromatograph, an HP 5973 mass selective detector and a Wiley 275.L data base system. The gas chromatographic conditions were as follows: separation column, a 30 m×0.25 mm internal diameter fused 5% phenyl methyl siloxane capillary HP-5MS with a film thickness of 0.25 µm; injector temperature, 220 °C; injection mode, split ratio ca.10 ml/min; injection volume, 1 µl. The column temperature program was as follows: 50 °C (4 min), from 50 °C at a rate of 10 °C/min to 280 °C (10 min). The carrier gas was He, at a flow rate of 0.7 ml/min, and the interface temperature was 280 °C. The mass spectrometer was operated under the following conditions: 70 eV electron energy and 230 °C ion source temperature.

Results and discussion

No measurable amounts of contaminants (either specific recycling compounds or compounds coming from the prior use of PET) were identified in the extracts of the samples R2, G and V. In the other two samples (R1 and B), only compounds originating from the first use of the PET bottle, i.e. limonene and traces of other soft drink flavorings like γ-terpinene and *p*-cymene were detected. More specifically, the concentration of limonene determined in the extract of sample R1 was 6.2 µg/g of plastic and the corresponding concentration in the sample B ex-

Fig. 1 GC profile of sample B extracts (extracted by HFIP/2-propanol combination)
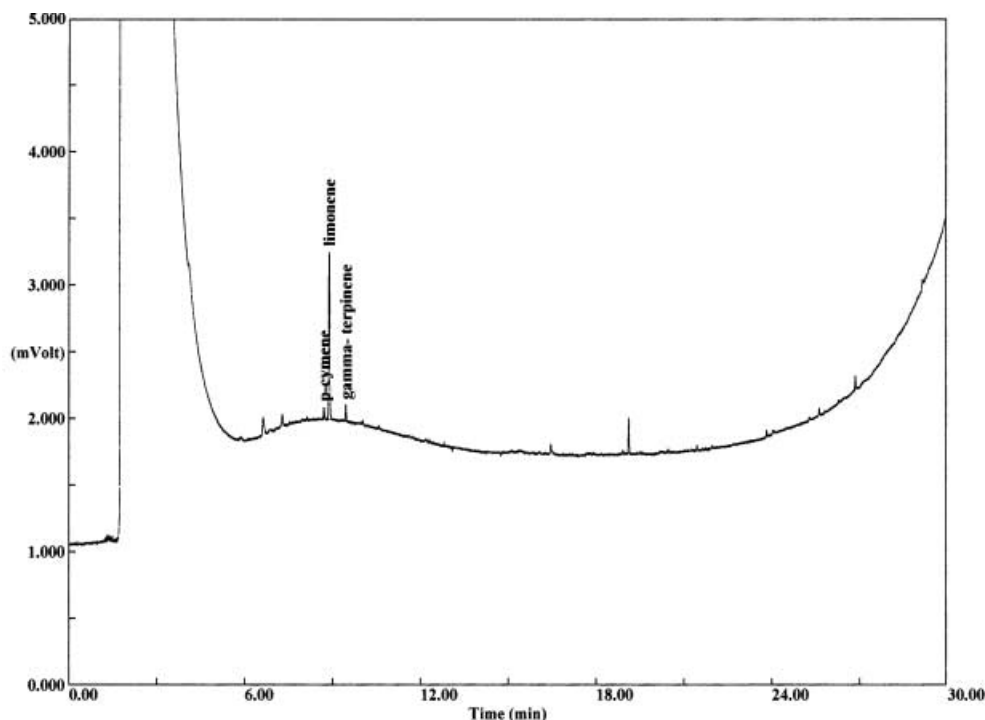
tract was 10.3 μg/g. Our results on limonene concentration in sample B (a single-use PET bottle containing a cola-type carbonated beverage) were comparable to those of Nielsen [14] who measured an average limonene sorption of 9.90 μg/g from carbonated orange juice into PET bottles after 12 weeks' storage at 25 °C. The lower concentration of limonene found in sample R1 (conventional recycling PET flakes) can be justified by the washing and drying steps during the recycling process, resulting in a reduction of the contaminant concentrations [15].

Concerning extraction efficiency, the results obtained show that both HFIP/2-propanol and $CHCl_3/CH_2Cl_2$ combinations seem to be suitable extraction solvents. It should be noted, however, that the possible contaminants in the recycled PET material are mainly located inside and not on the surface of the flakes, as surface contaminants are mostly removed during the recycling process. HFIP is a very aggressive solvent causing extensive swelling of the polymer even at room temperature and extracts all PET substances more indiscriminately. Therefore, the extraction procedure using HFIP/2-propanol combination was eventually considered to be the most appropriate extraction method in the present study.

Identification of the nature and extent
of contaminants in recycled PET samples

Several investigations have shown that considerable amounts of aroma compounds in juices can be dissolved in plastics packaging material. The extent of sorption was dependent on temperature and carbon-chain length. PET is relatively inert to these interactions and the loss of flavor components is of little significance for the product [14, 15, 16, 17].

Identification of any chemical substances coming from the earlier use and remaining in the PET was performed by compositional analysis of the PET sample extracts in direct comparison with analysis of virgin material extracts. In this way the typical virgin PET components can be identified and distinguished from recycling related substances. Attention was also given to semi-quantification of unknown substances. A total of 17 recycled PET samples (coming from both conventional and super-clean recycling processes) were analyzed. The identification of the compounds was performed by GC/MS analysis. A typical GC/MS chromatogram of the extract of a conventional recycling PET sample is presented in Fig. 2. Similar chromatograms were also obtained for the other PET extracts. As can be seen in this figure, two peak groups can be recognized. The first group is a post-consumer typical peak group with flavor compounds from the soft drink. The results on the quantitative determination of the identified substances in the extracts of the 17 recycled samples are summarized in Table 2.

The data presented did not indicate the presence of measurable recycling-specific compounds other than those originating from the first use of the PET bottle. These compounds included soft drink flavorings like limonene and γ-terpinene as well as *p*-cymene, a substance that could result from the dehydrogenation of γ-terpinene or limonene or both [18]. Of the 17 recycled PET samples tested, the 13 samples of the conventional

Fig. 2 GC/MS chromatogram (total ion current) of the extract of a recycled polyethylene terephthalate (PET) sample
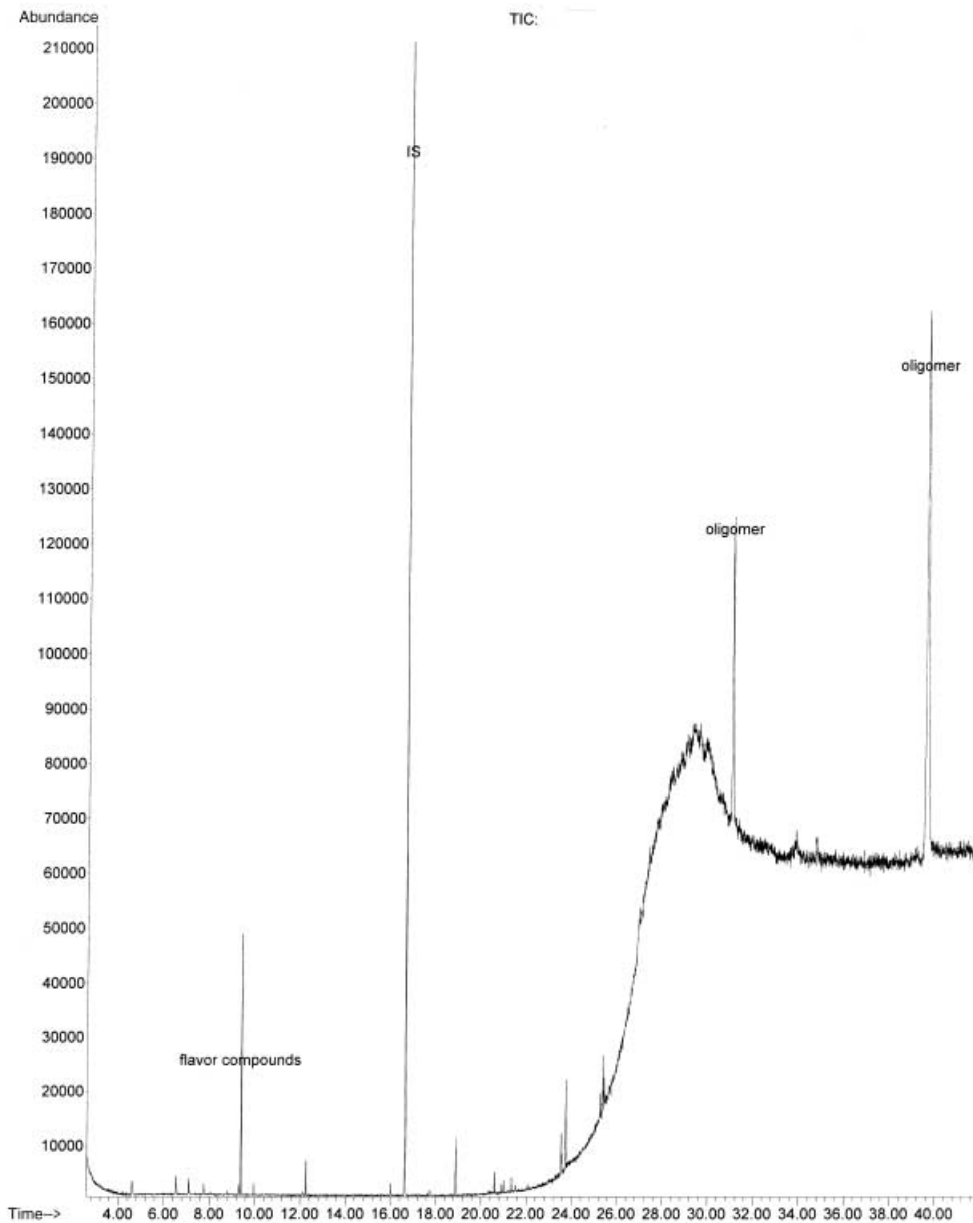

Table 2 Quantitative estimates (micrograms/gram of plastic) of residual flavor components in recycled PET samples. Detection limit: 0.10 μg/g plastic. *ND* Non-detected

Sample no.	Recycling method	Limonene	γ-Terpinene	*p*-Cymene
1	Conventional	5.7	<1	<1
2	Conventional	4.3	<1	<1
3	Conventional	4.2	<1	<1
4	Conventional	7.9	<1	<1
5	Conventional	6.4	<1	<1
6	Conventional	4.6	<1	<1
7	Conventional	5.2	<1	<1
8	Conventional	3.8	<1	<1
9	Conventional	4.4	<1	<1
10	Conventional	2.6	<1	<1
11	Conventional	15.0	1	<1
12	Conventional	12.6	<1	<1
13	Conventional	3.5	<1	<1
14	Super clean	ND	ND	ND
15	Super clean	0.1	ND	ND
16	Super clean	ND	ND	ND
17	Super clean	ND	ND	ND

Fig. 3 Mass spectra of the
extracted PET oligomers
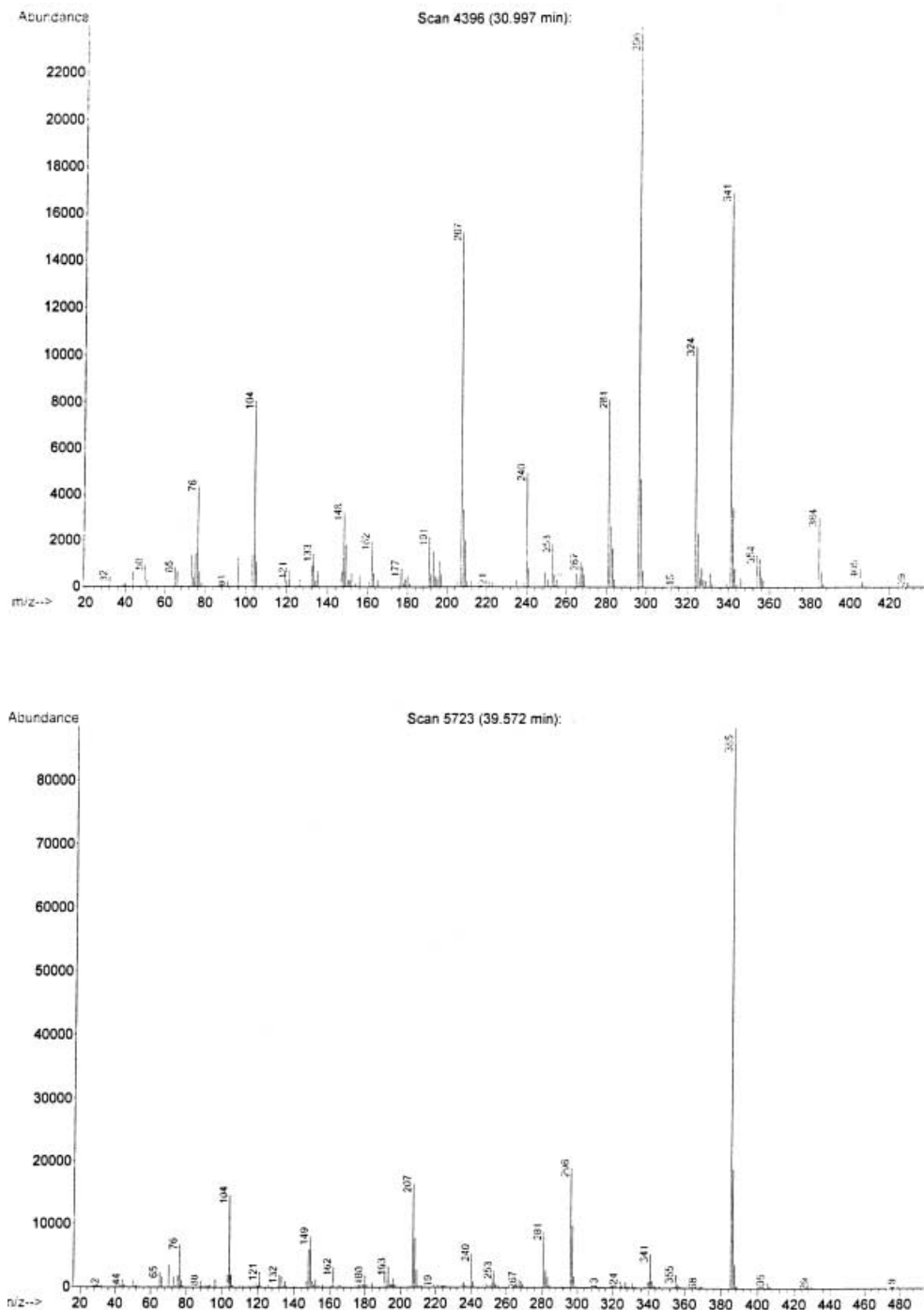
recycling contained limonene as the predominant species in the analyzed extracts. It was determined in concentrations ranging between 2.6 and 15 ppm, whereas γ-terpinene and *p*-cymene were semi-quantified at around one-tenth the level of limonene (Table 2). Limonene, a non-polar and volatile substance, diffuses so rapidly that it is probably present in the matrix of the polymer and therefore cannot be easily removed by washing. Analogous findings have been reported by other investigators [16]. On the other hand, in the extracts of the recycled samples produced by the super-clean recycling process, no measurable amounts of limonene or other recycling-related compounds have been detected. This is indicative of the excellent cleansing efficiency of the commercially applied super-clean recycling process. These materials are identical to the virgin PET and could be safely used for direct food contact applications.

In order to identify the second peak group of Fig. 2, GC/MS analysis was also carried out. The corresponding mass spectra are shown in Fig. 3.

The spectral library was not able to positively identify these compounds. The first peak of this group showed a molecular weight of 385 and the second peak showed a molecular weight of 428. The molecular weights of these peaks have also been confirmed by other investigators [19, 20] who have suggested that these peaks correspond to cyclic oligomers of PET. According to the above observations, the first of these peaks could be attributed to a cyclic dimer ($C_{20}O_8H_{16}$) and the second peak to the same dimer with an extra ethylene glycol unit ($C_{22}O_9H_{20}$). PET oligomers, identified in both virgin and recycled PET sample extracts, are inherent to the PET matrix and are not recycling related contaminants.

In conclusion, the above method can be used to quantify flavoring compounds (limonene, γ-terpinene, p-cymene etc) and other recycling-related residues in recycled PET samples with very little test sample preparation. Other methods are often laborious, time-consuming and performed using health-hazardous organic solvents [13].

A re-use of post-consumer recycled PET for direct food contact applications is possible. New recycling processes with high cleaning efficiency are in principle able to produce such a high quality recycled material. However, the cleaning efficiency of the recycling process should be evaluated by appropriate test methods. It is also necessary to ensure the quality assurance of the recycled material production under consideration of the expected contact conditions. The proposed simple and rapid analytical GC method could be used for a fast quality control of the production of recycled PET, through the quantitative determination of flavorings and other recycling specific compounds in recycled PET samples. The results of the present study indicate that post-consumer PET samples obtained from the conventional recycling process might not always be adequate to allow the material to be used directly for food contact applications. On the contrary, recycling processes including additional ("deeper") cleaning procedures (the so-called super-clean processes) usually produce material suitable for direct food packaging applications.

Further measurements of real life contamination levels in recycled PET samples are in progress. The results of these studies will be published in due time.

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