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Development of a rapid micro-Raman spectroscopy approach for detection of NIAS in LDPE pellets and extruded films for food packaging applications

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ABSTRACT

Identification and quantification of Non Intentionally Added Substances (NIAS) at low concentrations and eventually their distribution on Low Density Polyethylene (LDPE) films is an important issue. As Raman spectroscopy techniques are innovative and sensitive analytical methods and do not require pretreatment and manipulation of the sample, these were used for the identification of NIAS in LDPE pellet and films, which are commonly used for food packaging applications. The aggregation state of NIAS in LDPE were observed by Raman imaging with micrometric resolution. Four main NIAS compounds were identified in granule and film surfaces by confocal Raman spectroscopy: calcite (CaCO_3), calcium sulphate (CaSO_4), polystyrene (PS) and titanium dioxide (TiO_2) in anatase form. By a semi-quantitative evaluation of the inorganic NIAS, 9.93 mg/kg of CaCO_3 , 1.62 mg/kg of CaSO_4 and 0.17 mg/kg of TiO_2 were estimated. The experimental findings achieved by Raman analysis were confirmed by the results obtained by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Moreover, the toxicity of the identified compounds was examined according to the Cramer rules.

Keywords: NIAS; Confocal Raman spectroscopy; Micro-Raman imaging; Food packaging.

1. INTRODUCTION

In the last decades, concerns over food safety issues, such as possible contaminations due to migration of dangerous substances in food matrices from food packaging materials, have increased among consumers. Non Intentionally Added Substances (NIAS) in Food Contact Materials (FCMs) represent a major issue for the food packaging and FCM industry. In general, NIAS are chemical compounds that can be present in food packaging matrices and whose presence is unexpected and often undesired [1]. NIAS originate from break-down products of food contact materials, impurities of starting materials, unwanted side-products and various contaminants from recycling [2]. It is generally accepted that only compounds below 1000 Da are considered NIAS. Substances with a higher molecular weight are regarded as inert towards migration due to their larger sizes [3].

The safety of FCM must be evaluated on the basis of the amount of chemicals that can migrate from the materials into food. The materials must be manufactured in compliance with EU regulations, including good manufacturing practices, so that any potential transfer into food does not raise safety concerns. The main risks concern the presence of unexpected and undesired chemicals which could be threaten human health; other possible risks regard the change of the food composition with adverse effects on the taste and odor. The Commission Regulation (EU) No. 10/2011 on plastic materials and articles intended to come into contact with food states that potential health risks in the final food packaging products or articles should be assessed by the manufacturer in accordance with the internationally recognized principles of risk assessment. In that regard, the European Food Safety Authority (EFSA) published a draft scientific opinion on recent developments in the risk assessment of chemicals in food related to the safety assessment of substances used in FCM, for public consultation [4] in which assessment of NIAS is briefly discussed. At the same time, the International Life Sciences Institute (ILSI) published a guidance on best practices for NIAS evaluation in FCM [5,6]. Central to NIAS risk assessment and the first step towards demonstrating NIAS compliance is to determine which substances are present in the FCM. While NIAS derived from side reactions and degradation products can broadly be predicted and used as a starting point for developing an analytical strategy, the NIAS due to contamination can occur at any point in the life cycle of the FCM and their identification is considered a significant challenge. Consequently, their individuation and quantification have to be carried out on the finished materials and articles.

An effective approach to the NIAS testing and risk assessment solution is based on the following steps: information gathering, analytical screening, identification of hazardous substances and final risk assessment. Currently, screening programs to identify and semi-quantify the presence of NIAS are executed with different sample preparation techniques (e.g. extraction with solvents under controlled

conditions) and analytical techniques (e.g. gas chromatography - quadrupole time-of-flight mass spectrometry (GC/Q-TOF), gas chromatography - mass spectrometry (GC-MS), liquid chromatography - mass spectroscopy (LC-MS) and inductively coupled plasma - mass spectrometry (ICP-MS)). By using sensitive advanced analytical techniques most NIAS are regularly detected but not their distribution. In the food packaging industry, the analytical techniques that are usually employed for detecting NIAS rely on mass spectrometry, mainly GC-MS to quantify volatile [7–10] and semi-volatile substance and triple quadrupole - Liquid Chromatography Mass Spectrometry (QqQ-LCMS) to quantify non-volatile and polar compounds [11–13]. These are targeted analytical methods which need internal standards composed of the same or similar chemical structures of the NIAS under investigation. Moreover, for an accurate determination of the amount of NIAS present in the food package, internal standards with also similar concentrations should be used.

Although GC-MS and LC-MS are powerful techniques, they have some limitations. In general, these techniques are more suited for the evaluation of targeted chemical compounds or at least belonging to the reference database for this reason unexpected chemical compounds could be difficult to identified. Moreover, these two techniques have limitations with regard to the range of analytes that can be handled. In addition, relatively to the ionization techniques compatible with to the LC-MS, MS fragment determination is difficult when there is no *a priori* knowledge on the structure and origin [1,3]. Lastly, all these determinations based on mass spectrometry are expensive and time-consuming, thus their use in a lab as a possible in-line detection is infrequent. In addition, these techniques do not provide any information about the distribution and the aggregation state of the contaminants in the sample, which is an important parameter the packaging industry production process and for the risk assessment purposes [4].

To overcome these issues, alternative techniques can be taken into account. Vibrational spectroscopies have already proven to be powerful techniques for the identification of chemical compounds, thanks to the unique chemical spectra they provide. Moreover, these are able to perform spectra in few seconds, and no pre-treatment of the sample is required. In particular, confocal Raman spectroscopy has the additional advantages of not undergoing water interference and having a high spatial resolution, thus allowing a chemical mapping of Raman active compounds on x-y plane with spatial resolution below 1 μm . In principle, confocal Raman spectroscopy enables an in-line characterization of granules and films for what concern Raman active NIAS, since a single spectrum can be recorded in few seconds and can provide information about their presence, their distribution and their aggregation state in the FCM.

Thanks to these characteristics, Raman spectroscopy techniques have already been widely used in food science for many years ([14–20] and they are promising candidate techniques for analysis in the food packaging industry [21] to quickly detect the possible contamination of raw material and final products by NIAS and their distribution in the FCM. Furthermore, by implementing these analytical methods, i.e. using signal enhancement techniques such as Surface Enhanced Raman Spectroscopy (SERS) and Tip-Enhanced Raman Spectroscopy (TERS), the limit of detection is further increased of orders of magnitude and the resolution reaches the nanometer scale.

Nowadays, at industrial level the routine procedure for a preliminary screening of possible inorganic impurities in granules and films intended for food packaging uses is the gravimetric ashes analysis [22]. However, this analysis has the main limitation of being a destructive technique, with a poor limit of detection (limited to 0.01 mg for a commercial analytical balance) and no specificity. The operating procedure consists in heating the organic matrix at high temperature (500 °C) so that this burns and, if

the resulting inorganic residues are significant by weight, these latter are subjected to further analysis based on mass spectrometry.

In this work a versatile, simple and reproducible procedure to detect, discriminate and semi-quantify NIAS in granules and extruded films of Low Density Polyethylene (LDPE) for food packaging applications was proposed. The analytical procedure was set up on the raw material as a model system to standardize the methodology for both qualitative and quantitative analyses. Moreover, micro-Raman mapping was exploited to measure the distribution and the identification of contaminants on industrial LDPE granule and films. The foreseen advantages rely on the rapidity and the low limit of detection of the technique, on the possibility to use untreated raw materials, to not use internal standards and to map the distribution of the contaminants and their aggregation state.

For a tentative semi-quantitative analysis of the inorganic NIAS, the ashes of the pellets were measured by Raman spectroscopy. For a comparison, NIAS were determined also with established analytical methods such as by gravimetric analysis and by ICP-MS. The toxicity of the identified compounds was estimated on the basis of the Cramer classes.

2. Materials and methods

LDPE was chosen in this study as a representative of the common FCMs for food packaging applications. In particular, the surface of 50 LDPE granules, their cross sections, and 10 portions of a LDPE film were investigated for the possible presence of NIAS.

The LDPE samples were provided by Plastotecnica SpA. The film (width 100 cm and thickness 40 μm) was obtained from the processing of the granules using a production blown line (die diameter 280 mm, die gap 1.2 mm, mono-extrusion, line's speed 41 m/min). The density of LDPE was in the range of 0.921 g/cm^3 – 0.923 g/cm^3 and the melt flow index was in the range of 1.8 $\text{g}/10$ min – 2.0 $\text{g}/10$ min

(measured at 2.16 kg). The pellets were colorless and no additives were added in the samples in any stage of the production, except commercial antioxidants.

Nitric acid (HNO₃ 68%) was purchased from Sigma-Aldrich (Milan, Italy) and was used for the preparation of the external standard solutions (1% in water) by dilution of a certified reference material and for the preparation of the solution samples to be injected in the ICP-MS. The solutions were prepared with Milli-Q quality water (18 MΩcm).

2.1 Qualitative analysis of LDPE granules and films

The LDPE granules and the extruded film were analyzed by Raman spectroscopy techniques for detection of possible NIAS both on the surface and in the bulk material. The samples were characterized without any preliminary treatment. In order to perform bulk material analyses, the granules were cut by a disposable scalpel and the internal surfaces were investigated by Raman spectroscopy. Confocal Raman spectra were obtained by a Thermo Scientific™ DXR™ Raman instrument. The microscope was equipped with a motorized stage with 1 μm of resolution in the X-Y plane and a charge-coupled device (CCD) detector. A preliminary optical investigation by using a 10× magnification objective of the surface of granules and film was performed for detecting possible inhomogeneities in the LDPE matrix. The spectra were then acquired in different points of the samples surface, by using a laser excitation source of 532 nm, 3 mW laser power and a 100× microscope objective, in the range from 50 cm⁻¹ to 3500 cm⁻¹ with a grating resolution of 5 cm⁻¹. In the case of detection of agglomerations which include contaminants, these latter were further characterized by micro-Raman imaging, which was carried out by a Thermo Scientific™ DXR^{xi} Imaging microscope, considering the same experimental parameters set for confocal spectra. This microscope is equipped with an Electron Multiplying CCD camera that allows to collect 600 spectra per second. In this way,

optical and chemical mapping of the contaminants was obtained, thus providing information of the agglomeration state and dimensions of the NIAS with real-time data visualization.

2.2 Ashes analysis of the LDPE granules

For the ashes analysis, a 1.5 g of sample taken from LDPE granules were weighted on a glass crucible and brought to a temperature of 500 °C. Then, the possible inorganic residues detected by gravimetry. The calcination temperature of 500 °C has been chosen since all the organic components are thus burned and removed, without any possible contamination from the crucible (the glass melting temperature is 1723°C). As preliminary cleaning procedure, the crucible was soaked in aqua regia (HCl:HNO₃ 3:1 v/v), rinsed thoroughly in water and dried with nitrogen. Then, it was degassed, keeping it in the furnace at 105 °C for 2 h, and then it was weighted. These steps were repeated as many time as needed for the crucible to be stable in weight.

An analytical balance SI 114 from Denver Instruments (maximum weight 110 g and resolution 0.1 mg) was used to estimate the weight of the LDPE granules after thermal treatment. The thermal treatment was carried out with a muffle Carbolite furnace RHF1400 and it consisted of a heating ramp from 20°C to 500°C in 30 min and then in keeping the temperature at 500°C for 30 min. By this thermal treatment, all the organic compounds of the samples burned and only inorganic residues, oxides and metals, remained for the analysis.

After the thermal treatment, the inorganic residues possibly present in the crucible were detected by optical inspection and analyzed by Raman spectroscopy and Raman imaging. The transparent glass crucible allowed the back-illumination of the sample, thus helping in the detection even of the smallest residual particles.

Then, ICP-MS technique was used for confirming by elemental analysis the presence of contaminants detected by Raman characterization. A Thermo Scientific ICAP-Qs ICP-MS equipped with a quadrupolar mass analyzer and a quadrupolar collision/reaction cell with flat electrodes (flatpole) was used for the detection of Ca and Ti. This instrument was calibrated with the external standard solutions composed of HNO₃ (1% in water) prepared by dilution of a certified reference material at 1 g/l, by using ⁴⁵Sc (100 ppb) as internal standard. Interference from polyatomic ions were removed by operating the collision cell He mode (the presence of He gas in the collision cell) with discrimination of the ions kinetic energy (He – KED). The following ions were used for quantitation: ⁴⁴Ca, ⁴⁶Ti and ⁴⁷Ti. Other operating parameter were: RF power 1450 W, Argon plasma gas flow 15 l/min, auxiliary gas flow 1.0 l/min, nebulizer gas flow 0.90 l/min, sample flow rate 1.0 ml/min, nebulizer type concentric, spray chamber impact bead, interface cones (sampler and skimmer) Ni collision cell, He flow 5.0 ml/min, extraction lenses potentials and KED bias optimized through the auto-tuning procedure by using the tuning solution suggested by manufacturer.

2.3 Evaluation of the toxicity of the identified NIAS

Cramer classes were applied in order to estimate the toxicity of the identified compounds. Toxtree v3.1.0 (Ideaconult Ltd., Sofia, Bulgaria), based on a decision tree approach, was the used software. The substances are classified into three classes taking into account their chemical structures: class I corresponds to a low toxicity, class II corresponds to an intermediate toxicity and class III corresponds to a high toxicity ([23]).

3. Results and discussion

After a preliminary investigation with an optical microscope of the whole surface of granules and film, Raman spectra of the homogenous parts of LDPE samples were carried out (Fig. 1). The inset of Fig. 1 summarizes the assignment of the Raman bands to LDPE. The assignments are supported by Raman spectra of several kinds of polyethylene obtained in previous studies [24]. The characteristic bands of LDPE, clearly visible in Fig. 1, are: the symmetric CH₂ stretching mode at 2847 cm⁻¹, the asymmetric CH₂ stretching mode at 2882 cm⁻¹, the unresolved feature near 1439 cm⁻¹ due to anisotropic parts (CH₂ Fermi resonance), CH₂ twisting features near 1295 cm⁻¹ and the amorphous C-C stretching at 1128 cm⁻¹ and 1062 cm⁻¹.

Thanks to the micro Raman spectroscopy was possible to observe inhomogeneous parts in LDPE granules and films, composed of agglomerations with dimension of the order of μm². In fact, in the optical image of Fig. 2 the agglomerations are visible in white, while the black background represents the homogeneous parts of LDPE. The relatively large dimensions of these agglomerations are probably due to the fact that contaminants tend to migrate within the polymer and to form aggregates. By confocal Raman spectra four main compounds were identified as contaminants, as reported in Fig. 3 (a), (b), (c) and (d): calcite (CaCO₃), calcium sulphate (CaSO₄), polystyrene (PS) and titanium dioxide (TiO₂) in anatase phase. Fig. 2 also shows the micro-Raman maps with CaCO₃, CaSO₄ and TiO₂ superimposed on the optical images. The combination of these images demonstrates the consistency of the chemical and the morphological information. The same study was repeated for the bulk of the granules. It was not possible to analyze inclusions of PS by micro-Raman imaging because in the time needed to take the maps the laser degrades the organic materials, even if the laser power is reduced to the minimum (1mW). The CaCO₃ was found on the surfaces both of the granules and film. Traces of CaSO₄ were detected only on the surface of the granules. PS was found both on the surface and in the bulk of the granules. TiO₂ anatase was found both on the surface of granules and film.

In order to establish if the possible source of contamination was the 25 kg sack containing the LDPE pellets, a homogeneity study of the contaminants in granules accommodated in different location of a sack was performed. Ten granules were allocated at different distance with respect to inner surface of the sack and were analyzed in order to establish a possible contamination by the sack. Since no differences were found in this sense, as an alternative it was assumed that the contamination originate from the production process.

After the thermal treatment, micro-Raman imaging were used for the characterization of residues. An area of about 1 cm × 2 cm of the crucible containing the residues was characterized (See Fig. 4(a)). In this area 22 aggregates were observed. Fig. 4(b) reports that 9 aggregates were composed of CaCO₃ (yellow squares), 2 of CaSO₄ (green squares), 8 of TiO₂ anatase (blue squares) and 3 of TiO₂ rutile (black squares). The presence of TiO₂ rutile was due to the polymorph changes caused by the thermal treatment, where a portion of TiO₂ anatase changed in rutile phase. Fig. 4 (c) and (d) show the residues of CaCO₃ and of TiO₂ in anatase obtained by optical images and superimposed to the corresponding micro-Raman images. No traces of PS were detectable after the thermal treatment.

Since these compounds, already present before the thermal treatment, were neither expected nor desired, they can actually be considered as NIAS.

By gravimetric analysis, i.e. by weighting the crucible before and after the thermal treatment, no residues were determined because the residues amount is below the resolution of the used analytical balance (0.1 mg).

The analysis of residues of the LDPE granules by ICP-MS after the thermal treatment shows the presence of Ca and Ti, with a measured concentration of 0.10 mg/kg and 3.585 mg/kg respectively, with an instrumental uncertainty of about 20 % for both them. In this sense, the Raman and ICP-MS analysis are consistent, since the results of Raman analysis show the presence of CaCO₃, CaSO₄ and

TiO₂ in the LDPE matrices, and the ICP-MS data confirm the presence of Ca and Ti in the ashes residues. Despite the concentration of these compounds is very low, at trace levels, the following consideration can be done: i) assuming that all the Ti present in the LDPE samples is in form of titania polymorph (TiO₂), a semi-quantitative estimation of the concentration of TiO₂ in the granules and film can be carried out. Indeed, considering that the ratio between the atomic weights of O (15.999 u) and Ti (47.867 u) in TiO₂ is 0.334 and that for each Ti atom two O atoms are present, from the results obtained by ICP- MS that for Ti was of 0.1 mg/kg, a concentration of 0.17 mg/kg for TiO₂ was calculated. ii) The large amount of Ca found in granules and film by elemental analysis is confirmed also by Raman analysis by the presence of two compounds containing Ca (40.078 u): CaCO₃ and CaSO₄. The deductions on the respective concentration of the latter are more difficult than in case of TiO₂. On the other hand, by micro Raman imaging of the ashes on the crucible, a large abundance of CaCO₃ was found compared to that of CaSO₄ (9 and 2, respectively, out of 22 aggregates in the investigated area). Based on this consideration, a preliminary evaluation of the concentration of CaCO₃ and CaSO₄ was done, with a similar consideration as above in the case of TiO₂. If all the Ca present in the granules is in form of either CaCO₃ (molecular weight 100 mg/mol) or CaSO₄ (molecular weight 136 mg/mol) in the proportion of 9:2 then the concentration of CaCO₃ and CaSO₄ can be evaluated of 9.93 mg/kg and 1.62 mg/kg, respectively.

According to the Cramer classes, the inorganic NIAS, CaCO₃, CaSO₄ and TiO₂, detected by Raman spectroscopy belong to the class III because they are not the normal constituents of a human body.

Moreover, NIAS contains substances other than C, H, O, N, divalent S, which don't curs only as a Na, K, Ca, Mg, N salt, phosphate, sulphamate, sulphonate, sulphate and hydrochloride.

Concerning the traces detected by ICP-MS, any Raman active molecule was also detected by spectroscopic analysis, therefore any further consideration can be done in this respect, except to the fact

the some NIAS are present in the samples, in the form of chemical compounds containing both transition metals and an alkaline earth metals (Mg). The largest abundance is measured for Al (1.19 mg/kg), Zn (0.67 mg/kg), Mg (0.56 mg/kg), Fe (0.45 mg/kg) and Cu (0.41 mg/kg).

In conclusion, Raman spectroscopy was demonstrated to be a sensitive technique for detecting NIAS in the LDPE granules and films intended for food packaging applications. The distribution of the NIAS between the surface and the cross-section of LPDE granules seem to indicate that CaCO_3 and CaSO_4 originate from the environmental contamination, since their presence was detected only at the surface of the granules, while the PS and TiO_2 contamination came from the production process of the granules, such as, for instance, from previous batch of other material, as they were found in bulk material as well. By micro Raman imaging it is possible to understand the distribution of inclusions in the sample, and their agglomeration state. On this base it could be considered as a suitable technique for a semi-quantitative analysis of inorganic impurities in the surface of granules and films.

The limit of detection of Raman spectroscopy is below that of the gravimetric method, and it is able to discriminate the different types of contaminant. The results obtained by Raman spectroscopy were confirmed by the ICP-MS analyses.

This approach can be implemented for performing non-destructive and in-situ analysis of the surface of granules and films without any pre-treatment of the sample, in a little time-consuming and in very much effective way, thus addressing the stringent needs in food packaging industry related to food safety and risk assessment issues.

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Data availability

The raw data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study. The processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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FIGURE CAPTIONS

Fig. 1 Raman spectra of the LDPE matrix and the assignments of Raman bands in the inset.

Fig. 2. Micro-Raman imaging of inhomogeneous parts of LDPE samples (white parts) inclosing the agglomerations with CaCO_3 (a), CaSO_4 (b) and TiO_2 in anatase phase (c).

Fig. 3. Raman spectra of CaCO_3 (a), CaSO_4 (b), TiO_2 in anatase phase (c) and PS (d).

Fig. 4. Distribution of inorganic residues on the crucible (a) and their abundance (b). Optical images and micro-Raman maps of CaCO_3 (c) and TiO_2 in anatase phase (d) residues in the crucible after thermal treatment.

Fig. 1

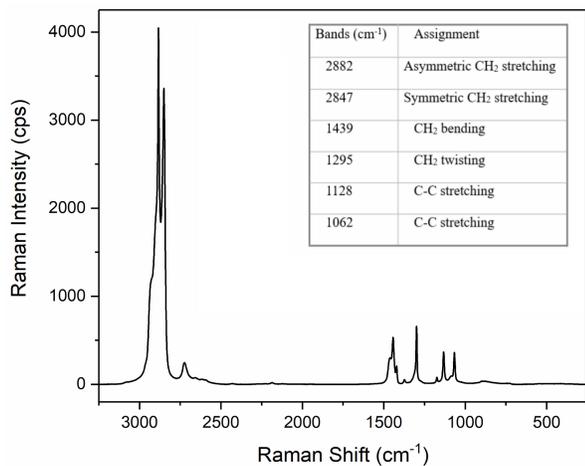


Fig. 2 (printed in colors)



Fig. 3

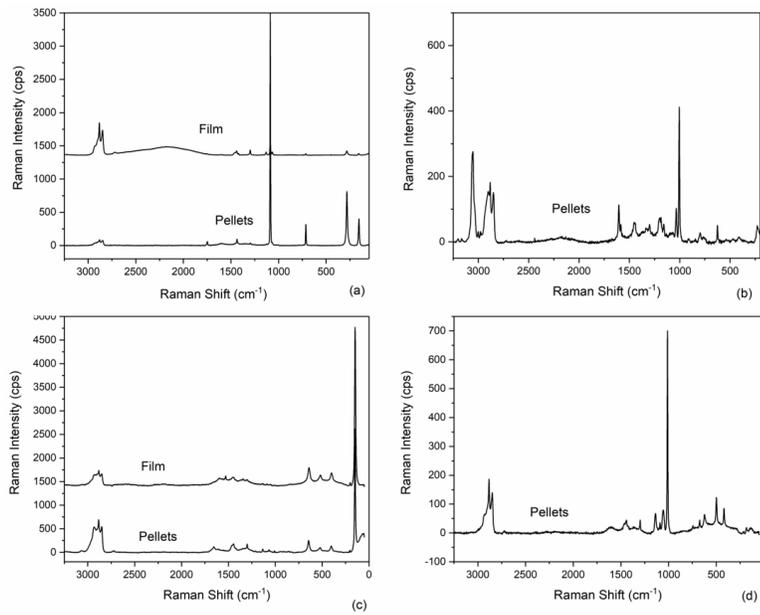


Fig. 4 (printed in colors)

