Contaminanti emergenti negli oli vegetali

Il giorno 15 novembre 2019 si è tenuto a Palazzo Turati, sede della Camera di Commercio di Milano, Monza-Brianza e Lodi un convegno organizzato da INNOVHUB - Stazioni Sperimentali per l'Industria, Area Oli e Grassi con la collaborazione di Assitol e Federolio.

Il convegno si è focalizzato sulla presenza di due classi di contaminanti che stanno creando da qualche tempo problemi e preoccupazione nel settore degli oli vegetali.
Si tratta della categoria dei derivati del glicerolo, quali esteri del glicidolo e dei monocloropropandioli, che si generano nel corso dei procedimenti di raffinazione e degli idrocarburi di origine minerale quali MOSH (Mineral Oil Saturated Hydrocarbons) e MOAH (Mineral Oil Aromatic Hydrocarbons).

Nel corso della giornata sono state presentate relazioni che per ciascun contaminante hanno analizzato la genesi del fenomeno, le tecniche analitiche a disposizione per la loro determinazione quantitativa, i riferimenti normativi, le problematiche relative al commercio e all'esportazione.

Nella sessione conclusiva inoltre due relazioni hanno esaminato la possibilità di mitigare la contaminazione nei prodotti finiti.

L'evento ha visto la partecipazione di specialisti a livello nazionale e internazionale, rappresentanti del mondo accademico e industriale, tecnici di laboratorio e ricercatori.

Pubblichiamo di seguito il titolo di tutte le relazioni presentate complete dei riferimenti dell'Autore e corredate, quando disponibile, di un breve riassunto redatto dall'Autore.

Abstract

MOSH AND MOAH: HISTORY AND STATE OF ART
MOSH E MOAH: STORIA E STATO DELL'ARTE

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UNI/CT/003/GL18 COMMITTEE: PROGRESS OF WORK
COMMISSIONE UNI/CT/003/GL18: STATO DEI LAVORI

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Currently, the most efficient method for the separation and analysis of MOSH and MOAH, is considered the ISO UNI EN 16995:2017. This method allows the determination of saturated and aromatic hydrocarbons (from C10 to C50) through the use of an High Performance Liquid Chromatography – Gas Chromatography – Flame Ionization Detector on-line approach. The principle on which the procedure is based is the separation of the two fractions, MOSH and MOAH, on a HPLC column taking advantage on an elution gradient; subsequently, through an Y-interface, the two fractions are sent singularly at the GC-FID system, where the actual detection occurs. On one hand, the advantages which this kind of analysis offers are several: by the elevated level of automation that includes an high efficiency in pre-separation, to low detection limits with high levels of reproducibility and accuracy. On the other hand, the main disadvantage

is that, although the Liquid Chromatography – Gas Chromatography on-line system is efficient and automated, it also has a high cost and is not readily available to all laboratories. Reason for which, it has been highlighted the need to develop a method that could be applied by multiple laboratories possible and that would not require the use of the on-line system Liquid Chromatography – Gas Cromatography. Within the experts participating to UNI CT/003/GL18 is emphasized the need to develop an alternative method able to detect, distinguish and measure the two fractions MOSH and MOAH that is available for multiple laboratories possible and that is not strictly related to the use of the HPLC GC online system, that was the main objective of a thesis work developed in INNOVHUB in 2018-2019. In this thesis an alternative method to the official ISO is proposed, which involves a SPE approach for the purification and separation of saturated and aromatic fraction eventually present in vegetable oil samples, followed by a revelation in Gas Chromatograph with Flame Ionization Detector. The results obtained applying this new methodology showed a congruence between the results obtained from the method proposed and the results of samples analyzed from other laboratories with their internal method. The method has been sent to UNI and is currently in draft status to receive comments, integration and for its validation process.
Moreover, in parallel way the MOAH problematic was treated in a way that could lay the foundations for future analysis of the aromatic fraction of mineral oil in a HPLC-Fluorimetric system. Thanks to its specific answer for the analytes' aromatic functional groups, the fluorescence detector has proved to be a valuable investigative tool. Thanks to the selection of two different channels of detection in the fluorimeter, the proposed approach also aims to lay the foundations for a future distinction between monoaromatic and polyaromatic molecules, since, the latter are the most relevant toxicologically. The results obtained show that there is scope to continue to investigate this issue and the need to do so with external standards even more representative for the analytes under consideration.

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- ISO UNI EN 16995:2017 - Foodstuffs. Vegetable oils and foodstuff on basis of vegetable oils. Determination of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) with on-line HPLC-GC-FID analysis

STANDARDIZATION WORK FOR DETERMINATION OF MINERAL OIL SATURATED HYDROCARBONS (MOSH) AND MINERAL OIL AROMATIC HYDROCARBONS (MOAH) IN VEGETABLE OILS, SEEDS AND MEALS

ATTIVITÀDI STANDARDIZZAZIONE PER LA DETERMINAZIONE DEGLI OLI MINERALI COSTITUITI DA IDROCARBURI SATURI (MOSH) E DEGLI OLI MINERALI COSTITUITI DA IDROCARBURI AROMATICI IN OLI VEGETALI, SEMI OLEAGINOSI E PANELLI

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Several cases of vegetable oil contamination with mineral oil hydrocarbons were reported (Biedermann, Bruhl, Fiorini). In each case, the contamination signal was characterized by gas chromatography (GC) as

a huge hump of unresolved complex mixture, with some thin peaks of odd-numbered n-alkanes that are naturally present in the seed.
According to the EFSA scientific opinion published in 2012, mineral oils are complex mixtures of hydrocarbons varying in carbon number and structure. Mineral oil saturated hydrocarbons (MOSH) consist of linear and branched alkanes (paraffins), and alkyl-substituted cyclo-alkanes (naphthenes), whilst mineral oil aromatic hydrocarbons (MOAH) include mainly alkyl-substituted polyaromatic hydrocarbons.
In 2019, JRC issued a guidance document covering sampling and analysis of MOSH and MOAH in food and food contact material in the frame of Recommendation (EU) 2017/84 for the monitoring of mineral oils (Bratinova & Hoekstra).
Meanwhile, three standardized methods were validated, covering the determination of mineral hydrocarbons in vegetable oils, in seeds and meals (Lacoste):

- in 2015, ISO/TC34/SC11 published a standard for the determination of MOSH in vegetable oils with a limit of application fixed at 50 mg/kg (ISO 17780: 2015);
- in 2017, CEN/TC275/WG13 published a standardized method based on on-line HPLC-GC/FID for both MOSH and MOAH determination, suitable above 10 mg/kg on basis on the results of the interlaboratory tests (EN 16995:2017),
- in 2019, CEN/TC327/JWG1 issued a draft method for the determination of MOSH and MOAH in animal feed by on-line HPLC-GC/FID.

The last listed method was validated by an interlaboratory study that was conducted in 2018. The fatty material is extracted from the commodity using organic solvent. After concentration of part of the solvent, the extract is submitted to an epoxidation step. The fractions of MOSH and MOAH are isolated and separated by an HPLC-GC-FID system. MOSH and MOAH fractions are separated on a silica gel column using a hexane- dichloromethane gradient and each one are transferred to GC while triglycerides are kept on the HPLC column. MOSH and MOAH are quantitated by internal standard added before analysis. Verification standards are added monitoring proper HPLC fractionation and GC transfer conditions.
A set of 3 oil samples and 8 feed samples delivered in double blind were assayed by 10 collaborating laboratories from five European countries. Sample matrices included refined sunflower oil, crude soybean oil, bleached palm oil, sunflower seeds, soybean meal, premix, chicken feed, pig feed ranging from 3 mg/kg to 286 mg/kg for MOSH, and from 0.3 mg/kg to 16 mg/kg for MOAH. Reproducibility (RSDR) ranged from 11.1 % to 25.3 % for samples containing more than 10 mg/kg of MOSH. Reproducibility (RSDR) ranged from 8.6 % to 25.9 % for samples containing more than 10 mg/kg of MOAH. Based on the precision data, the limit of application of the method was fixed at 10 mg/kg for both MOSH and MOAH with the method as described.

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SURVEY ON THE CONTENT OF MOSH AND MOAH IN VEGETABLE OILS

INDAGINE SUL CONTENUTO DI MOSH E MOAH NEGLI OLI VEGETALI

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ASPECTS CONCERNING TO THE EXPORT OF OLIVE OIL

ASPETTI RELATIVI ALL'ESPORTAZIONE DELL'OLIO DI OLIVA

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During the last few years, attention to the contamination of vegetable oils with mineral oils (MOSH and MOAH) by the large-scale retail trade, especially the German one, has increased up to the point of including very "restrictive" limits in the purchase specifications. Still remaining to the good practice of inserting into the commercial contracts higher or lower limits of analysis with respect to the current Regulations to improve the quality of the product, the reality of the facts in this case seems to have gone further. In the case of MOSH and MOAH contaminants, the bottling companies were forced to accept specifications with different limits according to different distribution chain, without the possibility to understand how the counterpart set these so restrictive values, sometime even not justified.

For producing companies therefore, it is more and more difficult to find feedstocks complying with the required specifications. The results from the German laboratories (recognized in the GDO specifications) are delivered within 7 working days after receiving the sample. This additional time has many consequences in the procurement of raw materials. At the moment it is not known if there is an analytical method that could be shared between the various laboratories and manufacturers. The fact that each laboratory uses an internal method of analysis also implies a poor reproducibility, and difficult repeatability of the data. Given the great uncertainty of measurement at these low concentrations, the difficulty arises for companies to understand whether a given lot of oil can be accepted or not. The consequence of this is that with these limits there is the risk of eliminating raw materials that could be of excellent quality, for a value of MOSH slightly exceeding the value of the specification (e.g. limit value of the specification for C17-C35 4.0 mg / Kg, measured value 4.3 mg / kg) and this seems completely meaningless. The various specification limits do not specify the criteria that led to the inclusion of the same and the reasons why a large retail chain takes into consideration only certain intervals of chain length of the interval (each with its own limit), while others take into consideration the whole spectrum of chain length. Therefore, the initial difficulties of selecting raw materials that conform to the specifications have been much greater, having also to fulfil different MOSH values in the interval between C10 and C50.

As a consequence, the bottling companies at the time of purchase of the raw material do not know whether this product will be accepted by the GDO or not, until the results of the different laboratories are received.

HISTORY AND STATE OF THE ART: NEW THRESHOLDS AND STATE OF ART FOR VEGETABLE OILS

INQUADRAMENTO STORICO E STATO DELL'ARTE: NUOVE SOGLIE E SITUAZIONI OLI VEGETALI

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3-MCPDe is one of the most discussed contaminant at European level related to vegetable oils and fats over the last three/ four years.

This contaminant, formed during the refining process of vegetable oils at high temperature, so far has no limit applicable to oils and fats.

At European level, some Countries proposed to set two different limits for different oils: first one at 1.250 ppb and second one at 2.500 ppb, while others prefer to have just one single limit for all oils and fats set at 2.500 ppb.

At International level, Countries producing palm oil are much interested to be involved in this discussion, because the new European Regulation under discussion could have many impacts for their productions.

Assitol (the Italian Association of vegetable oils and fats) is supporting actively the "one single limit proposal".

ANALYTICAL METHODS: EXPERIENCES AND PERSPECTIVES

METODI DI ANALISI: ESPERIENZE E PROSPETTIVE

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The problem of the presence of 3-monochloro-1,2 propanediol (3-MCPD), 2-monochloro-1,3 propanediol (2-MCPD), their fatty acid esters and the glycidyl fatty acid esters (GE), formed in heat processed fat-containing foods from glycerol or acyl glycerides in the presence of chloride ions, has attracted the attention of researchers since the end of the 70s and of the European health authorities since 2006.

The European Commission Regulation (EC) No1881/2006 prescribes maximum levels of 3-MCPD of 0.02 mg/kg (20 µg/kg) for hydrolysed vegetables proteins (HVP)) and soy sauce. This has since been revised with (EC) 290/2018 setting maximum levels for GE's in vegetable oils and fats of 1,000 µg/kg for the general population.

Consequently, the food oil producers must carefully monitor the levels of GE and, therefore, must have at their disposal reliable, specific, robust and validated analytical methods.

In response to the urgency of this problem, in the last few years several analytical methods have been developed and proposed. The foremost available methods are here reviewed and their relevant limits and advantages are discussed.

Innovhub-ISS is active in this field and, after a thorough analysis of the various available methods, laboratory experimentation and proficiency testing, the choice has fallen on AOCS Cd 29b-13 method. The activity and the future programs of Innovhub-ISS are here reported.

COMPANY EXPERIENCE ON THE MITIGATION OF GLYCIDIL ESTERS (GEs) IN VEGETABLE OILS

ESPERIENZA AZIENDALE SULLA MITIGAZIONE DEI CONTENUTI DI GLICIDIL ESTERI (GEs) NEGLI OLI VEGETALI

PAOLA TAMPIERI – TAMPIERI SPA, FAENZA

USE OF REFINED OLIVE HUSK OIL AS A TECHNICAL FLUID IN THE ORCHARD

IMPIEGO DELL'OLIO DI SANSA DI OLIVA RAFFINATO COME FLUIDO TECNICO IN OLIVETO

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This presentation deals with a research project recently started with the purpose of a complete or partial substitution of mineral oils in use in the agronomic procedure related to the olive oil production in plantations.

The final scope is to reduce the impact of undesirable contaminants in the olive oil and in all products of the production chain. Several possible intervention points have been individuated and for each of them the possible substitution Olive Husk Oil (OHO) will be tested:

a) Two stroke engines that deliver some non-combusted lubricants in the exhaust. OHO will be used for the lubrification of engines in use of pruning, shaking, blowing, cutting the grass, etc.
b) Chain save lost lubricants, even though in this case some vegetable oils of unknown nature are already in use. Also lost lubricants are used for the operation of moving hands and shakers during olive ripening.
c) Hydraulic fluids used in machines moving in the orchards and in the OHO extractions plants. A very important contamination with hydrocarbon product can be caused by the delivery of hydraulic oils in the environment caused by pipe failure or blowby.
d) The formulation of agronomic fluids against pests and microbes, where in classical use a light petroleum is used as a carrier or as a solvent of active substances.

The working programme consisting of a number of different actions is presented:

a) selection of orchards based on the presence of potential contaminating machines and on the presence of amounts of MOSH and MOAH to be determined after the olive oil extraction in a laboratory plant.
b) Tests on two stroke engines on bench test: if the preliminary evaluation will provide promising perspectives the machines will be transferred on the field
c) Test on chain saw and other lost lubricant machines, in order to understand if some problems can occur during the daily use, mainly during the cold season
d) Bench test for hydraulic acid formulation in a circuit mimic the hydraulic use in hard conditions. During this test all parameters related to oil degradation will be monitored.

e) Laboratory tests using OHO as the solvent for the dilution/dispersion of active agents to be used in case of need against pests and/or microorganisms. Active substances will be based on Brassicaceae meals and extracts.

A critical evaluation of each application, with PROs and CONs for each possible substitution is finally presented.

Le presentazioni autorizzate alla pubblicazione sono reperibili alla pagina web:

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