1. Introduction

No one wants to eat food that is unsafe and that can put their health at risk in any way or form. However, it is not that widely understood who is responsible for the evaluation of food safety and what is the foundation upon which they base their decisions. Therefore, a cold “risk assessment” of a food or of a single ingredient is a scientifically driven and complex process that intends to quantify the risk of adverse health effects that result from exposure of humans to hazards present in food or the environment over a specified period of time. It is complex because it consists of four steps that must be taken before we can evaluate the hazards and risks associated with a particular food. First, we need to identify hazards in a prospective (in vivo and in vitro tests) or retrospective (reviewing scientific data, incidents reports, and epidemiological surveys) way [1]. Then, for the identified hazards, we need to evaluate scientific data to determine whether the evidence is strong enough to demonstrate that a substance has the potential to cause harm. This step is called “hazard characterization”. Afterwards, we need to establish who may be harmed and at what level the exposure may be harmful. The answers are provided through the “exposure assessment” process in which we estimate the dose of a hazard to which a certain population may be exposed, usually through surveys of dietary intake. Both dose and duration need to be considered since the exposure can be “acute” and thus calculated over a short period of time using a meal or a day, or “chronic” with an estimate over the entire lifespan. Therefore, the actual risk estimate is obtained by comparing the level of exposure that can (theoretically) cause harm with the level of exposure that someone or a certain population would (realistically) experience.

If the real-life-exposure level is higher than that which theoretically causes harm, we can conclude that there may be a safety concern for consumers in the general population or for specific (vulnerable) groups [2].

The safety evaluation of food is a joint effort between risk assessors (organizations that evaluate the potential harmfulness of a food or ingredient) and risk managers (legal decision makers). In Europe, the risk managers are organizations such as the European Commission and the risk assessors are organizations such as the European Food Safety Agency (EFSA). Risk assessment has changed considerably since its first steps in the 1980s and contemporary risk assessment methods include conceptual models; uncertainty analyses [3]; and deterministic, probabilistic, and tiered approaches [4]. However, scientific information about the magnitude and extent of risks experienced by people and about the causes of those risks is a critical factor in any risk assessment and risk management decision process [5].
In recent years, we have seen an enormous development in all fields of food analysis. In particular, new analytical strategies were studied to improve the analytical sensitivity and to control new emerging contaminants. Despite this, the main target substances of analytical controls remain some categories of contaminants, such as residues of veterinary drugs or pesticides; presence of trace elements, particularly heavy metals; and several substances that can contaminate food in particular climatic or storage conditions, such as mycotoxins and biogenic amines.

The World health Organization estimates that around 600 million people worldwide die from foodborne diseases due to food contamination each year [6], highlighting the need to develop new analytical methods capable of verifying the actual presence of contaminants, even at trace levels. Furthermore, for greater control of contaminants, it is also essential to carry out monitoring focused on verifying the critical points and strategies useful for mitigating all food-safety issues.

Some major topics relating to novel approaches in food analytical chemistry have been indicated by the scientific community as being worthy of attention and improvement. The first is related to the so-called “green analytical chemistry” (GAC). This discipline was derived from Green Chemistry in the early 2000s, and it is devoted to the study of sustainable and more environmentally friendly laboratory practices. The GAC tries to find the right compromise between increased quality of the analytical results (in terms of sensitivity, selectivity, accuracy, and robustness) and improved environmental friendliness. It is based on 12 main principles that aim to reduce the sample amount and pretreatments, the use of reagents, the manual operations, and the energy consumption and to increase the automatization, the number of analytes detectable by a single analysis, and the analytical determinations made in situ [7]. Thus, all new procedures developed and proposed should be evaluated under the GAC point of view. In this regard, some mathematical and statistical tools have been proposed [8].

Another very interesting food safety aspect coming to the forefront in recent years is the possible simultaneous presence of different chemical contaminants in the same food, the so-called “cocktail effect”. Indeed, more than one contaminant may be present in the same food, and there are many interactions among these that can be hypothesized. These interactions may lead to an increase in toxicity as well as to partial detoxification. All of these effects must be statistically evaluated before confirming an effective risk. Moreover, the range of food to consider within these studies is very wide. Therefore, a large amount of data is needed. This concept (also known as “Cumulative Risk Assessment”) is that the health effect derived from the exposure to multiple agents or stressors, also at very low levels, can be higher than that caused by a single agent present at a level close to the limit for human consumption. In 2019, the European Food Safety Authority (EFSA) released a scientific report focused on understanding chemical mixtures in food. The report concluded that consumer’s level of concern from being exposed to combined effects of chemicals in food is high [9]. Studies about the cocktail effect have only been developed for multiple pesticides in food [10]. Thus, from this point of view, there are many gaps in our knowledge. For instance, taking as an example a widely consumed food such as meat, at least four main categories of chemical contaminants can be found, especially after cooking: heterocyclic aromatic amines, nitrosamines, polycyclic aromatic hydrocarbons, and acrylamide. Given the high toxicity of such contaminants, undoubtedly, the study of possible “cocktail effect” is urgent [11].

Another topic that requires special attention in food control is the availability of standardized procedures, properly validated. “Validation” is a term referring to the procedures adopted and developed by the laboratories in order to ensure the reliability of analytical methods. This procedure is essential in certifying an analytical method, according to the International Standard ISO/IEC 17025:2017, and for ensuring the method quality and performances. Today, it is still possible to find articles describing a novel analytical approach with no reference to validation parameters. In this way, the reliability of the proposed method is only argued by the authors, but it is not properly ensured through
the evaluation of validation parameters. These parameters are essential to both ascertain the compliance to the reference parameters and to compare the analytical method to other available methods. The full validation of a novel protocol is also important because it can be considered the first step when the standard method adopted for a certain analytical determination is outdated and the standardization of a novel procedure is desired. In this case, only fully validated methods can be considered for further standardization procedures. From this perspective, a particular effort and new analytical strategies are needed, especially for determining most harmful contaminants, such as mycotoxins, drug residues, pesticides, heavy metals, etc. [12,13].

This Special Issue is focused on new chemical approaches in food safety controls. We collected articles relating to new procedures, strategic approaches, and innovative technologies. The focus of the method development was the determination of contaminants in food, as well as risk assessment or monitoring of and other surveys dealing with food contaminants.

2. Review of Special Issue Contents

This Special Issue features eight original documents dealing with new analytical methods and their use for monitoring contaminants in food. These articles highlight how essential is to verify the presence of treatment residues, such as pesticides and veterinary drug residues, and of contaminants that often develop under opportune environmental and food storage conditions, such as biogenic amines, mycotoxins, and others. The present Special Issue also provides practical examples of risk and exposure assessment for different hazards and (populations) countries.

Four original articles report new findings in food analytical chemistry. The first paper describes a novel method for the determination of β-agonists in urine samples, developed by combining analyte separation, obtained by reversed-phase high-performance liquid chromatography, coupled with pulsed amperometric detection at a glassy carbon electrode. Other than the development of this method and its application to real samples, the authors described the validation procedure and its conformity with the European directives in terms of linearity, selectivity, precision, and recovery. The second paper reports a comparison between two analytical approaches, ELISA and ultra-high performance liquid chromatography with fluorescence detection (UPLC/FLD) for the determination of two important mycotoxins in cereals: T-2 and HT-2 toxins.

The authors describe the approach used to compare the two methods, developed by taking into account both the results obtained by analyzing 100 cereal samples and the validation parameters (sensitivity, linearity, selectivity, precision, and ruggedness). The authors conclude that the combination of both approaches is very effective for official control activities of cereals and derived products. The third analytical document focuses on a highly selective, sensitive, and reliable method for the simultaneous determination of 13 insecticides in vegetables.

This method is based on a pre-concentration of analytes, obtained by a three-dimensional microporous reduced graphene oxide/polypyrrole nanotube/magnetite hydrogel (3D-rGOPFH) synthesized as a magnetic solid-phase extraction (MSPE) sorbent. The analytical determination, by gas chromatography-tandem mass spectrometry, is validated in terms of sensitivity and accuracy, representing an effective novel tool for determining multiple classes of insecticide residues in vegetables. The last paper describes how the microbial assay for risk assessment (MARA) can be used for ecotoxicological testing in food safety. 

Boletus edulis, one of the most consumed wild mushrooms worldwide, was considered in this study as it is capable of accumulating many potentially toxic elements. After a comparison/confirmation by instrumental determination of 10 elements (Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, and Zn), the authors conclude that the MARA system can be applied for toxic identification if the targeted toxin is highly extractable in water.

Four original articles describe surveys of the most significant contaminants in food safety, such as pesticides, histamine, and aflatoxins. The first paper reports the evaluation...
of cereal-based product contamination by pesticide residues. The authors used a validated multi-residual analytical method based on gas chromatography and tandem mass spectrometry coupled with a rapid QuEChERS procedure. This method is used for the determination of 37 pesticides (pyrethroids, organophosphorus, and organochlorine compounds) in 209 commercially available samples of cereals and 11 legumes placed on the Italian market in 2018 and 2019. The results confirm that there are no trace of pesticides in legume samples, while 18 cereal samples are contaminated by at least one pesticide. However, none of these residues exceeded the maximum level demanded by the European Regulations. The second monitoring was carried in freshwater fish (carp) and the related contamination by DDT and DDT metabolites was evaluated. A survey about dietary habits was also conducted among fish consumers. The authors concluded that, although DDT contamination was sometimes verified, it was not found to be risky concerning the complete diet of the clusters. The third paper is focused on histamine contamination in fish products collected in Puglia and Basilicata (Italy), using a high-throughput two-tier approach involving a screening (ELISA test) and confirmatory method (HPLC/FLD with o-phthalaldehyde derivatization). Histamine concentration was detected in 51% of total batches with 2.5% non-compliance. Among 111 fresh tuna batches, 9 had a high content of histamine, up to 5542 mg kg$^{-1}$, which caused scombroid poisoning cases. The authors concluded that proper processing technology and storage practices are crucial for ensuring food safety of fish products and that a control is needed. The fourth article reports the assessment of exposure associated with aflatoxin M1 (AFM1) of the adult population in Serbia from the consumption of milk and dairy products through a Monte Carlo simulation. The study revealed moderate exposure risks compared with similar studies worldwide, confirming at the same time the need for continuous monitoring of AFM1 in feed and dairy supply chains.

3. Conclusions

This Special Issue is focused on food contaminants, their possible presence in food, and the new analytical methods developed for their identification and quantification. This Special Issue is subdivided into two sections: the first focuses on new analytical methods for food contaminants determination, and the second focuses on different methods of monitoring food contaminants and of performing risk assessments.

The original research examples collected in this Special Issue highlight the need for official controls and new analytical methods that are more effective compared with those that are available, and that are capable of identifying the highest number of food contaminants with high sensitivity, selectivity and accuracy in accordance with the principles of the green analytical chemistry.

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