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A QUECHERS method for sample preparation in the analysis of pesticides in tomato*

Métodos QUECHERS: una metodología para la preparación de muestras en el análisis de pesticidas en tomate

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Abstract:

Objective: Tomato crops are highly susceptible to pests. The use of pesticides during tomato harvest has consequently increased in recent years. This use has raised concerns about the presence of chemical contaminants in food, which may have harmful effects on health.
Materials and methods: To efficiently and reliably identify and determine the presence of pesticides at any of the washing, peeling or sterilization stages, the fast, easy, cheap, effective, robust, and safe (QuEChERS) method was created. Today, this method is successfully implemented for the monitoring of pesticide residues in tomato with recovery percentages and relative standard deviations meeting international standards.
Results: This review analyzes the application of the QuEChERS method for the identification and determination of pesticides in tomato through a review of the recent literature. In addition, a bibliometric analysis of the Scopus database between 2007 and 2021 is performed, finding that the most published areas are chemistry and agriculture, with China being the leading country with the most publications.
Conclusions: It is concluded that in most research, modifications are made to the method, such as the use of dicyandiamide sludge, obtaining good results in the extraction and recovery percentages with the advantage of having a lower cost and environmental pollution.
Keywords: QuEChERS methods, modifications, pesticides, residues, dicyandiamide.

Resumen:

Objetivo: El tomate es uno de los cultivos más susceptibles de ser atacados por plagas, por lo que el uso de plaguicidas durante su cosecha ha aumentado en los últimos años. Este uso ha suscitado preocupaciones sobre la presencia de contaminantes químicos en los alimentos, que pueden tener efectos nocivos para la salud.
Materiales y metodología: Para identificar y determinar la presencia de plaguicidas de manera eficiente y confiable en cualquiera de las etapas: lavado, pelado y esterilización, se crea una metodología rápida, fácil, barata, efectiva, robusta y segura (QuEChERS). Hoy se implementa con éxito para el seguimiento de estos residuos en tomate con porcentajes de recuperación y desviaciones estándar relativas según estándares internacionales.
Resultados: Esta revisión analiza la aplicación de la metodología QuEChERS para la identificación y determinación de plaguicidas en tomate, a través de una revisión de la literatura de los últimos años. Además, se realiza un análisis bibliométrico de la base de datos Scopus entre 2007-2021, encontrando que las áreas más publicadas son Química y Agricultura, siendo China el país con más publicaciones.

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Conclusiones: Se concluyó que en la mayoría de las investigaciones se realizan modificaciones en la metodología, como el uso de lodos de diciandiamina, obteniendo buenos resultados en los porcentajes de extracción y recuperación con la ventaja de tener un menor costo y contaminación ambiental.
Palabras clave: Métodos QuEChERS, plaguicidas, diciandiamina.

Introduction

Agriculture plays a fundamental role in most countries worldwide since its contribution is vital from nutritional, industrial and economic points of view. The increase in population and quality demands have generated a greater demand for food [1, 2]. The excessive use of pesticides to maximize crop yields has become a common practice in recent decades [3, 4]. This makes it possible to control and counteract the spread of pests, insects, weeds and diseases, which significantly affect crops. Pesticides can be classified into various groups according to their chemical composition, and these groups include organochlorines (OCs), organophosphates (OPs), carbamates and pyrethroids. These pesticides act in different ways: a) by contact, i.e., they remain on the surface of plants, or b) systemically, i.e., they are absorbed by roots, stems and leaves [5]. These chemicals enter the plant in their original form or by means of their degradation products, which are sometimes more toxic than the original substance [6]. Pesticide contamination arises mainly from incorrect use and noncompliance with the principles of good agricultural practice [7].

The presence of these contaminants in food is increasingly worrying due to their possible harmful effects on health [7, 8, 9]. The most susceptible consumers are children [10] because they consume a greater proportion of fruits and vegetables relative to their body weight [11]. According to the European Food Safety Authority (EFSA), the most pesticide-contaminated vegetable is tomato since multiple residues are frequently detected [12] in both raw and processed products [7].

This scenario is highlighting the importance of food security worldwide to ensure that food is nutritionally adequate and safe for consumption. Many countries and health organizations, such as Europe, Japan, the United States and the Food and Agriculture Organization of the United Nations (FAO), have established maximum residue limits (MRLs) [7, 13]. It is possible to assess the level of acceptable risk, the compliance with which is increasingly strict in each country.

Given increasing public concern regarding food safety in the face of problems caused by the continuous use of pesticides, numerous residual agrochemical extraction methods have bee.

reported. These methods include solvent extraction (SE), liquid-liquid extraction (LLE), solid-liquid extraction (SLE), pressurized liquid extraction (PLE), supercritical fluid extraction (SFE), microwave-assisted extraction (MAE) and solid-phase extraction (SPE)[14, 15]. However, these methods generally have limitations since they require a long operation time, a large size and number of samples, high-cost extractions, the use of toxic organic solvents and low selectivity.

Therefore, the obvious need for an effective and reliable extraction method [16] has led to the introduction of the fast, easy, cheap, robust and safe method (QuEChERS) method, which replaces less efficient traditional methods [17]. This method is now widely recognized and used [18, 19] in the extraction of a wide range of analytes from various matrices, such as agri-food, environmental and biological matrices [19]. This method is even used for the analysis of pharmaceutical products, [20] polycyclic aromatic hydrocarbons, and mycotoxins, among other compounds [18, 19].

The widespread acceptance of this method, together with the combination of technologies such as liquid and gas chromatography (LC and GC), which allows for better sensitivity, selectivity, and specificity, has led to the publication of a large number of manuscripts utilizing this method. Therefore, the aim of this work is to update the evolution of and modifications made to the QuEChERS method by carrying out a bibliometric analysis of publications related to pesticides in tomatoes for the period of 2007-2021.

The remainder of this document is structured as follows: Section 2 shows the bibliometric analysis methods. Section 3 shows the obtained results, and it is divided into two subsections. The bibliometric indicators are analyzed in Section 3.1. Section 3.2 describes the QuEChERS method and its modifications. Finally, the conclusions are shown in Section 4.

Materials and methods

This bibliographic research was carried out based on the following scientific problem: "Tomato is considered one of the vegetables most contaminated by agrochemicals both raw and processed products. Therefore, maximum limits of residues have been established for tomato, which making it possible to assess the level of acceptable toxicological risk for human consumption".

The keywords defined for the search were QuEChERS, pesticides and tomato. These keywords were obtained from a specialized dictionary concerning the area under investigation. The Scopus database was chosen for the bibliographic search. The results were filtered by year, author, knowledge area, and number of documents.

The Vosviewer software tool was used to build and visualize bibliometric networks [21]. This made it possible to identify the occurrence visualization network and the keyword clustering. In addition, it allowed us to visualize the keyword density of referring to the fundamental concept and the keyword density in general.

Results

Analysis of bibliometric indicators

Scientific texts related to the QuEChERS method for the preparation of samples containing pesticides in tomatoes were identified in the Scopus database. After searching for the term 'QuEChERS, pesticides in tomatoes' for the period 2007-2021, 171 documents were identified (Figure 1). As will be noted, there has been an increase in publications since 2011, with two maximum peaks in the years 2012 and 2020, in which a total of 20 articles were published. It is also noteworthy that almost 10 related articles have already been published in the first four months of 2021.

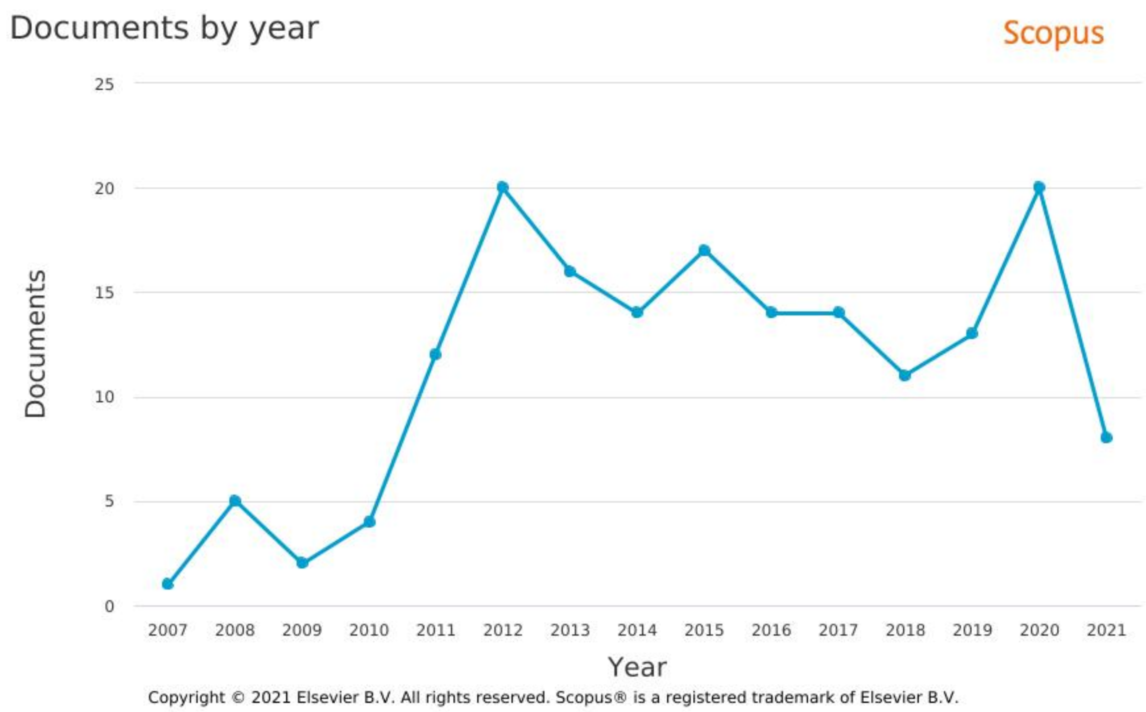

FIGURE 1.
Documents per year regarding the QuEChERS analytical technique when used with tomato
Source: Scopus analysis from 2007-2021.

Figure 2 shows the areas of further research into this subject in relation to the total number of documents within the same database. The research areas with the highest number of publications were chemistry, constituting 26.1% of publications, and agriculture, comprising 17.2%.

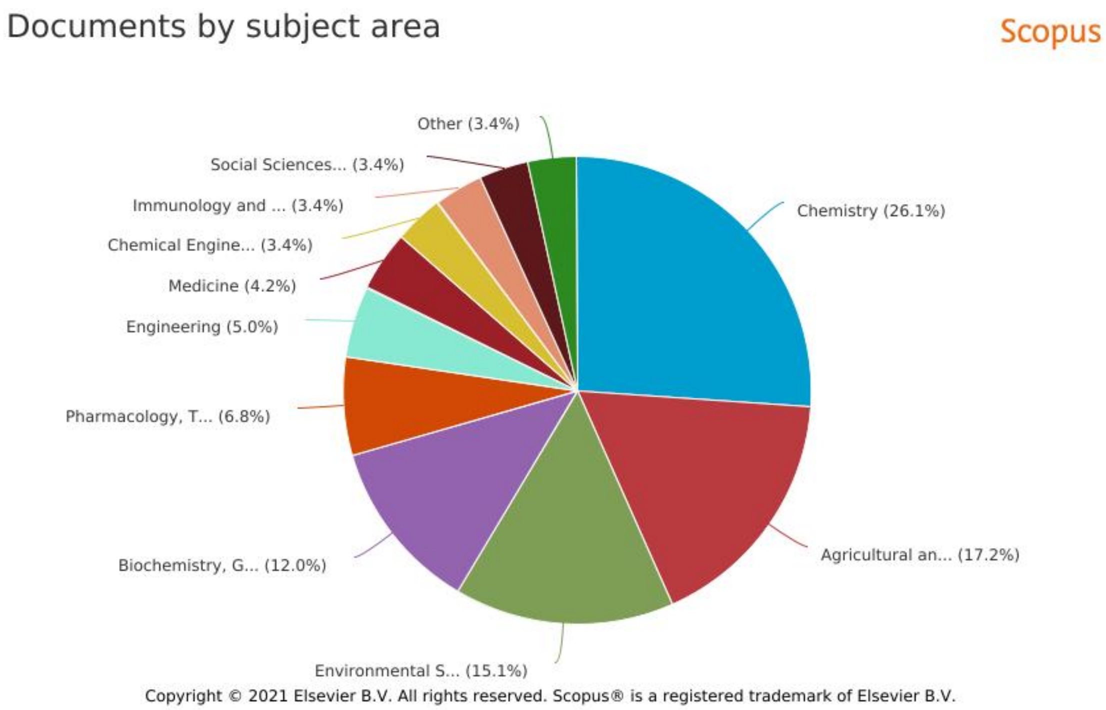

FIGURE 2.
Documents concerning the QuEChERS method for the preparation of samples containing pesticides in tomatoes shown by subject area
Source: Scopus analysis 2007-2021.

Figure 3 shows the types of published documents. Most of them (97.7%) are scientific articles. This indicates that the QuEChERS method remains of interest for scientific research and applicable for sample preparation.

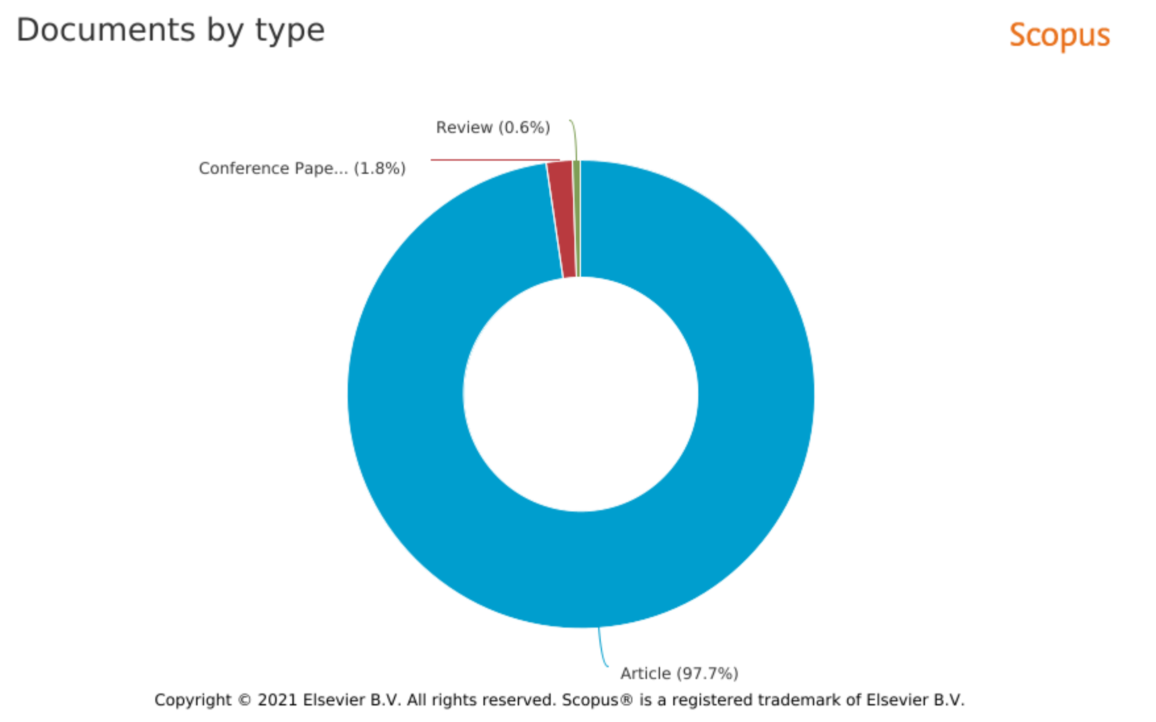

FIGURE 3.

Documents concerning the QuEChERS method for the preparation of samples containing pesticides in tomatoes shown by type (article, review or conference paper)

Source: Scopus analysis from 2007-2021.

Regarding the authors, the four with the most published articles on this topic are Dong, F.; Liu, X.; Xu, J.; and Zheng, Y., each of which has published 7 articles (Figure 4). These authors belong to the Chinese Academy of Agricultural Sciences. This institution has the second highest number of articles, with a total of 11 (Figure 5).

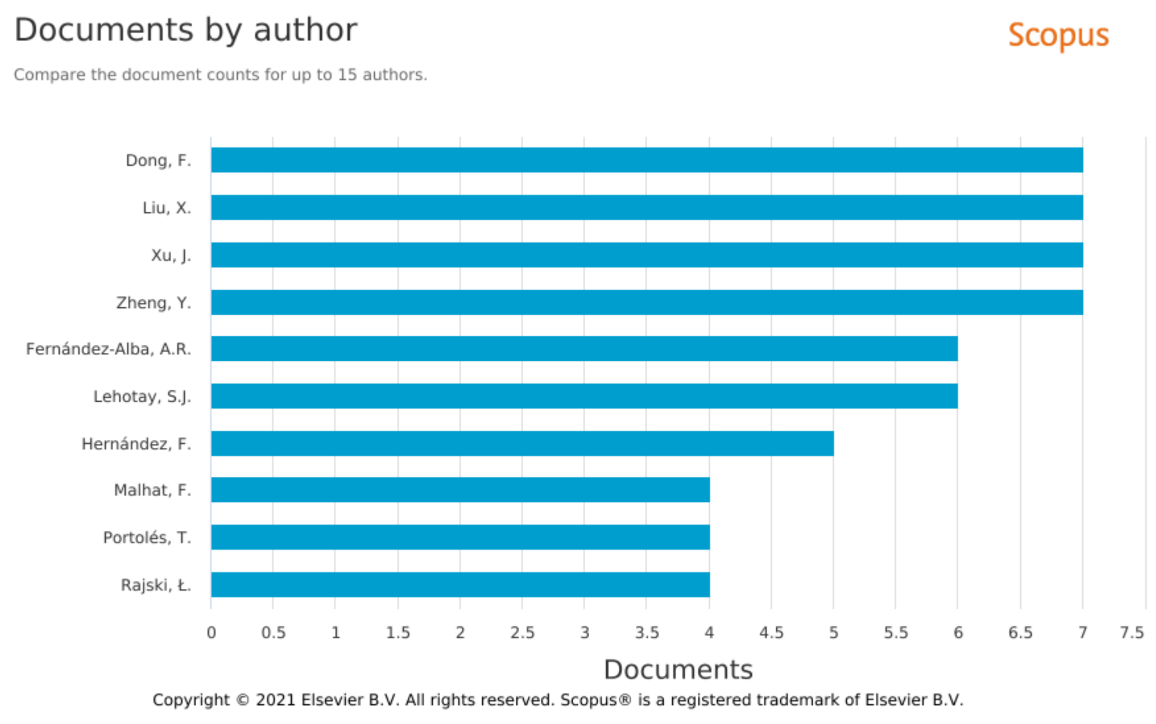

FIGURE 4.

Comparison of the documents on the use of the QuEChERS method for the preparation of samples containing pesticides in tomatoes, produced by up to 15 authors

Source: Scopus analysis from 2007-2021.

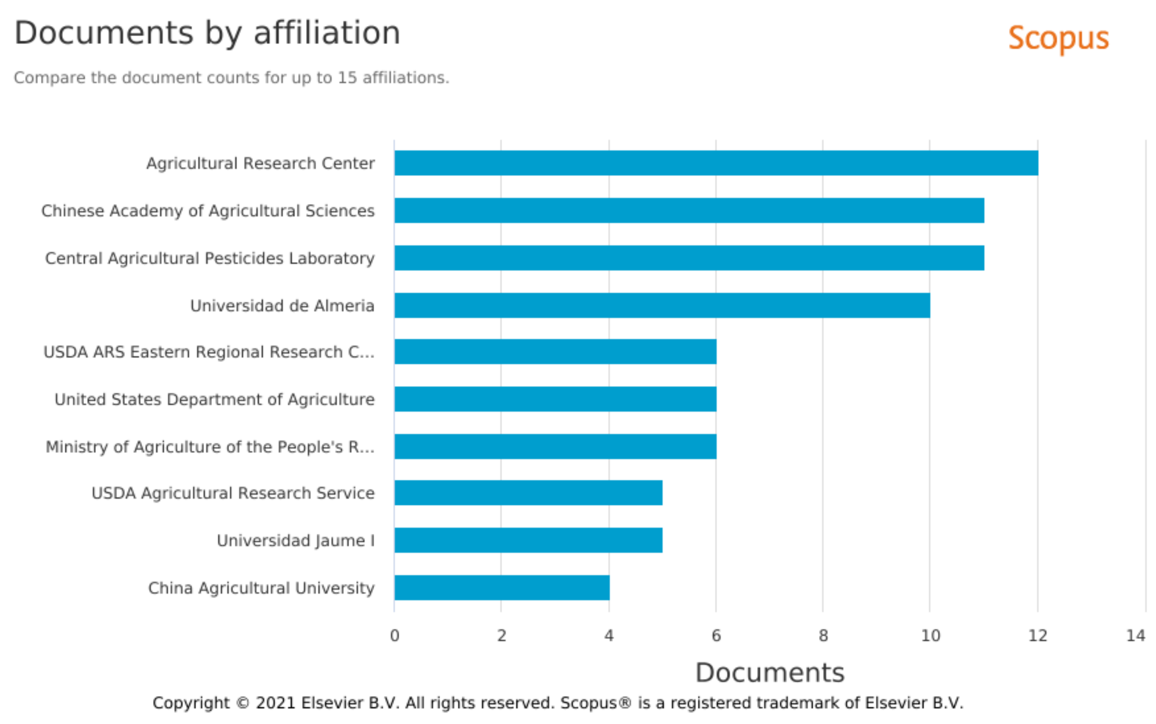

FIGURE 5.

Document collection comparison of the use of the QuEChERS method for the preparation of samples containing pesticides in tomatoes, produced by up to 15 affiliations

Source: Scopus analysis from 2007-2021.

It is also worth noting that in 2014, the four aforementioned researchers collaborated to publish an article related to the determination of phthalanilic acid residues in beans, fruits and vegetables using a modified QuEChERS method and tandem ultra-performance liquid chromatography-mass spectrometry (HPLC-MS).

China exhibits the most publications on QuEChERS and pesticides on tomatoes between 2007 and 2021 (40 papers), followed by Spain (25 papers) and Egypt (18 papers) (Figure 6).

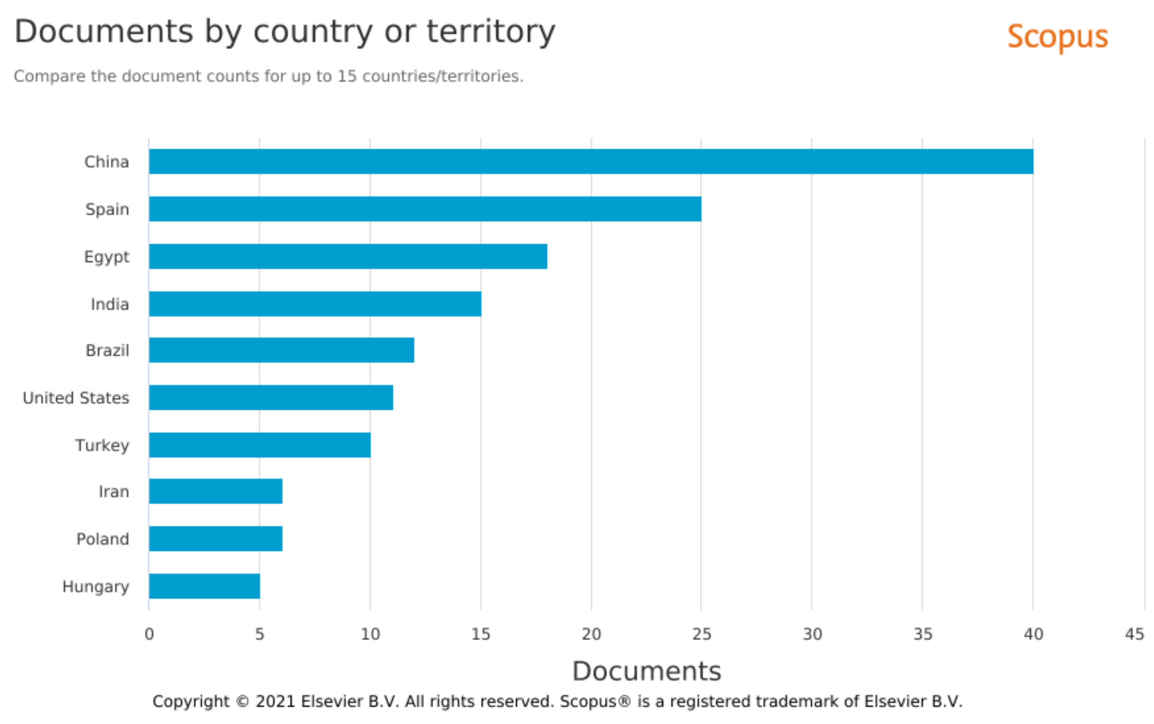

FIGURE 6.

Comparison of documents on the use of the QuEChERS method for the preparation of samples containing pesticides in tomatoes originating from up to 15 countries / territories

Source: Scopus analysis from 2007-2021.

The largest sponsor of research funding related to QuEChERS and tomato pesticides from 2007-2021 was the National Foundation of Natural Sciences of China, with a total of 13 articles, followed by the European Commission with 9 articles and the Generalist Valencia with 5 research works (Figure 7).

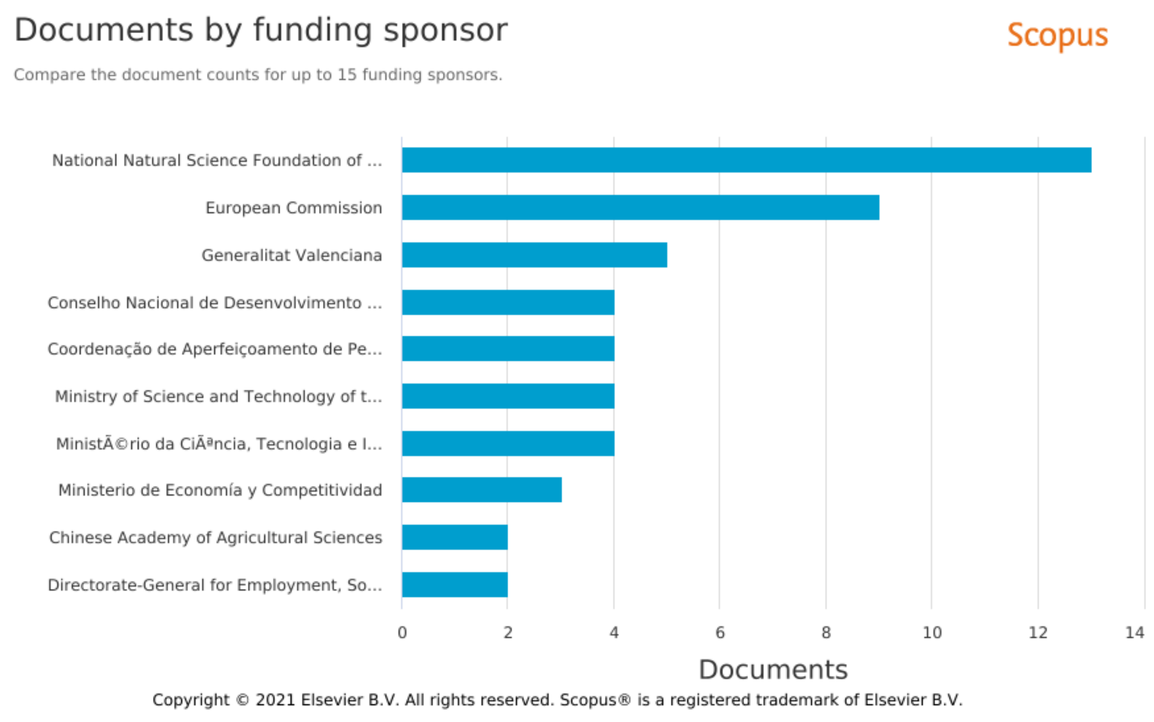

FIGURE 7.

Comparison of documents on the QuEChERS method for the preparation of samples containing pesticides in tomatoes funded by up to 15 sponsors

Source: Scopus analysis from 2007-2021.

Figure 8 shows the publications about QuEChERS and tomato pesticides in 5 journals considering their impact index according to their InCites Journal Citation Reports (SJR) and Source Normalized Impact per Paper (SINP) from 2007 to date. This shows that the Bulletin of Environmental Contamination and Toxicology exhibited the largest number of published articles in 2012 (4). Moreover, there are 3 published articles in Food Analytical Methods (2013) and the Journal of Chromatography A (2012, 2014 and 2017). It is important to note that the four authors, who have the most articles published and who are cited in Figure 4, have articles in these journals. Those are the highest impact index according to their SJR and SINP, thus showing the quality and novelty of the research carried out.

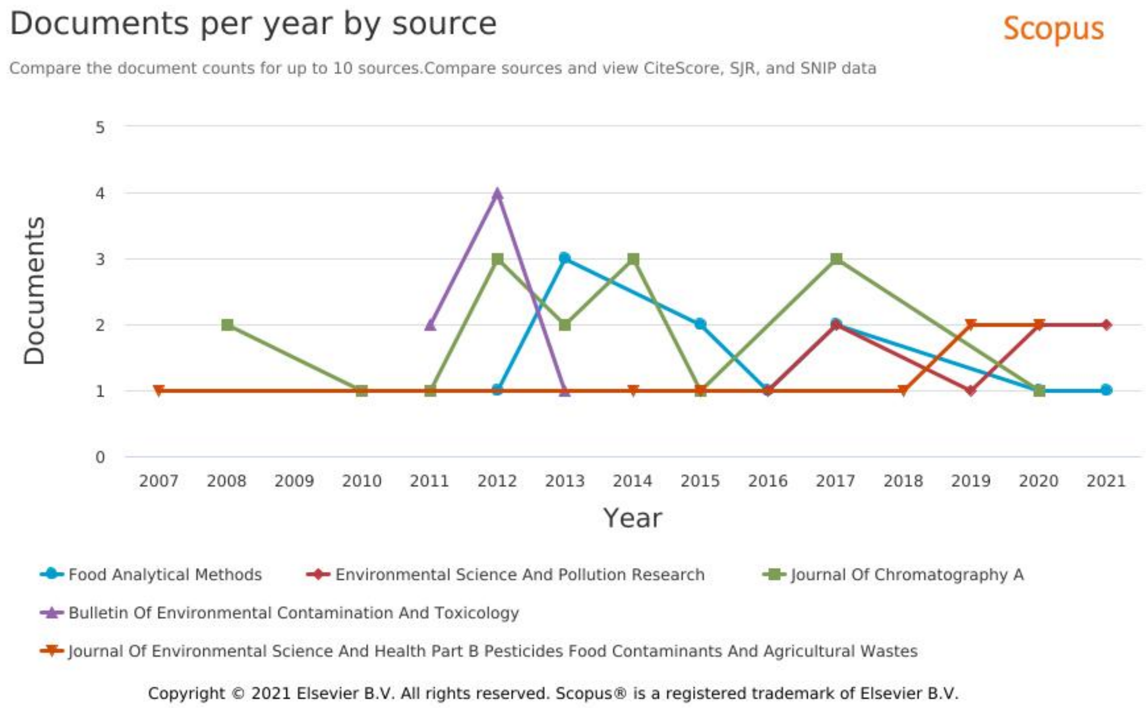

FIGURE 8.
Number of publications per year, taking into account the 5 journals with the highest impact index according to their SJR and SNIP
Source: Scopus analysis from 2007-2021.

To define the relationships among the keywords, an analysis was carried out using Vosviewer software. Figure 9 shows the visualization of keyword appearance and occurrence over the course of time from 2007-2021. The graph allows us to interpret that the QuEChERS method has a large number of nodes regarding the terms tomatoes and pesticides. The number of times the VOS clustering technique optimization algorithm runs was 1, with 1000 iterations of the technique. It was possible to identify 22 words grouped in two clusters. Cluster 1 (blue) has tomato at its center, while Cluster 2 (purple) shows the relationship between pesticides and the study technique.

Figure 10 shows the density of the elements and the grouping of the selected keywords. The highest density area is yellow. The areas represent the most extensive areas into which the words are grouped: tomato, pesticide, analysis, determination and pesticide residues. Areas of a lower density related to the terms QuEChERS method, study, detection, quantification and standard deviation can also be observed.

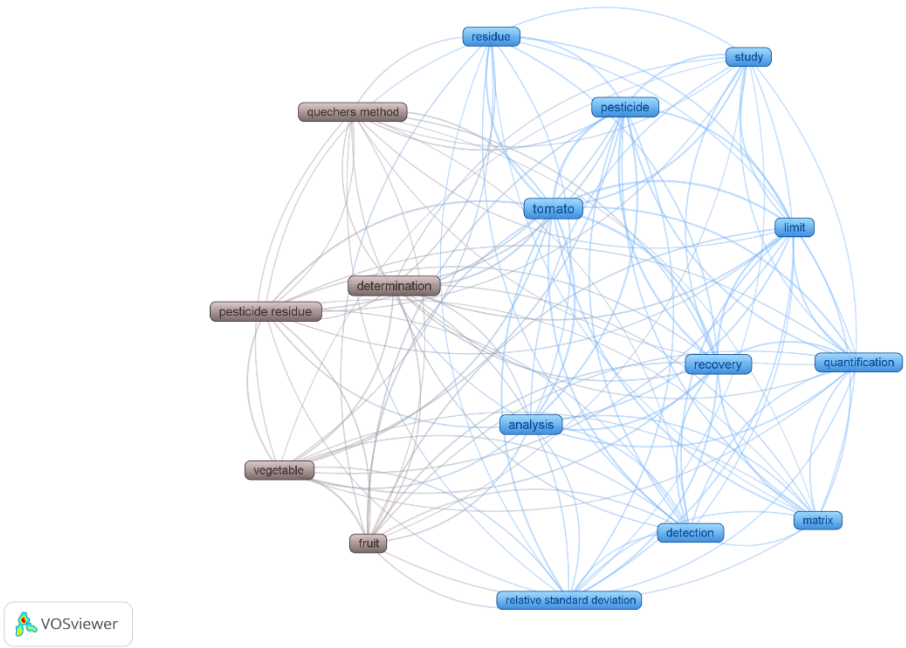

FIGURE 9.

Visualization of the appearance and occurrence of keywords 'QuEChERS' and 'pesticides on tomato' obtained with Vosviewer software

Source: Prepared by the authors.

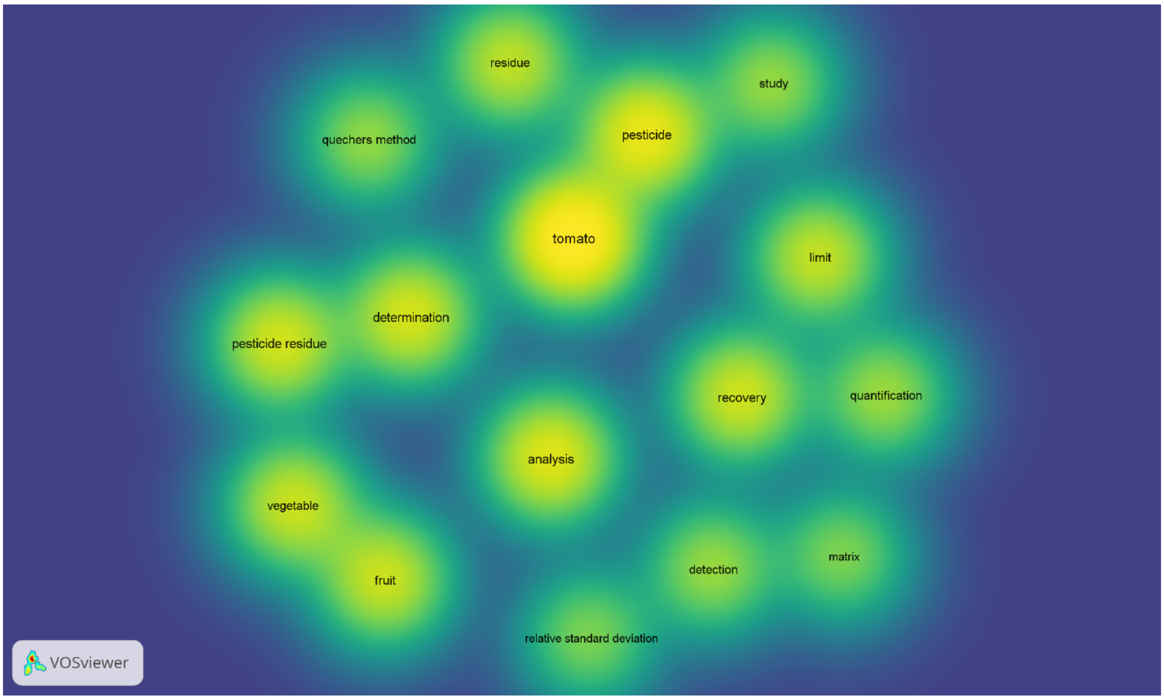

FIGURE 10.

Element density and clustering of keywords 'QuEChERS' and 'pesticides on tomatoes' obtained with Vosviewer software

Source: Prepared by the authors.

QuEChERS methods and their modifications

The extraction method was initially developed to determine multiclass pesticides and multiple residues in fruits and vegetables [16]. The original QuEChERS method was based on an initial extraction of 10 g of sample with 10 mL of acetonitrile (ACN) in the presence of 4 g of anhydrous $MgSO_4$ and 1 g of NaCl, aft er which the extract was cleaned by dispersive solid-phase extraction (d-SPE) with 25 mg of secondary primary amine (PSA) and 150 mg of anhydrous $MgSO_4$. The classic cleaning materials used in the QuEChERS method to eliminate interferences in tomatoes are graphitized carbon black (GCB) and primary/secondary amine (PSA) [22], since tomatoes are a rich source of natural antioxidants [23] such as lycopene, which represent 80-90% of the total carotenoid content [24] of organic acids and saccharides.

At the time of writing, the original article had been cited in the literature more than 5163 times. This method has been modified several times using buffered conditions to improve the extraction capacity of pH-dependent compounds. The two most important buffered versions validated by highly prestigious international laboratories stand out. These are the AOAC 2007.01 official method, which employs an acetate buffer [25], and the standard method of the European Committee for Standardization (CEN) EN 15662, which uses a citrate buffer [26]. Together, these two official versions have attained more than 860 citations.

One of the main advantages of this method is microscale extraction. It requires small amounts of sample and minimal solvent consumption, as detailed in Table 1. This table shows the applications and modifications to the QuEChERS method for pesticide analysis in raw and processed tomatoes.

TABLE 1.
Application of the QuEChERS methods to the pesticide analysis of raw and processed tomatoes

Analyte	Sample mass (g)	QuEChERS methods	Extraction		Cleaning salts	Analytical technique	References
			Solvent	Salt			
24 pesticides	10	15mL ACN	Triphenylphosphate (TPP), 10 mL ACN	4 g de $MgSO_4$ anhydrous y 1 g de AcONa	25 mg PSA 150 mg $MgSO_4$ anhydrous	UFLC-MS	[27]
10 insecticides and 7 fungicides	10	Modification of the QuEChERS version (Ahumada & Zamudio, 2011)	15 mL ACN y acetic acid 1 % (v/v)	6 g de $MgSO_4$ anhydrous y 1 g de AcONa	25 mg PSA 150 mg $MgSO_4$ anhydrous	LC-MS	[28]
Fungicides and insecticides	10	Anastassiades 2003	15 mL ACN	(6 g $MgSO_4$ anhydrous, 1 g NaOAc)	25 mg PSA, 150 mg $MgSO_4$anhydrous	UFL<C-MS	[29]
Thiophanate methyl and carbendazim	10	Anastassiades 2003	10 mL ACN and 0.1 mL formic acid	4 g $MgSO_4$anhydrous, 1 g NaCl	25 mg PSA, 150 mg $MgSO_4$anhydrous	UPLC-MS/MS	[30]
109 pesticides	15	Anastassiades 2003 with some modifications	15 mL ACN	6 g $MgSO_4$anhydrous, 1.5 g NaOAc	600 mg $MgSO_4$ anhidro200 mg PSA	LC-MS/MS	[31]
6 organochlorines 5 organophosphates	10		10 mL ACN	4g $MgSO_4$anhydrous, 1g NaCl	100 mg PSA, 600 mg $MgSO_4$, 30 mg activated carbon	GC-EDC (organochlorines) GC-FTD (organophosphates)	[4]
8 pesticides	15	QuEChERS described by Lehotay	15 mL ACN al 1 % acetic acid	6 g $MgSO_4$ anhydrous, 1.5 g anhydrous sodium acetate	150 mg $MgSO_4$ anhydrous, 50 mg PSA	LC-MS/MS	[32]
6 fungicides	10	EN 15662:2008	10 mL ACN	4 g $MgSO_4$ anhydrous, 1 g NaCl, 1 g dehydrated trisodium citrate y 0.5 g disodium hydrogen citrate sesquihydrate	150 mg $MgSO_4$ anhydrous, 25 mg PSA	LC-MS/MS	[5]
Fluxapyroxad	5		5 mL ACN/water (9:1 v/v)	4 g $MgSO_4$anhydrous, 1 g NaCl	50 mg C18 150mg $MgSO_4$anhydrous	UPLC-MS/MS	[33]
20 organochlorines, 6 organophosphates	10	Basado EN15662	10 mL ACN	4 g $MgSO_4$ anhydrous, 2 g NaCl, 1 g tribasic sodium citrate dihydrate Microwave irradiation	150 mg Na_2SO_4, 100 mg PSA, 10 mg graphitized carbon (GCB)	GC-μECD	[34]
Methomyl and acetamiprid	15	AOAC	15 mL ACN (1%) acetic acid	4 g $MgSO_4$ anhydrous, 1 g NaCl	25 mg PSA, 150 mg $MgSO_4$ anhydrous	LC-MS/MS	[35]
Ciazofamide and its metabolite CCIM	10	Anastassiades 2003	15 mL ACN	4 g $MgSO_4$ anhydrous, 1 g NaCl	50 mg PSA, 150 mg $MgSO_4$ anhydrous, 10 mg (GCB)	UPLC-MS/MS	[36]

Source: Prepared by the authors.

In this respect, one of the modifications made to the multiresidue method for the determination of 24 pesticides was based on the AOAC 2007.01 [25] method. Triphenylphosphate (TPP) was used in the extraction process, along with 10 mL of acetonitrile acidified with acetic acid at 1% (v/v), 4 g of anhydrous $MgSO_4$ and 1 g of sodium acetate (AcONa), while 25 mg of PSA and 150 mg of anhydrous $MgSO_4$ were employed in the cleaning stage [27]. These modifications make it possible to achieve recoveries better than 70% in tomato (*Solanum lycopersicum*) samples (Entry 1).

Bojacá, [28] and Liu, [30] made modifications to the QuEChERS method developed by Ahumada [27] for the analysis of pesticide residues in tomatoes grown in the open field and greenhouses in Bogotá, Colombia. These authors used 15 mL of ACN and acetic acid at 1% (V/V), after which 6 g of anhydrous $MgSO_4$ and 1 g of AcONa were employed without the use of an ultrasonic bath for the extraction. Additionally, they used the same sample cleaning process conditions as in the method of Ahumada (Entries 2 and 3).

Liu [30] and Golge [31] made modifications based on the original QuEChERS method for the extraction of carbendazim, thiophanate methyl and 109 pesticides in selected tomato samples. In the initial carbendazim and methyl thiophanate extraction, 10 mL of ACN with 0.1 mL of formic acid was necessary, while the amounts of the extraction salts and cleaning were the same proportions as those employed in the original QuEChERS method [16] (Entry 4). They extracted 109 pesticides by employing 15 mL of acetonitrile with 6 g anhydrous MgSO4 and 1.5 g of NaOAc, and for cleaning, they used 600 mg of anhydrous MgSO4 and 200 mg of PSA, achieving recovery yields between 77.1% and 113.2% [31] (Entry 5).

In Entry 6, 5 organophosphate and 6 organochlorine compounds were analyzed in raw, stored, washed and peeled tomato samples obtained from southern Bolivia [4]. The samples were treated by modifying the amounts of anhydrous MgSO4 and PSA, in addition to which activated carbon was used in the cleaning phase. In their work, Andrade et al.[32] also studied 58 tomato samples obtained from markets in Sao Paulo, Brazil, and analyzed the presence of 8 pesticides using 1% acetic acid and anhydrous AcONa. They were the most important modifications made to the QuEChERS method according to what was reported [16] (Entry 7).

In Entry 8, the QuEChERS method EN 15662, approved in 2008 by the European Union, was employed by means of trisodium citrate dehydration and disodium hydrogen citrate sesquihydrate, along with anhydrous magnesium sulfate and sodium chloride in the sample extraction process used with greenhouse tomatoes for the analysis of 6 fungicides [5]. Another modification based on the EN 15662 method used anhydrous magnesium sulfate, sodium chloride, tribasic sodium citrate dihydrate and microwave irradiation in the extraction process employed for the chonto tomato sample commercialized in Armenia (Quindío-Colombia). Moreover, GCD was used for the analysis of 20 organochlorine compounds and 6 organophosphates (Entry 10).

Cheng et al.[33] employed a combination of ACN and formic acid in the extraction stage and C18 in the cleaning stage to analyze the fungicide fluxapiroxad in tomato samples obtained from a market in Beijing, China (Entry 9). Rasolonjatovo et al. [35] employed the AOAC 2007.01 method for the analysis of the insecticide methomyl, along with the compound with the trade name acetamiprid (Entry 11). Finally, Yang et al. [36] used GCB in the cleaning stage. This was the most important modification made to the original QuEChERS method for the determination of cyazofamid and its metabolite 4-chloro-5-(4-methylphenyl)-1H-imidazole-2-carbonitrile (CCIM) during tomato growth and tomato paste manufacturing (Entry 12).

Other adaptations to the QuEChERS method have been those made by Chinese researchers to determine pesticides in tomatoes (Table 2).

TABLE 2.
Authors who have made modifications to the QuEChERS method for the determination of pesticides in tomatoes

Author/year	Agrochemical Classes	Modifications to the QuEChERS Method to determine agrochemicals in tomatoes
[37]	20 pesticides organochlorines	Carbon-based QuEChERS in the form of N-doped graphite using dicyandiamide sludge in conjunction with GC-MS / MS mass spectrometry tandem gas chromatography determination
[13]	101 pesticides	QuEChERS based on carbon-fixed Fe_3O_4 magnetic nanoparticles using primary / secondary amine (PSA) together with GC-MS / MS determination
[38]	10 pesticides	Carbon-based QuEChERS with carbon-fixed Fe_3O_4 magnetic nanoparticles using primary / secondary amine (PSA) in conjunction with GC-MS / MS determination

Source: Prepared by the authors.

Millions of tons of dicyandiamide sludge are dumped in China every year. This waste is difficult to dispose of, and companies spend a lot of money buying land on which to accumulate this waste, thus generating environmental pollution and damage to health [39]. The main components of dicyandiamide sludge are calcium carbonate, carbon, silicon dioxide, and a small amount of nitrogen-containing organic compounds.

However, studies carried out by the authors Kang and Wu and Yang in the last two decades have focused on the elimination and reuse of dicyandiamide sludge, including the production of cement, nonsintered brick and rubber, respectively [29, 30]. Despite this, carbon material, which comprises 10–20% of the content of dicyandiamide sludge, is rarely reused. The literature states that nitrogen-doped graphite carbon (NGC) can be synthesized by means of heat treatment of precursor nitrogen-containing carbon materials that include dicyandiamide, melamine, and urea [40, 41].

Xuemin Ye et al. recently reported the design of an adsorbent material used in the cleaning step of the QuEChERS method for organochlorine pesticide determination in carbon-based tomatoes in the form of nitrogen-doped graphite using dicyandiamide sludge as a precursor [37].

These authors found acceptable results in the experimental parameters that affect the efficiency of extraction and buffer systems and analyzed the optimal recovery conditions and effects of the matrix. They compared their results with other classical QuEChERS methods, and these showed that higher recoveries were obtained when employing the proposed method owing to the use of NGC. Furthermore, the proposed QuEChERS method had environmental and low-cost advantages.

Conclusions

The modifications made to the QuEChERS method by adding acetate and citrate in the extraction stage and graphite carbon in the cleaning stage, together with LC or GC chromatography or UFLC in tandem with MS, have allowed the identification and determination of a large number of pesticides in tomatoes. Moreover, after carrying out a bibliometric analysis in the Scopus database for the period 2007-2021 by employing the search terms QuEChERS, pesticides and tomato, we have concluded that the areas in which most research is being carried out are those of chemistry and agriculture. The country that publishes most is China, with four authors who have 7 articles each. In addition, China is the most prominent country with regard to the timeliness and quality of published works. Relevant publications from Chinese authors were mainly in the journals Bulletin of Environmental Contamination and Toxicology, Food Analytical Methods and Journal of Chromatography A. Finally, two validated modifications made to the QuEChERS method developed by Anastassiades were identified, which were those in the AOAC 2007.01 and UNE-EN 15662 (CEN2008) methods. Subsequently, Chinese researchers have made modifications in addition to these modified methods, specifically with the use of dicyandiamide sludge as a nitrogen source, thus modifying carbon in the form of graphite to obtain good results regarding extraction and recovery percentages, with the advantages of a low cost and reduced environmental pollution.

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Notes

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