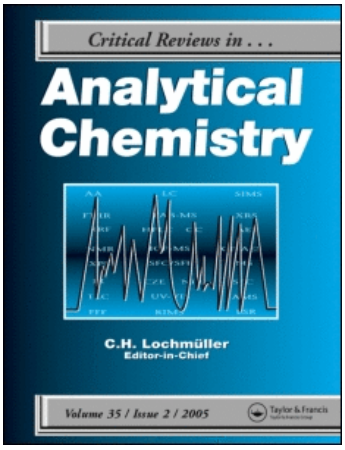

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Analysis of Pesticide Residues in Juice and Beverages

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Online publication date: 10 August 2010

To cite this Article Tadeo, José L. , Sánchez-Brunete, Consuelo , Albero, Beatriz and González, Lorena(2004) 'Analysis of Pesticide Residues in Juice and Beverages', Critical Reviews in Analytical Chemistry, 34: 3, 165 — 175
To link to this Article: DOI: 10.1080/10408340490888670
URL: http://dx.doi.org/10.1080/10408340490888670

Critical Reviews in Analytical Chemistry, 34:165–175, 2004

ISSN: 1040-8347 print
DOI: 10.1080/10408340490888670

Analysis of Pesticide Residues in Juice and Beverages

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The analysis of pesticides in juice and beverages is reviewed. Sample preparation is an important step in the analytical method, and the advantages of various new extraction techniques over the classical solvent extraction have been highlighted. Solid-phase extraction and solid-phase microextraction are widely used at present due to the simplicity and robustness of these extraction procedures, together with the low requirement of organic solvents. Determination of residues at the low levels found in juice has been performed mainly by chromatographic methods employing selective detectors or, in an increasing proportion, coupled to mass spectrometry for the quantification and simultaneous identification of residues. In addition, the pesticide concentrations reported in juice and beverages have been discussed in relation to the assessment of consumer exposure to these chemicals through the intake of the processed food products studied.

Keywords determination, gas chromatography, high-performance liquidchromatography, juices, pesticides, sample preparation

Pesticides are widely used in present-day agriculture to control pests, diseases, and weeds, which may affect crops and decrease their quality and yield. The frequent and broad use of these compounds initiates the contamination of the environment and the presence of their residues in food. Figure 1 shows the chemical structures of representative compounds of the principal pesticide groups used in agriculture.

Public concern about the contamination of food by pesticides has been increasing over the past years due to uncertainty about the adverse effect those residues may pose over a long-time exposure attributable to the toxicity of most pesticides and the high consumption of fruit and vegetables. Levels of pesticides in food are regulated by international and national organizations in order to protect human health and maximum residue levels (MRLs) have been established in many countries for the different commodity-pesticide combinations. In the case of processed food, such as juices, MRL corresponding to the original matrix is normally considered. The exposure to pesticides via consumption of fruit and vegetables is especially important for children because of their higher intake per body weight and their higher susceptibility to chemicals during developmental stages.

The treatment of crops with pesticides deposits these compounds on the surface of plants in the aerial treatments, or applies them to soil so they can be absorbed through the roots. In general, pesticides are often found at higher concentrations in peel and pulp than in juice. This fact makes the expected pesticide levels in juice and beverages low, which increases the difficulty of analysis. Therefore, analytical methods should be highly sensitive and selective to allow the determination of pesticides in those matrices and, consequently, the extraction and clean-up of extracts are important steps of the analytical procedure.

To allow for control of pesticide residues, many analytical methods have been developed for their determination in food and these methods have been reviewed in various publications (1–5). Nevertheless, although the consumption of processed food has increased nowadays, reviews on pesticide determination in these matrices are scarce. The aim of the present work is to critically review the analysis of pesticide residues in juice and beverages, particularly considering the preparation of samples, and to discuss the levels found in these matrices in relation to the consumer exposure.

SAMPLE PREPARATION

The presence of pesticides in juice and beverages at low levels generally requires the concentration of these compounds in

Financial aid from INIA, Project no. RTA01-41, is acknowledged by the authors.

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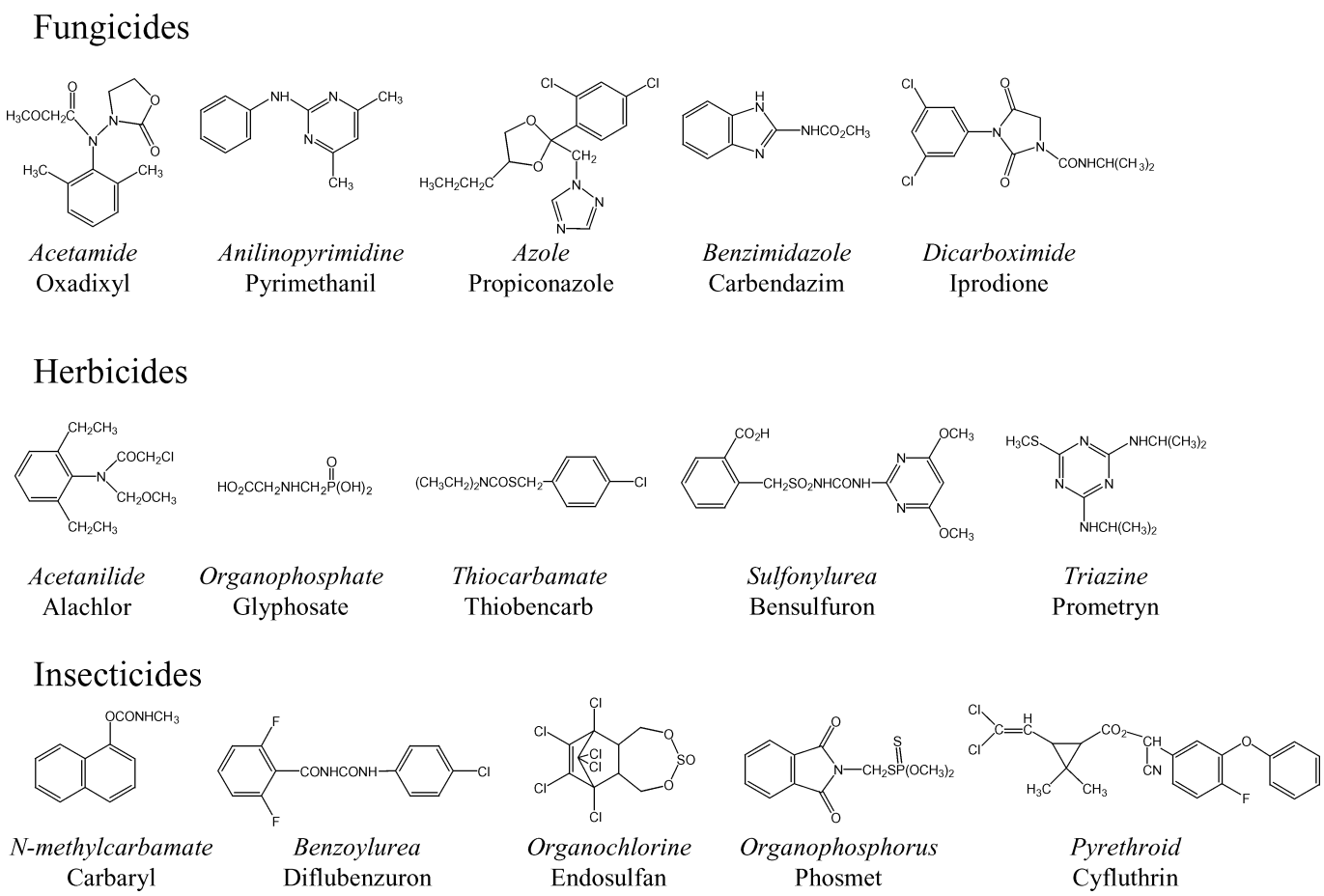

FIG. 1. Chemical structures of representative compounds of pesticides used in agriculture.

a clean extract before they can be determined. Classical analytical methodology is based on liquid-liquid extraction, whereas modern techniques have been developed based on solid-liquid extraction.

Liquid-Liquid Extraction

Pesticides usually have been extracted from juice and beverages by means of organic solvents. These classical methods are easy to use and do not require special equipment. Nevertheless, they have several disadvantages due to the use of large amounts of glassware and high volumes of toxic organic solvents. Moreover the glassware employed needs to be pesticide residue free, requiring the use of highly oxidizing reagents for cleaning, which in turn may cause the contamination of the environment. In addition, the organic extracts obtained have to be concentrated and cleaned up in order to obtain the low detection limits required. All these facts make classical methods laborious, time consuming, and difficult to automate.

Table 1 shows the different liquid-liquid extraction methods reported for the analysis of pesticides in juice and beverages. In general solvents of low polarity and immiscible with water, such as, hexane, ethyl acetate, or dichloromethane, are used. Mixtures of these solvents with a water-miscible solvent like acetone are also employed in order to facilitate the extraction, particularly of those pesticides with a higher polarity. With the aim of diminishing the drawbacks indicated above for this classical extraction technique, a decrease in the volume of extraction solvent, and consequently a miniaturization of the sample preparation method, has been carried out in recent publications (6, 7). Nevertheless when a selective and sensitive method is required, particularly necessary in multiresidue analyses, a further clean-up is needed, usually accomplished by column chromatography on silica gel.

Solid-Liquid Extraction

In the past years, modern extraction techniques have been developed and applied to the analysis of pesticide residues in food. These techniques are based mainly on the extraction of pesticides in a solid phase, which allows the concentration of analytes in the sorbent and their subsequent elution or desorption, frequently in a selective way. Solid-phase extraction (SPE), matrix solid-phase dispersion (MSPD), solid-phase microextraction (SPME), and stir-bar sorptive extraction (SBSE) are the main examples of these modern extraction techniques and they are reviewed below.

TABLE 1
Liquid-Liquid Extraction of Pesticides from Juice and Beverages

Solvent	Pesticide	Matrix	Clean-up	Ref.
Acetone-dichloromethane (1:1)	Fungicides and organophosphorus insecticides	Must and wine		(8–11)
Acetone-hexane (1:1)	Fungicides	Must and wine		(7)
Acetone-petroleum ether (1:1)	Fungicides	Must and wine		(6, 12)
Acetonitrile	Insecticides and fungicides	Tomato	Dichloromethane LLE-florisil	(13)
Acetonitrile-water (2:1)	Multiclass	Tomato and carrot	Dichloromethane LLE-florisil	(14)
Cyclohexane-ethyl acetate-acetone (2:2:1)	N-methyl carbamates	Fruit juices		(15)
Dichloromethane	Organochlorines, organophosphorus, and triazines	Wine	Silica gel	(16)
Ethyl acetate	Organochlorines, organophosphorus, and carbamates	Fruit juices and wines		(17–19)
Hexane	Organochlorines, organophosphorus, and fungicides	Fruit juices and wine		(20–23)
		Tea infusion	Florisil	(24)

Abbreviation: LLE, liquid-liquid extraction.

Solid-Phase Extraction and Matrix Solid-Phase Dispersion

Pesticides are, in general, low-polarity compounds that have to be extracted from an aqueous medium like juices or beverages. Therefore, a reverse-phase SPE, using silica gel end-capped with long alkyl chains (C_{18}), has been used frequently with that aim (Table 2). Pesticides are thus partitioned and retained in the C_{18} phase, while other more polar compounds are eluted. A subsequent elution with an organic solvent (methanol

TABLE 2
SPE and MSPD of Pesticides from Juice and Beverages

	Pesticide	Matrix	Elution	Clean-up	Ref.
SPE					
Cation exchange	Thiabendazole	Fruit juices	Methanol (0.3 M NH_4OH)		(30, 31)
C_{18}	Atrazine	Fruit juices	Methanol	Liquid extraction	(32)
	Benzoylureas and procymidone	Wine	Methanol		(33–35)
	Dithianon	Must and wine	Acetonitrile		(36)
	Herbicides	Wine	Ethyl acetate		(37)
	Multiclass	Fruit juices	Dichloromethane		(36, 38)
		Wine	Ethyl acetate		(39, 40)
Diatomaceous earth	Fungicides	Strawberry juice	Hexane (9)-dichloromethane (1)		(41)
	Thiabendazole	Citrus and apple juices	Hexane (3)-ethyl acetate (1)		(42)
Polymer (Oasis)	Multiclass	Beer and wine	Ethyl acetate-hexane	SPE-aminopropyl	(43, 44)
		Wine	Ethyl acetate	Florisil	(45)
MSPD					
Alumina	Thiabendazole	Orange juice	Ethyl acetate	SPE-propylsulfonic	(46)
Diatomaceous earth	Multiclass	Fruit juices	Ethyl acetate		(47)
Florisil	Multiclass	Fruit juices	Ethyl acetate		(48, 49)

Abbreviations: SPE, solid-phase extraction; MSPD, matrix solid-phase dispersion.

is often used) allows one to obtain pesticides in a concentrated organic extract, which is normally clean enough and amenable to be analyzed by gas chromatography (GC) or high-performance liquid chromatography (HPLC). Recently a polymeric phase (Oasis), formed by a vinyl benzyl and a vinyl pirrolidone copolymer, has been used with good results. In addition, diatomaceous earth, or cation exchange columns for ionic compounds, have also been employed in SPE analysis of pesticides from juices (Table 2).

An alternative solid-liquid extraction technique used in pesticide residue analysis is MSPD. This technique is based on the dispersion of the sample over the surface of the phase-support material with the aim of providing a new mixed phase for the isolation of analytes from various matrices. It has been used mainly for the analysis of pesticides in fruit and vegetables by placing the sample in a glass mortar containing the solid support material and blending it with a glass pestle (25, 26). MSPD has also been applied to the analysis of liquid samples such as milk and fruit juices (27–29). In contrast to SPE, where much of the sample is retained in the first millimeters of the column, the sample is dispersed throughout the length of the column in MSPD. The new phase created, together with the pesticide distribution and its interactions, as well as the polarity of the extraction solvent are the main controlling factors of this sample preparation technique. Florisil, alumina, and diatomaceous earth are the solid supports most often employed in MSPD analysis of pesticides in fruit juices (Table 2).

Solid-Phase Microextraction

SPME is a recently developed solventless technique based on the partition of analytes between the matrix and a fiber coated with a solid phase, where the analytes are retained due to their higher affinity for this phase. SPME can be applied to the analysis of liquid and gas matrices, and pesticides can be extracted by direct immersion (DI) in liquids or by headspace (HS) analysis. Several factors may affect pesticide extraction by SPME, such as, temperature, adsorption time, pH, matrix effect, and addition of salt.

Temperature favors volatilization of pesticides and their concentration in the headspace, although at high temperature desorption of analytes from the fiber will occur. Temperatures in the range of 50°C to 90°C are normally used in HS-SPME. In general a long time (more than 60 min) is necessary for achieving equilibrium concentrations of pesticides in the fiber. Nevertheless if agitation and adsorption time are maintained constant, the amount adsorbed is proportional to the initial concentration in the matrix and sampling time can be reduced to values around 20–30 min with reasonable reproducibility and sensitivity results.

The influence of pH on SPME analysis of pesticides in juice and beverages is generally limited, because values found in those matrices are not far from neutral pH. On the other hand, matrix effect is an important factor in SPME. Undissolved particles or low-volatility compounds may interfere either in the chromatographic analysis, or by saturating the fiber. Matrix effect is often found in immersion analysis; this problem is usually solved by dilution of samples in variable proportions from 1 to 100 times. In these cases, for pesticides with a certain vapor pressure, HS analysis is a good alternative to avoid matrix effect. In HS-SPME of liquid samples, the addition of salt is a normal practice to increase the concentration of pesticides in the gas phase by decreasing the solubility of pesticides in the liquid matrix. Nevertheless salting out of pesticides is not often employed in direct immersion, due to the reduction of recoveries sometimes found which may be explained by the formation of a salt layer around the fiber.

The other important step in SPME is the desorption of analytes from the fiber. The determination of analytes extracted by SPME is usually performed by thermal desorption and gas chromatographic analysis, although it can also be achieved by solvent desorption and liquid chromatographic determination. In the case of GC, the desorption takes place in the injection port of the gas chromatograph at a temperature chosen in accordance with the recommended maximum temperature for the particular fiber used and the analyzed compounds. Temperatures close to the maximum recommended temperature can shorten fiber life and increase bleeding. In the case of solvent extraction, static or dynamic processes can be used. The dynamic extraction is usually recommended to fully extract analytes and avoid carry-over effects. The application studies reported for SPME analysis of pesticides in juice and beverages are shown in Table 3.

Variations on the SPME technique have been developed recently. In-tube SPME is a technique based on the retention of analytes in a capillary internally coated with a stationary phase. Several draw/eject cycles of the liquid are performed to achieve retention in the stationary phase of the analytes, which are subsequently extracted with an adequate solvent for HPLC analysis (50). Another variation is the use of a stir bar externally coated with a stationary phase. This technique, called stir-bar sorptive extraction (SBSE), has been used recently for the determination of pesticides in beverages (51, 52). It has been claimed that the detection limits obtained with this technique are higher than those of SPME, due to the higher amount of solid phase coating the bar in comparison to that used in fibers. Nevertheless, it has to be taken into account that a selective retention of analytes versus matrix components is necessary in order to achieve better detection limits.

DETERMINATION OF RESIDUES

Pesticide residues in juice and beverages are generally determined by chromatographic methods. The confirmation of residues at the low levels usually present in those matrices is a necessary and difficult analytical task, which is mainly carried out by mass spectrometry. Other analytical techniques, such as immunoassays and capillary electrophoresis, have also been employed.

Chromatographic Methods

Many pesticides are low-polarity, thermally stable, and volatile compounds, and therefore they can be determined by GC. Moreover, the availability of selective and sensitive detectors has made GC the preferred option for the analysis of

TABLE 3
Solid-Phase Microextraction of Pesticides from Juice and Beverages

Fiber (thickness)	Type	Pesticide	Matrix	Ref.
PDMS (100 μm)	HS	Organophosphorus	Fruit juice	(53)
		Oxadiazon	Wine and must	(54)
PPMS (70 μm)	HS	Organochlorines	Tea	(55)
CAR-DVB (65 μm)	DI	Multiclass	Fruit juices and wine	(56)
DVB-CAR-PDMS (50/30μm)	DI	Fungicides	Wine	(57)
PA (85 μm)	DI	Organophosphorus	Fruit juices and wine	(58)
		Triazoles		(59)
PDMS (100 μm)	DI	Multiclass	Wine	(60–62)
PDMS-DVB (60 μm)	DI	Fungicides	Wine	(63)
		Organophosphorus	Fruit juices	(64)

Abbreviations: PDMS, polydimethylsiloxane; PPMS, polyphenylmethylsiloxane; CAR-DVB, carbowax-divinylbenzene; DVB-CAR-PDMS, divinylbenzene-carbowax-polydimethylsiloxane; PA, polyacrilate; PDMS-DVB, polydimethylsiloxane-divinylbenzene; HS, head space; DI, direct immersion.

pesticide residues. At present these analyses are performed using fused silica capillary columns, normally with low-polarity stationary phases such as dimethylpolysiloxane or phenyl-substituted methylpolysiloxane. Insecticides and fungicides often are applied directly to fruits to control pests and diseases; hence, these compounds are frequently determined in juice and beverages. Table 4 summarizes the studies reported on GC determination of pesticides.

TABLE 4
Determination of Pesticides in Juice and Beverages by Gas Chromatography

Detector	Pesticide	Matrix	LOD (μg/kg)	Ref.
ECD	OC	Fruit juices and tea	0.05–8	(52, 55, 65)
	Fungicides	Wine and must	2–11	(8)
	Pyrethroids	Tea	5–100	(66)
	Multiclass	Fruit juices	1–5	(14, 15, 18, 67, 68)
		Tea	0.05 ng	(24)
		Wine and must	0.01–12	(9, 16, 45, 69–72)
FPD	OP	Fruit juices	8	(20, 64, 67)
		Tea	0.015–0.035	(52)
MS	OC	Tea	0.05	(55)
	OP	Wine and must	2–30	(10, 58)
		Fruit juices	0.025–0.050	(53)
	Fungicides	Beer	0.5	(43)
		Wine and must	0.1–50	(7, 8, 12, 51, 57, 73)
		Fruit juices	<5	(41)
	Oxadiazon	Wine	<0.02	(54)
	Pyrethroids	Tea	5–100	(66)
	Triazoles	Wine	0.03–0.1	(59)
	Multiclass	Fruit juices and wine	0.1–10	(39, 40, 44, 56, 61, 62)
MS-MS	Multiclass	Fruit juices and wine	2–50	(56)
NPD	OP	Wine	0.3–50	(10, 19, 74)
		Fruit juices	0.025–2	(17, 21, 49, 53)
	Fungicides	Wine and must	25–50	(6–8)
	Thiabendazole	Fruit juices	10	(42)
	Multiclass	Fruit juices	5–10	(14, 18)
		Wine	0.1–10	(16, 37, 45, 70, 71)

Abbreviations: ECD, electron capture detector; FPD, flame photometric detector; MS, mass spectrometry; NPD, nitrogen phosphorus detector; OC, organochlorines; OP, organophosphorus.

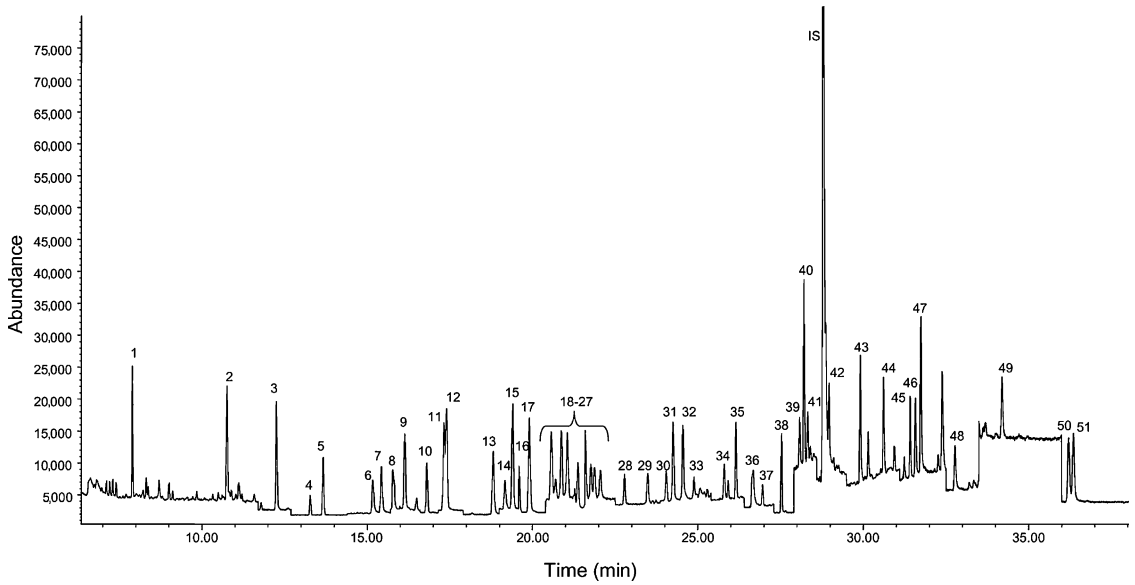

FIG. 2. GC-MS-SIM chromatogram of a grape juice sample fortified with pesticides at 0.02 μg/mL. Peak identification: 1, EPTC; 2, molinate; 3, propachlor; 4, ethalfluralin; 5, trifluralin; 6, simazine; 7, atrazine; 8, lindane; 9, terbuthylazine; 10, diazinon; 11, chlorothalonil; 12, triallate; 13, metribuzin; 14, parathion-methyl; 15, tolclofos-methyl; 16, alachlor; 17, prometryn; 18, terbutryn; 19, fenitrothion; 20, pirimiphos-methyl; 21, dichlofluanid; 22, aldrin; 23, malathion; 24, metolachlor; 25, fenthion; 26, chlorpyrifos; 27, triadimefon; 28, butralin; 29, pendimethalin; 30, phenthoate; 31, procymidone; 32, methidathion; 33, endosulfan I; 34, profenofos; 35, oxadiazon; 36, cyproconazole; 37, endosulfan II; 38, ethion; 39, ofurace; 40, benalaxyl; 41, endosulfan sulfate; 42, nuarimol; 43, bromopropylate; 44, tetradifon; 45, cyhalothrin; 46, fenarimol; 47, pyrazophos; 48, coumaphos; 49, cypermethrin; 50, fluvalinate tau-I; 51, fluvalinate tau-II; IS, internal standard (hexazinone).

Electron capture detection (ECD) has been the technique usually employed in the determination of halogen-containing pesticides, generally organochlorine compounds, due to its very good response for this class of pesticides. Nevertheless ECD does not have a high selectivity, which makes it necessary to confirm the residue identity in order to avoid false-positive residues, particularly at the low levels found in juice and beverages.

TABLE 5
HPLC Determination of Pesticides in Juice and Beverages

Detector	Pesticide	Matrix	Column	LOD (μg/kg)	Ref.
CL	Carbamates	Fruit juices	C_{18}	2–3	(15)
	Glyphosate	Beer	Anion exchange	5	(75)
DAD	Benzoylureas	Wine	C_{18}	4–5	(33, 35)
	Carbaryl	Fruit juices	C_{18}	0.8	(38)
	Benzimidazoles	Fruit juices	C_{18}	20	(30, 31)
	Multiclass	Wine and fruit juices	C_{18}	0.4–27	(36, 63, 76)
FD	Thiabendazole	Orange juice	C_8	0.15	(46)
MS	Benzimidazoles	Fruit juices	C_{18}	2	(30)
	Multiclass	Wine	C_{18}	0.01–6	(34, 77)
MS-MS	Fungicides	Beer	C_8	0.5–5	(78)
	Multiclass	Fruit juices	C_8	0.2–30	(47, 79, 80)
UV	Fungicides	Wine and must	C_{18}	1–10	(34)
	Multiclass	Wine	C_{18}	0.3–8	(77, 81)

Abbreviations: CL, chemiluminescence; DAD, diode array detector; FD, fluorescence detector; MS, mass spectrometry; UV, ultraviolet.

TABLE 6
Pesticide Levels (μg/kg) Found in Juice and Beverages[a]

Pesticides	Orange	Apple	Pineapple	Grape	Tomato	Tea	Wine	Beer
Organophosphorus								
Acephate		0.6						
Azinphos-methyl	20–40							
Chlorpyrifos	1.0–2.1	0.4–1.4	1.1					
Diazinon	2.1–3.7	4.0–4.7	1.4–5.5	2.6				
Dimethoate		0.5–100		0.7–3.0			7–25	
Ethion	0.6–8.0							
Fenitrothion							50	
Methamidophos		1			0.9–14.0	1		
Methidathion	0.7–2.0							
Omethoate		1–6		1–3			1–13	
Parathion-methyl							50	
Phosmet	22	2.0						
Fungicides								
Benomyl							40	
Captan				0.7–15				
Carbendazim		1.6–48	3.3				60	
Cyprodinil							0.9–50	
Dicloran							1–5	
Folpet				4–14				
Iprodione				1–7	5		0.4–80	
Oxadixyl							10–120	
Pyrimethanil							10–100	
Procymidone							0.8–50	
Propiconazole							0.4–1.7	
Thiabendazole	20–90	20–271					53	
Triadimefon								28–35
Triflumizole								7
Vinclozolin							10–80	
Organochlorines								
Chlorothalonil						0.9		
DDE, p, p′	0.4				0.2			
Dicofol	0.7–3.0			7.0				
Dieldrin						0.7		
Endosulfan			0.2–2		0.2–5.0		1.0–4.2	
Lindane							2.4–95	
Others								
Aldoxycarb						7.0		
Carbaryl	3–9	1–500	3.6	2–25	3–6	3	3–110	
Chlormequat		0.9						
Flufenoxuron							10	
Methoxychlor							1.2–1.3	
Teflubenzuron							12	

[a]Range of values reported in several monitoring studies (20, 47–49, 52, 57, 59, 62, 78, 80, 84–87).

Another important insecticide group is the organophosphorus compounds. These pesticides have often been determined by using a nitrogen-phosphorus or a flame photometric detector, due to the good selective and sensitive response obtained.

Nowadays, mass spectrometry (MS) coupled with GC is the analytical technique most often used. The need to analyze pesticides belonging to different classes requires the use of universal detectors able to determine them at residue levels. MS detection

TABLE 7
Estimated Daily Intake of Pesticides from Juice and Beverage Consumption

		Estimated daily intake (μg/person)				
		Juices		Tea		Wine
Pesticide	ADI (μg/person)	Child	Adult	Child	Adult	Adult
Organophosphorus						
Acephate	550	0.019	0.010			
Azinphos-methyl	275	1.455	1.559			
Chlorpyrifos	550	0.146	0.208			
Dimethoate	110	0.096	0.050			0.276
Ethion	110	0.161	0.172			
Fenitrothion	275					0.364
Methamidophos	220	0.033	0.026	0.030	0.117	
Methidathion	55	0.073	0.078			
Omethoate	110	0.088	0.047			0.218
Parathion-methyl	165					0.364
Phosmet	550	1.130	1.143			
Fungicides						
Benomyl	5500					0.291
Captan	5500	0.025	0.059			
Carbendazim	1650	0.722	0.359			0.437
Cyprodinil	1650					0.204
Dicloran	550					0.017
Folpet	5500	0.039	0.091			
Iprodione	3300	0.015	0.044			0.997
Procymidone	5500					0.207
Propiconazole	2200					0.007
Thiabendazole	5500	5.467	2.783			0.386
Vinclozolin	550					0.327
Organochlorines						
Chlorothalonil	1650			0.027	0.105	
Diazinon	110	0.293	0.273			
Dicofol	110	0.113	0.112			
Endosulfan	330	0.005	0.007			0.007
Lindane	275					0.691
Others						
Carbaryl	440	0.767	0.682	0.091	0.351	0.095
Chlormequat	2750	28.647	14.324			
Methoxychlor	5500					0.002
Teflubenzuron	550					0.087

is a good option, because it can be employed as a universal detector at full scan and also as a selective detector in the selected ion monitoring (SIM) mode. In addition the use of selected main ions from the pesticide mass spectrum, together with the particular retention time in GC for each compound, provides a very good confirmation of the residue identity. Moreover, the development of robust ion trap MS/MS equipment provides an alternative sensitive technique for the determination and confirmation of pesticides at residue level. Figure 2 shows a GC-MS-SIM chromatogram of a fruit juice spiked with pesticides at 20 μg/kg. Nevertheless, some pesticides are thermally unstable or not volatile, which hinders their determination by GC; consequently, they usually are determined by HPLC. As most pesticides are low-polarity compounds, they often are analyzed by reverse-phase HPLC employing a C_{18} stationary phase and mixtures of acetonitrile or methanol with water as the mobile phase.

Ultraviolet (UV) detection is frequently used in the determination of pesticide residues, due to its low cost and good response for many compounds. However, the selectivity in UV

detection is low, which is an important drawback for determination at the levels found in juices. This problem can be overcome for compounds showing fluorescence, due to the increase in sensitivity and selectivity obtained with the fluorescence detector (FD). The improvement in robustness and the decrease in prices achieved in MS coupled to HPLC has made MS a good option for pesticide detection, not only for the determination of compounds not amenable for GC analysis but also as a general detection technique for pesticide residue analysis. In addition the use of tandem MS/MS coupled to HPLC can improve the selectivity of analysis and allow the confirmation of residues at very low levels, due to the elimination of interferences prior to ion measurement through the isolation of the parent ion and its ulterior fragmentation. Table 5 shows the literature on HPLC determination of pesticides in juice and beverages.

The limits of detection (LOD) achieved by means of the different detectors used are on the order of μg/kg or even lower, depending on the particular pesticide-matrix combination and on the detection technique employed. These LODs can be lowered and, overall, the selectivity greatly improved when MS or tandem MS-MS detection is used.

Other Techniques

Enzyme-linked immunosorbent assays (ELISA) have sometimes been employed in the analysis of pesticides in juice and beverages (21, 61, 82, 83). This technique is often used as a screening procedure rather than for accurate quantitative analysis. The application of ELISA is preferred because these methods are cost-effective, not laborious, do not require sample clean-up, and can be performed without sophisticated instrumentation.

Nevertheless immunoassays are specifically developed for single pesticides, or in some cases class-specific immunoassays have been developed, but it is not possible at present to perform multiresidue pesticide analysis.

Another analytical technique that has been applied, although more scarcely, is capillary electrophoresis with UV detection (32). This technique has several advantages, such as very high resolution, small sample volumes, rapid analysis, and low solvent consumption, but it often suffers from low sensitivity for pesticide residue determination.

PESTICIDE LEVELS AND ASSESSMENT OF CONSUMER EXPOSURE

Pesticide residues have often been found in juice and beverages, although generally at low concentrations. Table 6 shows the pesticide levels found in the monitoring studies carried out by different authors. It can be observed that widely used fungicides and organophosphorus insecticides are the compounds more often detected at levels around a few μg/kg or lower.

Human exposure to environmental toxicants, and particularly to pesticides, is a current public health concern, due to their toxicity and the long-term exposure to these compounds. The risk posed by the presence of pesticides in food must be avoided, and therefore pesticide tolerances, expressed by their maximum residue limits (MRLs), have been established in many countries.

In order to estimate the population's exposure to pesticides from food ingestion, the information on dietary composition and data on residue concentrations in the food consumed have to be considered. Table 7 shows the estimation of daily intake of pesticides based on the amount of juices and beverages consumed by adults and children in a standard diet (84) and the pesticide concentrations found. The daily intake values estimated are very low in comparison with their corresponding acceptable daily intakes (ADI). These values show that the risk associated with the exposure via juice and beverage consumption is very low.

In the case of organophosphorus or carbamate pesticides, a cumulative risk should be considered, because compounds belonging to these groups may have a common mechanism of action. Nevertheless, owing to the low values encountered, this cumulative risk also can be considered low. A special precaution should be taken with children due to their higher susceptibility to chemicals during growth and the possible aggregate exposure from multiple sources, including the domestic use of pesticides.

CONCLUSIONS

The consumption of juice and beverages has clearly increased and many analytical procedures have been reported for determining pesticide residues in those matrices, due to increasing public concern about the presence of pesticides in food commodities. The use of classical extraction techniques requiring large volumes of harmful solvents has been overcome by new techniques based on the SPE of pesticides. Sample preparation using SPE followed by the determination of residues by a chromatographic method provides rapid, reliable, and sensitive procedures for the analysis of pesticides at levels usually found in juice and beverages. The reported levels are generally very low, and therefore they represent a low consumer exposure to pesticides through the consumption of these processed food commodities.

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