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Multiresidue analysis of seventeen pesticides in wine by gas chromatography with mass-selective detection

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Abstract

We have developed a multiresidue method permitting the simultaneous quantitation of 17 pesticides in wine: dicloran, dimethoate, diazinon, chlorpyrifos-methyl, vinclozolin, carbaryl, methiocarb, dichlofluanid, parathion-ethyl, triadimefon, procymidone, myclobutanil, iprodione, imidan, dicofol, phosalone and azinphos-methyl. Solid-phase extraction of 0.5 ml of wine sample is followed by direct injection of 1 μl of the eluent onto a DB-5 MS gas chromatographic column followed by mass-selective detection using one target and two qualifier ions for each pesticide. The extraction and injection steps are carried out with automatic instrumentation. Good resolution of all compounds was achieved with a run-time approximating 23 min. Detection and quantitation limits were around 2 μg/l and 10 μg/l, respectively, with linear calibration curves up to 3 mg/l for most constituents. Recovery in half the compounds was >90%, and >80% in most of the remainder. Imprecision (relative standard deviation) was <10% for most pesticides and <18% in all. Further analytes can be added to the repertoire without difficulty. The method merits consideration together with four other multiresidue methods now available that offer similar analytical characteristics, slower run-times, and a different selection of analytes.

Keywords: Wine; Food analysis; Sample preparation; Pesticides

1. Introduction

The widespread use of pesticides in grape production has led to the presence of pesticide residues in wines offered commercially for public consumption [1–3]. There is at present a great deal of uncertainty surrounding the limits in wine that can be safely tolerated for these potentially noxious agents [4,5]. The number of pesticides available to grape-growers has been steadily increasing as products have been introduced targeting specific pathogens [6,7]. Some of these newer agents are permitted in some jurisdictions but not in others. Since 1986, the Liquor Control Board of Ontario has maintained a Quality Assurance Program to monitor a wide range of pesticide residues in wines prior to permitting their sale to the public, irrespective of the country of origin. To consolidate a range of different technologies previously used for different families of pesticides, viz. gas chromatography (GC) with nitrogen–phosphorous detection for residues containing these atoms, GC with electron-capture detection for halogenated pesticides, high-performance liquid chromatography (HPLC) with fluorescence detection for carbamate pesticides [8], we have developed a GC method with mass-selective detection (MS)

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employing one target and two qualifier ions for each of 17 pesticides that are commonly or occasionally found in commercial wines. This paper describes the method itself and its performance characteristics under routine operating conditions.

2. Method

2.1. Chemicals

Ethyl acetate and ethanol were pesticide grade and glass distilled (Caledon, Georgetown, Canada). Fresh batches were run as blanks in the GC–MS system to ensure absence of interference. All water was double-distilled, deionised and charcoal-purified. Pesticide standards were as indicated in Table 1.

2.2. Sample preparation

Solid-phase extraction was performed by first washing cartridges (3 ml) containing 500 mg of C_{18} bonded porous silica (Supelco, Oakville, Canada, catalog No. 5-7012) with 3 ml of ethyl acetate followed by 3 ml of 96% aqueous ethanol and finally twice with 3 ml of 10% (v/v) ethanol in water. A 0.5-ml volume of wine sample was passed through the cartridge which was then dried for 60 min using a mechanical high vacuum pump under a 20 in.Hg vacuum (Edwards E2M2, Crawley, UK) (1 in.Hg= 338.638 Pa). Forty-eight extractions were performed simultaneously by coupling two Supelco VISIPREP-24 manifolds to the above pump. The absorbed pesticides were eluted by adding 2 ml of ethyl acetate and collecting the eluent in a graduated conical tube, thereby representing a four-fold dilution of the original wine sample. Since all pesticides eluted within the first ml, it is feasible to save time by using this volume (two-fold dilution). The cartridge can be reconditioned at least 10 times by washing alternately with 96% ethanol and water, and storing in 96% ethanol.

Table 1
Source of pesticide standards

Chemical name	Commercial name	M_r	Catalog No.[a]
Dicloran	Botran	207.00	RH 45435
Dimethoate	Cygon	229.28	RH 45449
Diazinon	Diazinon	304.35	RH 45428
Chlorpyrifos-methyl	Brodan	322.50	RH 45396
Vinclozolin	Ronilan	286.11	RH 45705
Carbaryl	Sevin	201.22	RH 45367
Methiocarb	Mesurol	225.31	PS-543
Dichlofluanid	Euparen	319.23	RH 45433
Parathion-ethyl	Parathion	291.26	RH 45607
Triadimefon	Bayleton	293.75	RH 45693
Procymidone	Sumilex	283.02	RH 36640
Myclobutanil	Nova	288.35	RH 34360
Iprodione	Rovral	330.17	RH 45536
Imidan	Phosmet	317.33	RH 45621
Dicofol	Kelthane	370.51	RH 36677
Phosalone	Rubitox	367.80	RH 45620
Azinphos-methyl	Guthion	345.37	RH 45333

[a] All from Riedel-de Haën, Wunstorfer, Germany, except methiocarb which was from Chem Service, West Chester, PA, USA.

2.3. Analysis

The HP5890 GC system coupled to an HP5972 mass-selective detection system (Hewlett-Packard, Mississauga, Canada) was fitted with a DB-5 MS column (J & W Scientific, Folsom, CA, USA) 30 m×0.25 mm I.D., 0.25 μm thickness. This column is stable up to 500°C. The carrier gas was ultra-pure helium at a flow-rate of 1 ml/min at the start of the temperature program (70°C) and had been previously passed through hydrocarbon and moisture traps.

The temperature program was as follows: initial temperature 70°C, held for 0.5 min; 10°C per min to 270°C, held for 0.1 min; 25°C per min to 290°C, held for 2 min; total run time, 23.4 min; injector and detector temperatures, 270°C. Injection of 1 μl of the ethyl acetate eluate was in splitless mode. One-hundred samples were sequentially introduced without manual intervention by means of the HP7673 Autosampler/Autoinjector. The MS system was routinely set in the selective ion monitoring (SIM) mode and each compound was quantitated based on peak area using one target and two qualifier ions (Table 2).

Instrument settings were as follows: solvent delay, 12.5 min; EM volts, 400; detector off at 21.0 min. Six-point calibration curves were constructed for each compound by dilution of stock standards and used to calculate its concentration in the wine samples. These were checked by two-point cali-

Table 2
GC–MS monitoring parameters for pesticides analysed

Compound	Retention time (min)	Target ion (*m*/*z*)	Qualifier ions (*m*/*z*)
Dicloran	12.70	206	176, 208
Dimethoate	12.85	87	93, 125
Diazinon	13.50	179	199, 304
Chlorpyrifos-methyl	14.42	286	125, 288
Vinclozolin	14.51	285	212, 287
Carbaryl	14.79	144	115, 116
Methiocarb	15.09	168	109, 153
Dichlofluanid	15.19	123	224, 226
Parathion-ethyl	15.52	109	139, 291
Triadimefon	15.59	208	210, 293
Procymidone	16.39	96	283, 285
Myclobutanil	17.40	179	181, 288
Iprodione	19.52	314	187, 316
Imidan	19.64	160	161, 317
Dicofol	19.89	139	111, 141
Phosalone	20.31	182	184, 367
Azinphos-methyl	20.38	160	77, 132

brations with each run; fresh calibration curves were generated if both calibrations were >2 standard error (SE) from the slope in the same direction.

Recovery of all 17 compounds from a composite mixture was checked once weekly.

Fresh standards were prepared if the recovery differed from the target value >2 standard deviations (SDs) on two consecutive occasions. The column was baked at 400°C once weekly, and cropped when necessary.

3. Results

3.1. Peak resolution

Fig. 1 illustrates the chromatographic resolution obtained when all 17 compounds were simultaneously added to pesticide-free wine. All peaks were satisfactorily separated with adequate sensitivity, although for parathion and triadimefon, as well as for phosalone and azinphos-methyl, the differences in retention times (min) were at the second decimal place. Resolution of these four peaks was not satisfactory when a deactivated fused-silica pre-column of 0.25 μm and 1 m length was used; the latter procedure also reduced the sensitivity of a number of constituents and was therefore not employed. These problems were caused by tailing after a few injections and seemed to be attributable to adsorption and decomposition inside the column. Retention times are listed in Table 2.

Column life averaged 4000 samples. Deterioration was first indicated by upward shifts in retention time and/or baseline, peak shouldering, or increased background noise.

3.2. Sensitivity

The criteria were based on standard definitions [9]. The limit of detection (LOD) for each compound was defined as the lowest concentration to exceed the mean baseline value by>3 SD (Table 3). For 11 pesticides this value was 2 μg/l, and 5 μg/l for the remaining six. The limit of quantitation (LOQ) was determined as the lowest concentration of each compound that gave a signal-to-noise ratio of 10 (Table 3). This was as low as 5 μg/l for carbaryl, methiocarb and procymidone; as high as 20 μg/l for dicofol and azinphos-methyl, and around 10 μg/l for the remaining compounds.

3.3. Linearity and calibration

Excellent linearity was obtained for all compounds as gauged by six-point calibration curves. The parameters of the linear regression equation $y=mx+c$ and the correlation coefficient r [10] yielded slopes with low SE and intercepts that in most cases did not differ significantly from zero, together with r-values close to unity (Table 3), except for the following: myclobutanil and azinphos-methyl, where there were small but significant ($P<0.05$) positive and negative intercepts, respectively, and the SE of the slopes was >5%. The linear range extended to relatively high values (at least 2 mg/l) for all constituents (Table 3), dilution of the sample rarely being required.

3.4. Recovery

Recovery was calculated by adding all constituents to 10 samples of pesticide-free white wine in a final concentration of approximately 250 μg/l and analysing the spiked wines (Table 4). The mean recovery of 10 constituents was very satisfactory (>90%).

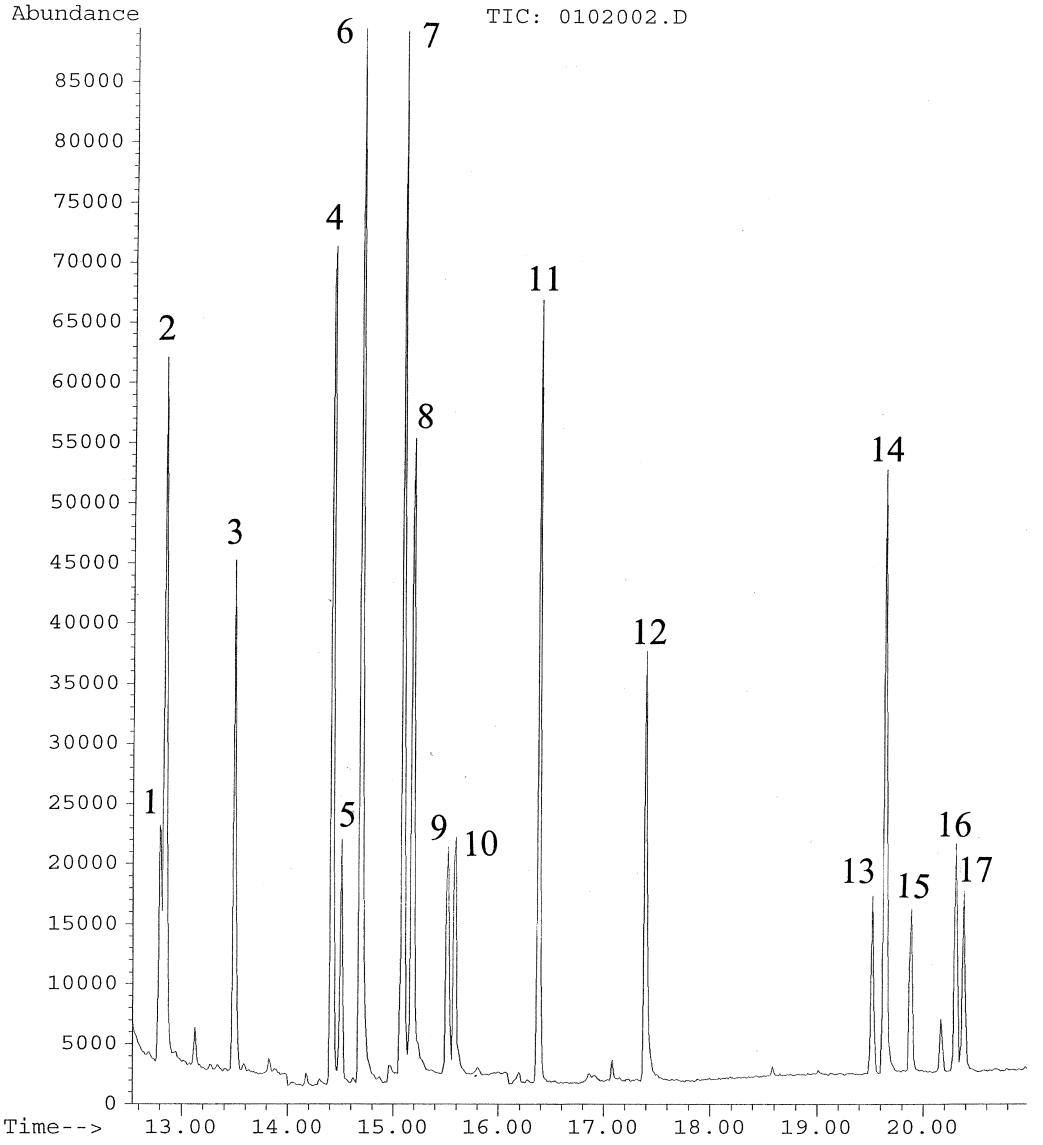

Fig. 1. Total ion chromatogram of a composite standard in pesticide-free white wine. The numbered peaks are as follows: 1=dicloran; 2=dimethoate; 3=diazinon; 4=chlorpyrifos-methyl; 5=vinclozolin; 6=carbaryl; 7=methiocarb; 8=dichlofluanid; 9=parathion-ethyl; 10=triadimefon; 11=procymidone; 12=myclobutanil; 13=iprodione; 14=imidan; 15=dicofol; 16=phosalone; 17=azinphos-methyl. The pesticide concentrations were around 250 μg/l (range 230–270 μg/l). Time scale in min.

Five (diazinon, chlorpyrifos-methyl, vinclozolin, parathion and dicofol) yielded recoveries in the 80–90% range, while the recoveries of phosalone and azinphos-methyl were as low as 78.4% and 79.4%, respectively.

3.5. Imprecision

This was determined for the complete method (solid-phase extraction plus GC–MS) and also for the GC–MS component alone. For the first, four

Table 3
Sensitivity and linearity of GC–MS method for pesticide analysis in wine

Compound	LOD (μg/l)	LOQ (μg/l)	Parameters of linearity			
			r[a]	Slope	Intercept[b]	Upper limit (μg/l)
Dicloran	2	10	0.998	$1.93\cdot10^2$	$+3.57\cdot10^3$	2000
Dimethoate	2	10	1.000	$2.69\cdot10^2$	$-9.05\cdot10^3$	2000
Diazinon	2	10	1.000	$3.62\cdot10^2$	$+1.90\cdot10^3$	2000
Chlorpyrifos-methyl	2	10	0.999	$1.90\cdot10^2$	$-7.41\cdot10^3$	2000
Vinclozolin	5	10	0.998	$2.10\cdot10^2$	$+1.74\cdot10^3$	2000
Carbaryl	2	5	0.999	$7.05\cdot10^2$	$+2.24\cdot10^4$	5000
Methiocarb	2	5	0.999	$7.16\cdot10^2$	$+3.01\cdot10^4$	2000
Dichlofluanid	2	10	1.000	$6.97\cdot10^2$	$+8.52\cdot10^3$	2000
Parathion-ethyl	2	10	0.995	$2.11\cdot10^2$	$-1.63\cdot10^4$	2000
Triadimefon	2	10	0.984	$2.17\cdot10^2$	$+1.72\cdot10^4$	2000
Procymidone	2	5	0.999	$5.68\cdot10^2$	$+1.52\cdot10^4$	3000
Myclobutanil	2	10	0.940	$1.92\cdot10^2$	$+3.54\cdot10^4$	2500
Iprodione	5	10	0.999	$9.75\cdot10^2$	$-1.32\cdot10^3$	5000
Imidan	5	10	0.996	$5.54\cdot10^2$	$-2.35\cdot10^4$	3000
Dicofol	5	20	0.995	$3.72\cdot10^2$	$-9.34\cdot10^2$	2500
Phosalone	5	10	0.995	$2.50\cdot10^2$	$-2.06\cdot10^4$	5000
Azinphos-methyl	5	20	0.964	$7.51\cdot10^2$	$-1.38\cdot10^4$	3000

[a] Correlation coefficient.
[b] In all cases this did not differ significantly from zero ($P>0.05$).

Table 4
Recovery and precision of wine pesticide analysis

Compound	Recovery[a] ± S.E.M. (%)	Method imprecision, RSD (%)				Instrument imprecision[b], RSD (%)	
		50 μg/l	100 μg/l	250 μg/l	1000 μg/l	250 μg/l	1000 μg/l
Dicloran	91.6±2.0	3.2	3.9	5.1	4.0	6.0	5.9
Dimethoate	97.3±1.8	7.7	7.0	8.2	6.2	2.6	4.6
Diazinon	84.0±2.5	6.1	6.3	9.9	7.9	8.7	8.6
Chlorpyrifos-methyl	80.3±1.5	7.1	7.1	9.6	9.1	8.1	8.1
Vinclozolin	86.7±1.4	4.0	3.0	3.4	3.0	6.8	7.2
Carbaryl	102.7±1.9	7.2	5.7	8.9	8.2	11.9	6.8
Methiocarb	98.7±1.6	4.8	7.7	7.6	6.9	3.4	3.9
Dichlofluanid	99.4±1.2	10.1	5.0	6.2	6.3	10.1	3.4
Parathion-ethyl	86.2±1.4	6.9	9.4	13.3	11.9	6.4	10.1
Triadimefon	101.9±1.3	12.0	7.2	9.3	8.2	4.3	6.4
Procymidone	97.2±1.1	10.9	11.8	13.1	12.4	7.4	4.3
Myclobutanil	91.7±1.1	11.1	9.9	13.9	10.4	7.9	7.4
Iprodione	96.1±1.4	13.0	11.6	13.1	9.9	11.4	7.9
Imidan	94.5±1.2	12.0	10.9	13.9	9.1	10.8	11.4
Dicofol	83.4±1.3	9.9	10.6	12.3	10.1	11.4	10.5
Phosalone	78.4±1.9	16.4	13.4	17.3	10.3	10.4	11.4
Azinphos-methyl	79.4±1.9	14.5	13.6	17.7	12.6	12.3	12.2

[a] Each pesticide was added to pesticide-free white wine in a concentration of 250 μg/l ($n=10$).
[b] $n=10$.

concentration levels of all pesticides (50 μg/l to 1 mg/l) were spiked into a single pesticide-free white wine and 10 replicate analyses were performed at each concentration. For the second, one eluate at two concentrations was directly injected 10 times into the GC–MS system. The relative standard deviation (RSD) was calculated for each set of replicates (Table 4). For seven constituents, the method RSD was <10% at all concentrations. For eight, values up to 16.4% were derived at the lowest concentration. The differences in RSDs at all concentrations for these 15 pesticides were not dramatic. Phosalone and azinphos-methyl gave the highest values for method RSD at the lowest concentration (up to 16.4%), with lesser values at the highest concentration. Surprisingly, the instrument RSD was around the same percentage as the method RSD (or somewhat higher) for most pesticides, suggesting that the solid-phase extraction contributes very little to the analytical variance.

3.6. Stability

This was assessed by preparing and analysing a fresh composite solution of wine containing all constituents, storing at 4°C (in sealed individual vials completely filled to exclude air) under a blanket of nitrogen, and re-analysing at weekly intervals for 6 weeks. All constituents were fully stable under these conditions except for the following which decreased in concentration at the end of that period by the percentage stated: imidan (17.5%); phosalone (24%); azinphos-methyl (15.5%); diazinon (82% after 1 week, 100% after 2 weeks). At 4°C, the stock standards were stable for 1 year, the dilutions used to calibrate for 1 week, and the composite solutions in sealed vials for 8 weeks.

4. Discussion

Many investigators have described methods for the determination of single pesticides in wine predominantly utilising GC or HPLC techniques. These include the carbamate dikar [11]; parathion [12]; methiocarb [13]; procymidone [14]; ethyl carbamate [15]; metalaxyl [16] and folpet [17].

Other papers have focused upon a group of pesticides, usually related but not necessarily so. Representative samples include the following; dialifor, dimethoate and methiathion [18]; 32 carbamate pesticides [19]; vinclozolin, iprodione, procymidone and dichlozolinate [20]; four fungicides including metalaxyl and folpet [21]; iprodione and vinclozolin [22]; and six pesticides among which were several not listed above, such as chlorpyrifos and fenarimol [23,24]. Further, the group headed by Cabras in Italy have made extensive contributions in addition to the paper already cited above [20], describing GC methods for four pesticides [25] and five different pesticides [26] in the last few years.

These approaches are well suited to vineyard-based laboratories, where the pesticides used will be known and relatively few. The task of a regulatory laboratory is infinitely more complex. Here, the objective is to test for all possible pesticides, most of which have defined allowable limits while others are banned completely. This testing is not restricted to domestic products but also embraces wines and other beverages from any country in the world seeking to export its products. Although a combination of different techniques as used previously in our laboratory can meet these needs, the costs (especially in labour) are high, and the risks of mis-matching results and other transcription and identification errors are increased many-fold compared with a multiresidue method capable of analysing and quantitating all the desired analytes in a single run. The trade-off is that analytical quality will not be the same for all constituents and compromises will have to be made in setting acceptable limits for imprecision and recovery.

The first multiresidue method for the analysis of pesticides in wine utilised HPLC preceded by solid-phase extraction on a C_8 cartridge [27]. The limits of detection for the 15 compounds measured ranged from 6 to 20 μg/l and recoveries were 85–108%, but only six were among the pesticides included in our repertoire. Kaufman [28] presented a fully automated method to assay 21 pesticides in wine, in which solid-phase extraction is followed by GC–MS. Detection limits were stated to range between 5 and 10 μg/l. Recoveries for 17 pesticides ranged between 80 and 115%, but were much lower (down to 5%) for three and 585% for a fourth. No data for imprecision were provided, but the RSDs for recovery based on five replicates ranged from 1 to 29%, all except one value being <10%. Five of the

above 21 pesticides were among those measured by our method.

GC–MS coupled to solid-phase microextraction (SPME) was used to measure 14 pesticides, five of which were also measured by us [29]. Limits of detection ranged from 0.1 to 5.5 μg/l, and the method was clearly much more sensitive than the previous two, in line with the use of SPME. However, this level of sensitivity is not required since the allowable limits for pesticides in wine approximate 0.1–1 mg/l in most jurisdictions, values up to 5 mg/l being permitted in some instances. Imprecision for individual pesticide assays (RSD) ranged from 8.6 to 18% at a concentration of 1 μg/l and 3.2–9.9% at a concentration of 100 μg/l. Data for recovery were not presented.

The most recent multiresidue method for pesticides in wine has been introduced by Hyötyläinen et al. [30]. This couples LC to GC (flame ionization detector) through a vaporizer interface. The method seems capable of measuring almost any desired pesticide, but the authors reported data on only seven, two of which overlapped with our selection. Linearity was excellent; imprecision (RSD) ranged from 6 to 12%; limit of detection was around 10 μg/l; recoveries ranged from 100 to 130% except for procymidone, for which recovery was only 35%.

It is axiomatic that a multiresidue method will not be optimal for all compounds analysed, forcing certain compromises in order to permit the inclusion of a broad range of analytes. The present method is a useful and practical option that offers the rapid (approximately 23 min) analysis of 17 pesticides. In this respect it is faster than previous multiresidue methods, viz. 40 min [27,29] and >60 min [30]; Kaufman [28] did not specifically provide this information, but a comparison of individual pesticides revealed much longer retention times with his method than with ours. Previous methods seem to have been tailored to pesticides favoured by European growers, whereas our method includes all of those used in North America that may be present in commercial wine. This does not apply to folpet and captan which, although used in many spraying programs and frequently present on grapes and in the pressed juice, are degraded during fermentation.

Many methods have been developed to measure the pesticide content of fruit and vegetables (e.g., [31,32]), some of which permit the analysis of many more compounds than we have undertaken to date, although in theory (and to some extent in practice as we have already shown, see below) any volatile pesticide for which a pure standard is available can be assayed subject to satisfactory peak resolution. However, only a small proportion of these compounds are used on grapes, and even fewer appear in commercial wines due to their degradation and precipitation during fermentation and clarification procedures [8]. Moreover, the time per analysis is much longer (requiring multiple extractions) and both recovery and precision are poorer than in methods developed specifically for wine analysis. It is not advisable to use GC–MS for many carbamates and ethylene bis-dithio carbamate (EBDC) derivatives. They are difficult to volatilise, lose sensitivity after a few injections, and can cause deterioration of the column and detector. They are now almost universally measured by HPLC with fluorescence detection after post-column derivatization.

Our method is versatile and is capable of allowing the inclusion of new pesticides released on the market. For example, we have recently added imidacloprid to the original 17 pesticides (together with α- and β-endosulfan, malathion, methoxychlor, chlorpyrifos ethyl, folpet and captan for analysis of juices) and achieved analytical characteristics matching those reported in this paper.

In terms of sensitivity, recovery, linearity and imprecision, the present method matches the performance of previously published techniques in most respects. The level of automation (extraction and injection) is an attractive feature. It has been in routine use for one year in the course of which >6000 products have been analysed from every wine-producing region of the universe without any problems coming to attention, and has also been recognised as matching the stringent standards required for regulatory and legal purposes by the Canadian Department of Agriculture. Laboratories desiring to expand their repertoire of pesticide analyses or unhappy with their current methods should find it worthy of consideration.

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