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Short communication

Optimization of a sample preparation method for multiresidue analysis of pesticides in tobacco by single and multi-dimensional gas chromatography-mass spectrometry

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ABSTRACT

A selective and sensitive multiresidue analysis method, comprising 4 7pesticides, was developed and validated in tobacco matrix. The optimized sample preparation procedure in combination with gas chromatography mass spectrometry in selected-ion-monitoring (GC-MS/SIM) mode offered limits of detection (LOD) and quantification (LOQ) in the range of 3–5 and 7.5–15 ng/g, respectively, with recoveries between 70 and 119% at 50–100 ng/g fortifications. In comparison to the modified QuEChERS (Quick-Easy-Cheap-Effective-Rugged-Safe method: 2 g tobacco + 10 ml water + 10 ml acetonitrile, 30 min vortexing, followed by dispersive solid phase extraction cleanup), the method performed better in minimizing matrix co-extractives e.g. nicotine and megastigmatrienone. Ambiguity in analysis due to co-elution of target analytes (e.g. transfluthrin-heptachlor) and with matrix co-extractives (e.g. δ-HCH-neophytadiene, 2,4-DDE-linolenic acid) could be resolved by selective multi-dimensional (MD)GC heart-cuts. The method holds promise in routine analysis owing to noticeable efficiency of 27 samples/person/day.

1. Introduction

India is the world's second largest producer of tobacco (*Nicotiana tabacum* L.) with $901.95 million/year worth of export [1,2]. Cultivation of tobacco receives frequent application of pesticides, the residues of which might sustain processing treatments and cause health hazards [3–5]. The need for a multiresidue analysis method for pesticides in tobacco is pertinent to support the Indian tobacco industry to comply with the Guidance Residue Levels (GRL)[6]. Considering the complex nature of its matrix, in most literature, only 2-7.5 g of tobacco has been considered for extraction [7–9] with selective determination by GC [10], two-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC-TOFMS) [11], GC-MS/MS [9,12], high performance liquid chromatography [13] etc. However, with these methods, we have recorded high matrix effect (ME) and false positives/negatives for several pesticides. In the present study, we therefore, aimed to develop an effective sample preparation method to minimize co-extractives and also attempted to resolve matrix interferences for target pesticides by GC-MS/SIM and MDGC heart-cuts.

2. Experimental

2.1. Selection of pesticides and tobacco matrix

A total of 47 GC amenable compounds out of the GRL list (23 organochlorines, 8 organophosphates, 16 pyrethroids) were considered [6]. Sample preparation was optimized and validated in KLS (Karnataka Light Soil) tobacco (highest exported type), and further evaluated in three other tobacco matrixes viz. NLS (Northern Loamy Soil), SBL (Southern Black Soil) and SLS (Southern Light Soil) (Supplementary Table 1).

2.2. Reagents and materials

Certified pesticide reference standards (>98% pure) were purchased from Ehrenstorfer GmbH (Augsburg, Germany). The

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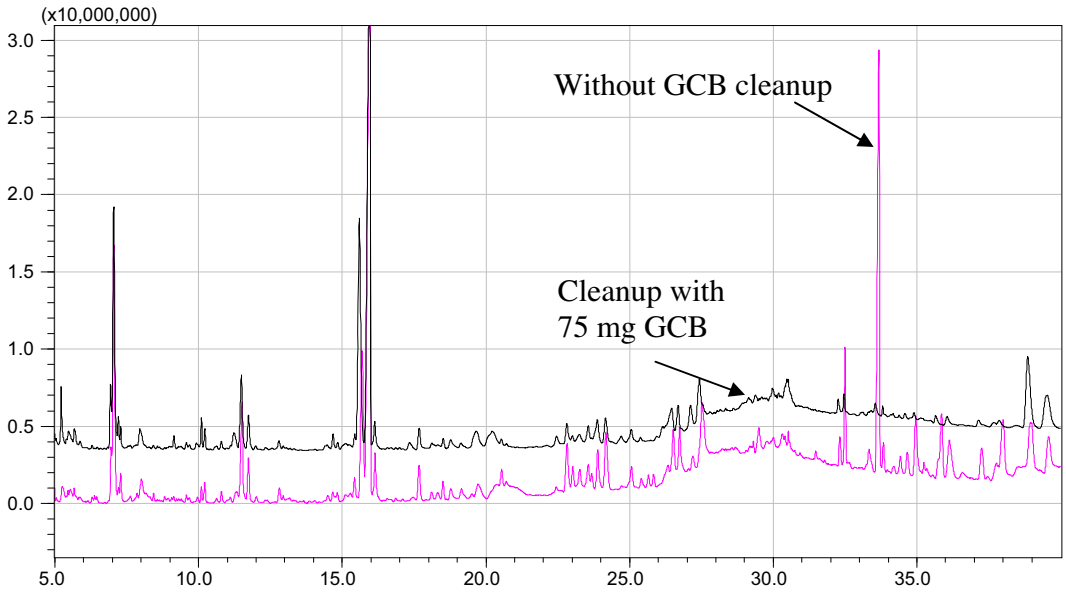

Fig. 1. Overlaid full-scan chromatogram of control matrix with and without GCB cleanup (75 mg) showing effect of cleanup on removal of matrix co-extractives.

solvents used were of pesticide residue analysis grade (Sigma–Aldrich, Bangalore, India). The dispersive solid phase extraction (d-SPE) sorbents viz. primary secondary amine (PSA), C18 and graphitized carbon black (GCB) were purchased from United Chemical Technology (Bristol, PA, USA). The other reagents were of analytical reagent grade. A homogenizer (Silent Crusher M, Heidolph, Saffron Walden, UK) was used for proper mixing of the sample with solvent during extraction.

2.3. Preparation of standard solutions

The stock solutions (w/w) of the individual pesticide standards were prepared by dissolving 10 mg of each analyte in 9 g ethyl acetate (EtOAc, 10 mL = 9 g). An intermediate mixture of 10 mg/L was prepared by mixing appropriate quantities of the individual stock solutions followed by requisite volume make-up, from which the calibration standards (5-250 ng/mL) were prepared by serial dilution.

2.4. Standardization of sample preparation technique

2.4.1. Pre-treatment

To obtain homogeneity, the dry tobacco samples (25 g) were soaked in water (225 mL, containing 0.5% acetic acid) for 30 min and subsequently homogenized (2 min) to form a fine paste with smooth appearance without any visual granules. Homogeneity test was carried out at 100 ng/g ($n = 6$). For this, 100 g of tobacco samples were spiked at 100 ng/g. The pretreatment was done as follows:(a) six samples (2 g) drawn from 100 g spiked sample(b) to 100 g sample, 900 mL water was added and soaked for 30 min. Further, the sample was homogenized in a grinder and 10 g sample was drawn for extraction.

The samples were extracted using the procedure described in Section 2.4.5.

2.4.2. Sample size optimization

Tobacco homogenates, 10 g (1 g tobacco + 9 mL of water) and 20 g (2 g tobacco + 18 mL of water), fortified with the pesticide mixture (100 ng/g), were extracted in separate batches ($n = 6$) with 10 mL EtOAc, followed by d-SPE cleanup using 150 mg PSA + 150 mg C18 + 75 mg GCB + 300 mg $MgSO_4$ for 10 g and proportionately double amounts for 20 g. The recoveries were statistically compared.

2.4.3. Sample:solvent ratio

To optimize the sample-solvent ratio, 20 g of the fortified tobacco homogenate (at 100 ng/g) was extracted with varying amounts (5 and 10 mL) of ethyl acetate in separate batches each in six replicates. The cleanup in each case was carried out with d-SPE sorbents in proportionate amounts as mentioned below:

- Solvent volume 5 mL: 300 mg PSA + 300 mg C18 + 150 mg GCB + 600 mg MgSO4
- Solvent volume 10 mL: 150 mg PSA + 150 mg C18 + 75 mg GCB + 300 mg MgSO4

The quantification of residues in the recovery samples was carried out using matrix-matched standards prepared separately with the strategies selective for 5 and 10 mL solvent volumes to ensure comparability of results.

2.4.4. Optimization of GCB for cleanup

Effect of variable quantities of GCB (0, 75 and 150 mg) was investigated in combination with PSA (150 mg), C18 (150 mg) and $MgSO_4$ (300 mg). Since GCB tends to adsorb planar pesticides like chlorothalonil [14], the effect of toluene addition (200, 500 and 1000 μl) on its recovery (at 100 ng/g) was also evaluated. In all cases, quantification was done using corresponding matrix-matched calibrations.

2.4.5. Optimized sample preparation method

Samples (20 g homogenate) were extracted with EtOAc (10 mL, +10 g Na_2SO_4) by homogenization (15000 rpm, 2 min), followed by centrifugation (5000 rpm, 5 min) for phase separation. An aliquot of 3 mL EtOAc extract was drawn, mixed with toluene (1000 μl), vortexed (30 s), and cleaned by d-SPE (150 mg PSA + 150 mg C18 + 75 mg GCB + 300 mg $MgSO_4$). The supernatant was filtered through PTFE membrane (0.22 μm, Chromatopack, Mumbai) before injection into GC-MS.

The performance of the above method was compared with the modified QuEChERS method [15] in terms of recovery and cleanup efficiency.

2.5. GC-MS

A QP-2010 Plus GC-MS (single quadrupole, Shimadzu Corporation, Kyoto, Japan) with VF-5MS (30 m × 0.25 mm, 0.25 μm)

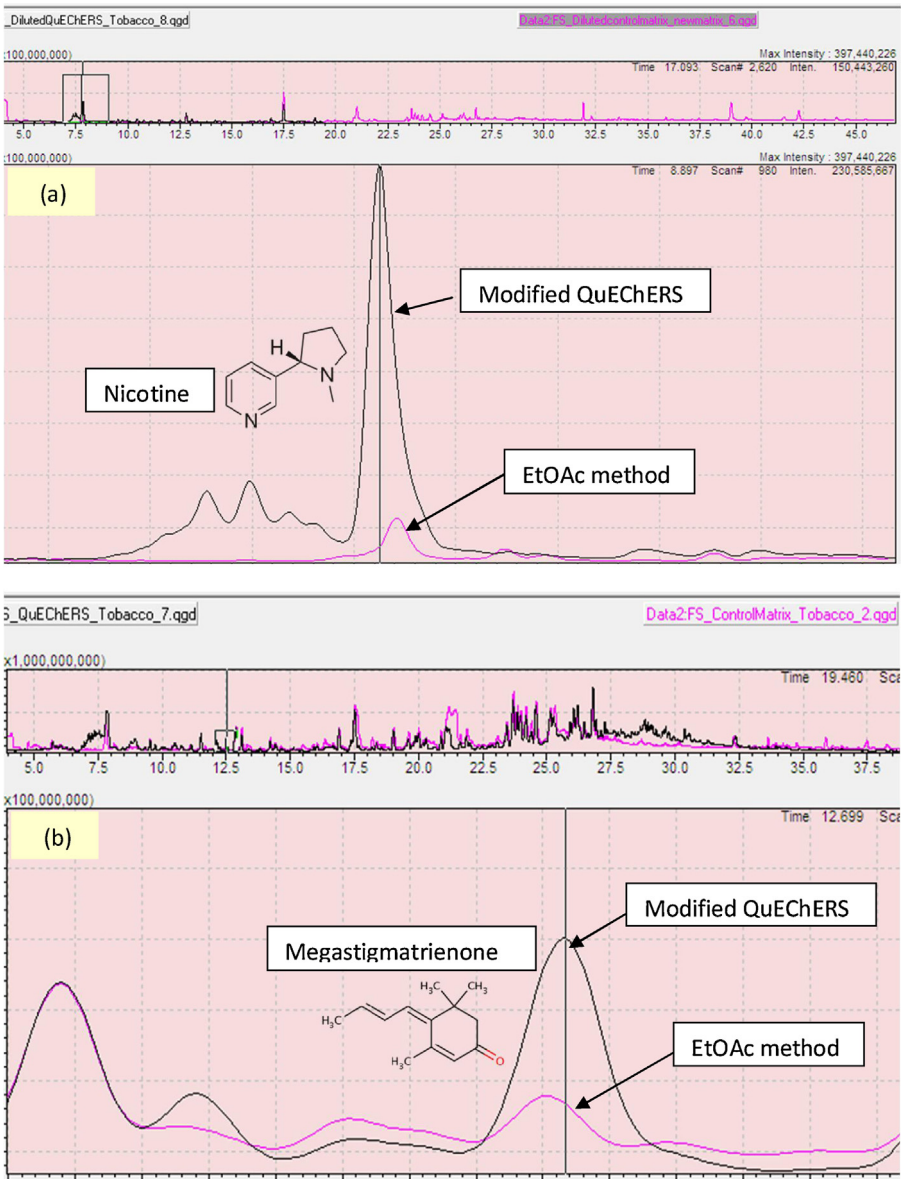

Fig. 2. Comparative cleanup effect: intensity of (a) nicotine and (b) megastigmatrienone by EtOAc against modified QuEChERS.

capillary column was used. GC separation was achieved through an optimized oven temperature program from 60 °C (1 min), ramped at the rate of (@) 25 °C/min to 160 °C (0 min), 2.5 °C/min to 190 °C (0 min), 3 °C/min to 205 °C (1 min), 5 °C/min to 220 °C (0 min) and finally 17 °C/min to 285 °C (10 min) with a total run time of 39.82 min. GC injection was performed through programmable temperature vaporizer (PTV) inlet utilizing a hollow glass liner with glass wool with large volume injection (LVI) (6 μl) for higher sensitivity. The initial injection temperature was 70 °C for 0.07 min. During the evaporation phase, temperature was ramped to 87 °C at a rate of 50 °C/min (0.1 min), then increased to 285 °C at 400 °C/min (0 min) during transfer phase. Initially, for 0.8 min, the split vent was kept open, then splitless condition was maintained for 2 min (transfer of analytes to the column), and further, the split vent was opened again for the rest of the run time. The carrier gas (Helium) flow was maintained at 1.10 mL/min. In MDGC-MS (described in Supplementary Information: MDGC setup), the VF-5MS column (in 1st GC oven with ECD at 300 °C) was connected in series to a mid-polar Rxi-624 SilMS column (6% cyanopropylphenyl, 94% dimethylpolysiloxane; 30 m × 0.53 mm) in the 2nd GC oven (connected to MS) through a Deans switch and the other end of the column was connected to MS detector. After confirming the identity of each target peak over ECD on retention time (t_R) basis, the chromatographic separation was optimized in the 2nd column with oven temperature program starting from 200 °C, then ramped @ 20 °C/min to 270 °C, with heart-cut switching recovery of 100%.

2.6. Method performance

The analytical method was validated as per the DG-SANCO guidelines [16]. On the basis of the solvent and matrix-matched calibration curves within 5–250 ng/mL, LOD and LOQs were determined by considering a signal to noise ratio (S/N) of 3 and 10, respectively. The precision in terms of repeatability (3 analysts prepared 6 samples each on a single day) and intermediate precision (3 analysts prepared 6 samples each on 6 different days) was determined separately at 100 ng/g. Precision was expressed as the ratio of the reproducibility standard deviation (RSD_R) to the predicted relative reproducibility SD ($PRSD_R$) and repeatability SD (RSDr) to the predicted repeatability SD ($PRSD_r$) using Thompson equation

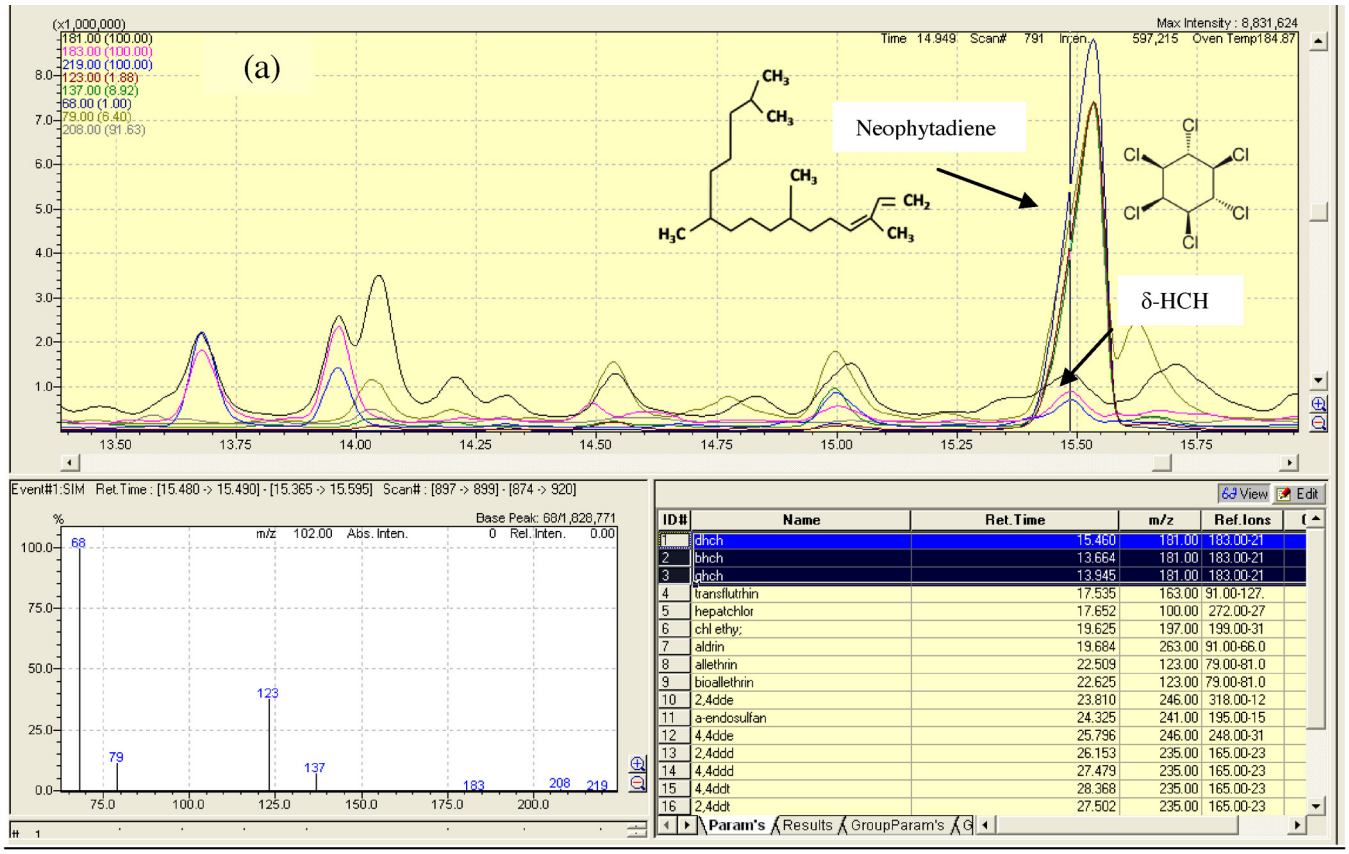

Fig. 3. Reduction of matrix interferences for δ-HCH by MDGC-MS (a) before heart-cut and (b) after heart-cut.

[17] which suggests that at concentration <120 ng/g, $PRSD_R = 22.0$ and $PRSD_r = 0.66\ PRSD_R$. The recovery experiments were carried out by fortifying the blank KLS matrix ($n = 6$) with the pesticide mixture separately at 50, 70 and 100 ng/g. ME was calculated as: (peak area of matrix-matched standard- solvent standard) x 100/peak area of solvent standard).

The method was applied for the analysis of 20 samples collected from the native parts of Karnataka and Maharashtra States.

3. Results and discussion

3.1. Standardization of sample preparation

3.1.1. Homogeneity

Soaking in water increased the recovery of the EtOAc phase from ~2 to 6–7 mL when 10 mL solvent was used to extract 20 g of tobacco homogenate. The homogeneity test results were

Table 1
Method validation data for multiresidue analysis of pesticides in tobacco.

Name	t_R (min)	Quantifier	Qualifier 1	Qualifier 2	GRL	LOD	LOQ	Recovery (% RSD) at spike level (ng/g)		
		m/z	*m/z*	*m/z*	(ng/g)	(ng/g)	(ng/g)	50	70	100
Dichlorvos	5.639	185	79	109	100	3	10	–	79 (2)	105(1)
4-Br-2-Cl phenol[a]	6.029	208	63	206	NA	3	10	–	78 (1)	88(4)
Fenobucarb	9.859	121	150	107	NA	5	15	83 (4)	91 (3)	92(2)
α-HCH	11.852	181	183	219	50	3	7.5	71 (3)	74 (2)	86(2)
Lindane	13.325	181	183	219	50	3	7.5	76 (6)	99 (3)	102(4)
β-HCH	13.328	181	183	219	50	3	7.5	72 (2)	74 (3)	86(2)
δ-HCH	14.986	181	183	219	50	3	7.5	74 (3)	75 (2)	98(3)
Dimethoate	12.507	93	87	125	500	5	15	–	–	89(5)
Diazinon	13.632	137	179	93	100	3	10	–	79 (7)	82(3)
Chlorothalonil	14.205	266	264	268	2000	3	10	–	71 (6)	79(6)
Chlorpyriphos methyl	16.11	286	125	288	200	3	10	–	75 (12)	96(4)
Transfluthrin	16.718	163	91	127	NA	3	10	–	84 (5)	103(2)
Heptachlor	16.779	272	100	274	20	3	7.5	88 (7)	103 (9)	93(3)
Fenitrothion	17.907	277	125	65	100	3	10	–	84 (6)	96(4)
Aldrin	18.713	263	66	91	20	3	7.5	94 (6)	100 (8)	102(3)
Chlorpyriphos ethyl	18.727	197	199	314	500	3	10	–	87 (1)	89(4)
Dichlorobenzophenone	19.7	139	111	141	NA	3	10	–	70 (6)	93(6)
Heptachlor epoxide	21.02	353	81	355	20	3	7.5	79 (9)	96 (6)	92(2)
Allethrin	21.559	123	79	81	NA	4	10	–	109 (8)	103(2)
Bioallethrin	21.738	123	79	81	NA	4	10	–	119 (9)	106(2)
cis-Chlordane	22.478	373	375	377	100	3	10	93 (5)	102 (5)	96(2)
2,4-DDE	22.74	246	248	318	200	3	10	99 (9)	111 (5)	93(2)
α-Endosulfan	23.206	241	195	159	1000	4	10	–	88 (10)	104(4)
trans-Chlordane	23.259	373	375	377	100	3	10	90 (2)	99 (5)	94(2)
Profenofos	24.69	339	337	208	100	4	10	–	110 (6)	87(6)
4,4-DDE	24.81	246	248	318	200	3	10	–	106 (2)	93(3)
Dieldrin	24.789	263	81	79	20	3	7.5	93 (9)	102 (7)	86(3)
2,4-DDD	25.199	235	237	165	200	4	10	–	81 (7)	88(2)
Endrin	26.022	263	81	67	50	3	7.5	84 (4)	88 (3)	93(2)
β-endosulfan	26.679	195	241	243	1000	4	10	–	85 (13)	76(4)
4,4-DDD	26.892	235	237	165	200	4	10	–	102 (5)	98(4)
2,4-DDT	27.033	235	237	165	200	4	10	–	113 (3)	88(4)
Endosulfan sulfate	28.053	272	229	237	1000	4	10	–	80 (8)	76(3)
4,4-DDT	28.159	235	165	237	200	4	10	–	94 (7)	92(3)
Bifenthrin	29.283	181	166	141	2500	4	10	–	100 (1)	96(3)
Fenpropathrin	29.48	181	97	55	NA	4	10	–	85 (9)	78(3)
Lambda cyhalothrin	30.352	181	77	150	500	4	10	–	76 (8)	81(2)
Permethrin-1	31.248	183	163	165	500	5	15	–	–	82(4)
Permethrin-2	31.412	183	55	181	500	5	15	–	–	79(3)
Cyfluthrin	31.665	163	165	127	2000	5	15	–	–	92(4)
Cypermethrin	32.221	163	165	127	1000	5	15	–	–	96(6)
Etofenprox	32.863	163	165	107	NA	4	10	–	80 (6)	79(4)
Fenvalerate	33.769	225	125	167	1000	5	15	–	–	75(3)
Esfenvalerate	34.375	167	125	225	NA	5	15	–	–	92(3)
Fluvalinate-1	33.905	250	252	55	NA	5	15	–	–	81(5)
Fluvalinate-2	34.096	250	252	55	NA	5	15	–	–	73(2)
Deltamethrin	36.468	181	253	172	1000	5	15	–	–	78(3)

[a] 4-Bromo-2-chlorophenol, the primary metabolite of the organophosphorus insecticide profenophos.

satisfactory [e.g. RSD of α-HCH (2.7%), trans-chlordane (2.5%), transfluthrin (2.5%), bifenthrin (2.6%)]. Addition of 0.5% acetic acid adjusted the homogenate's pH to ~4 which was optimum for the stability of all studied pesticides. Differences in recoveries for 10 and 20 g sample sizes were non-significant ($p = 0.05$). However, as the precision RSDs for 20 g homogenate were <3% in most cases vis-à-vis >6% for 10 g, it was selected as the optimum sample size.

3.2. Sample:solvent ratio

Extraction of 20 g homogenate by 5 and10 mL of EtOAc resulted in similar recoveries ($p = 0.05$). However, MEs were significantly lower for 10 mL vis-à-vis 5 mL solvent (e.g. MEs of α-endosulphan and dieldrin were 31 and 23% less, respectively), which could be due to the effect of dilution of matrix components. Hence, 10 mL solvent per 20 g homogenate was selected as optimum.

3.3. Evaluation of cleanup procedure

Optimization of cleanup was necessary to minimize ME and contamination of GC-hardware (liner, etc.) [18]. A comparison of the total ion chromatograms showed numerous additional signals in case of '0 mg GCB's (especially at retention times where pyrethroids elute), vis-à-vis 75 mg GCB (Fig. 1). GCB addition in d-SPE provided a better S/N for pyrethroids, and such effects (+ lower ME) were similar ($p = 0.05$) for 75 and 150 mg GCB except for organochlorines and organophosphates, where 150 mg GCB resulted in15-20% reduction in S/N vis-à-vis 75 mg GCB. The Supplementary Table 2 shows some matrix compounds which elute over the time frame of pyrethroids. The MEs for lindane and fenobucarb were 33 and 25% less with 75 vis-à-vis 150 mg GCB. Hence, 75 mg GCB in combination with150 mg PSA, 150 mg C18 and 300 mg $MgSO_4$ was considered as optimum for effective cleanup. However, inclusion of 75 mg GCB in d-SPE resulted in substantial adsorption loss of chlorothalonil and endrin residues. Addition of toluene to the solvent extract before d-SPE reduced such losses and the recoveries

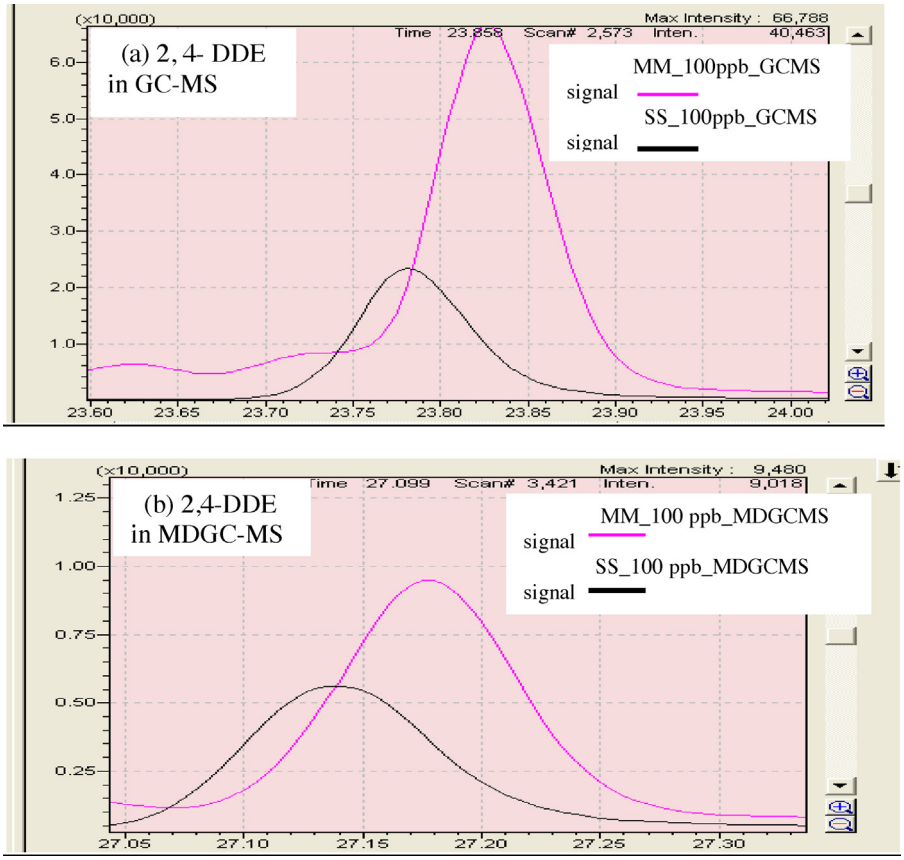

Fig. 4. 2,4-DDE showing higher matrix effect in (a) GC-MS as compared to (b) MDGC-MS after chromatographic separation from linolenic acid.

of chlorothalonil and endrin increased from 43 to 74% and 22 to 76%, respectively, when toluene level was increased from 200 to 1000 μl. Addition of toluene did not have any significant effect on matrix effect. If PSA and C18 are not used in cleanup, then matrix effect significantly increases. For example, in case of chlorothalonil and *o,p*-ddt, the matrix effects were reduced by 27 and 48% respectively when the optimized PSA and C18 were used. On gravimetric comparison, the optimized method had around 28–30% less residual matter than modified QuEChERS [15] when equal volumes of extracts were evaporated to dryness and compared on dry weight basis. The optimized cleanup was also effective in significantly minimizing the level of co-extracted nicotine (a major tobacco alkaloid) and megastigmatrienone (an aroma compound) by 85 and 60%, respectively [Fig. 2(a) and (b)], vis-à-vis modified QuEChERS.

3.4. Method validation

3.4.1. LOD, LOQ and recovery

The calibration linearity ($R^2 > 0.99$) was established for all the pesticides with LOD and LOQ values below the GRLs (Table 1). The recoveries were similar to modified QuEChERS ($p = 0.05$) and ranged between 70 and 119% with repeatability and intermediate precision-RSD < 10%, and Thompson ratios <2 indicating satisfactory precision. The optimized sample preparation method involves a dilution factor of 6.65.For those pesticides with LOQs < 10 ng/g, the recoveries are reported at all fortification levels (50, 70 and 100 ng/g). For those pesticides with LOQs at 10 and 15 ng/g, considering the dilution factor, the recoveries are reported at 70 and 100 ng/g respectively (Table 1). For aldrin, dieldrin, heptachlor and heptachlor epoxide, although the sample preparation method could provide good recoveries, it was not possible to achieve detection at the GRL of 20 ng/g due to the dilution of samples, which probably indicates inherent limitation of a single quadrupole GC-MS to achieve the desired LOQ (2–3 ng/g) and in such cases higher selectivity and sensitivity of GC-MS/MS selected reaction monitoring could provide required detection limits.

3.4.2. Evaluation of matrix influence

The ME ranged from 25 to 90% for most of the studied pesticides, including matrix induced signal enhancements (>50% for 4% pesticides) and suppressions (>50% for 34% pesticides), necessitating use of matrix-matched standards for quantification. For certain pesticides, lower analyte peak areas were observed when compared to the area of the analyte in solvent standard. For example, chlorothalonil ($t_R = 14.205$ min) showed only 54% area. Similar matrix effect was recorded for transfluthrin ($t_R = 16.718$ min, 67% area) and heptachlor ($t_R = 16.779$ min, 58% area). The ME for the test pesticides in NLS, SLS and SBS types of tobacco were mostly similar. In general, ME was higher in KLS as compared to the other types except for dimethoate, dichlorobenzophenone and fenpropathrin, where MEs in KLS were approximately 70, 20 and 70% less, respectively. Although KLS type had relatively less nicotine content (Supplementary Table 1) a higher ME for most of the pesticides indicates influence from matrix constituents other than nicotine.

Replacing lower *m/z* fragment ions with higher ones for quantification resulted in improved S/N and also reduced ME (Supplementary Table 3). This is due to the fact that the co-extractives from tobacco matrix generated many low m/z ions throughout the chromatographic run which might have interfered with the detection of the pesticides of interest when a lower *m/z* is selected [11]. For example, by selecting the quantifier m/z as 263 (S/N = 73) instead of the base peak *m/z* 79 (S/N = 17), and *m/z* 353 (S/N = 1236)

instead of 71 (S/N = 23), the MEs of dieldrin and heptachlor epoxide were reduced by ~90%. In case of fenpropathrin, the m/z 181 (S/N = 105) in place of 97 (S/N = 22), reduced ME by 70%. The signal of endrin, which was masked by geranyl-α-terpinene, a matrix compound, could be selectively quantified when m/z 263 was chosen.

Although the cleanup strategy effectively minimized MEs for most of the pesticides, however, selective co-elutions of specific matrix co-extractives still created ambiguity in identification and quantification of some pesticides. The δ-HCH signal was masked by neophytadiene (a natural constituent of tobacco) (Fig. 3a), which resulted in <30% matching with the NIST library in full scan. Although the relative abundance of *m*/*z* 181 and 183 was low in the neophytadiene mass spectrum, because of its high concentration (as co-extractive) in the final solution, the quantification of δ-HCH with the same *m*/*z* was erroneous. Such a strong co-elution could be resolved by MDGC-MS heart-cuts through a mid-polar Rxi-624SilMS column, where δ-HCH and neophytadiene got separated at the t_R of 17 and 17.8 min, respectively, ensuring accurate quantification of δ-HCH (Fig. 3b). Similarly, the co-elution of neophytadiene with endrin could also be effectively resolved by MDGC-MS with corresponding reduction in ME for endrin by 55%. Other such examples include resolving the close elutions of transfluthrin and heptachlor, and chlorpyriphos ethyl and aldrin, where MEs were reduced by 56, 46, 71 and 88%, respectively, after MDGC separations. The co-eluting signals of 4,4-DDD and 2,4-DDT could also be separated by MDGC heart-cuts (Supplementary Table 4) with corresponding reduction in MEs by 40 and 51%, respectively. Similar observations were noted for linolenic acid (t_R = 26.858 min) which eluted closely with 2,4-DDE (t_R = 27.162 min) causing high ME. After MDGC-MS separation, the signal intensities of matrix-matched and solvent standards were comparable and the ME for 2,4-DDE was reduced by 67% (Fig. 4a and b).

3.4.3. Application of method to real samples

The analysis of the real world samples reflected detection of the residues of captan and fluvalinate (fluvalinate-1 + fluvalinate-2) (Supplementary Fig. 1) at the concentrations of 33.6 and 50 + 53 ng/g, respectively, in two different samples. The residue level of captan was much below the GRL (700 ng/g) and no GRL is currently available for fluvalinate.

In conclusion, the multiresidue method reported in this paper offered satisfactory precision and accuracy in compliance with the regulatory guidelines. It performed comparatively better than the modified QuEChERs in minimizing MEs related to some major tobacco compounds like nicotine, megastigmatrienone, etc. Application of MDGC-MS heart-cut resolved matrix interferences and nullified co-elution related false detections. The method, with an output of 27 samples/person/day (including GC-MS run), holds potential for implementation in routine analysis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chroma.2014.03.080.

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