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Application of a system suitability test for quality assurance and performance optimisation of a gas chromatographic system for pesticide residue analysis

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Abstract

In pesticide residue analysis, screening for over 150 compounds has to be performed on a daily basis. As part of the quality control measures it is crucial to verify that the chromatographic system fits the purpose, or if any deterioration occurred during its previous use. The operation conditions of the chromatographic system can be best monitored with properly selected system suitability test (SST) mixtures, which provide information with one injection on the characteristic performance parameters of the whole system from the injector to the detectors. We developed SST mixtures that are also suitable for use with electron-capture, nitrogen–phosphorus and pulse flame photometric detectors. These SST mixtures were applied over 3 years to monitor the system performance parameters, such as the number of effective theoretical plates, resolution, asymmetry, detection limit and selectivity. The applicability and advantages of these tests are illustrated and discussed.

Keywords: System suitability test; Detection, GC; Quality assurance; Multiresidue methods; Pesticides

1. Introduction

Analysts have to demonstrate that the results obtained under particular application conditions are reliable and fit for the purpose. Internal quality control measures, comprising routine practical procedures, should be included in the analytical batches to enable analyst to decide whether they satisfy the pre-set quality criteria and a set of the results can be accepted. The GC determination was shown to be one of the major potential sources of the uncertainty of the analysis [1–3]. The performance of any chromatographic system is changing with time. For example, tailing of the peaks caused by dirty injection system and column may result in bad peak separation and incorrect integration, similarly the detector response may vary. These changes increase the uncertainty of chromatographic measurements. Therefore, before the instrumental analysis starts, the GC performance parameters should be checked to verify their suitability for the purpose of the analysis.

The first complex system suitability test giving information on a large variety of performance parameters of capillary columns was developed by Grob et al. [4]. His multi-component mixture has provided the basis for the elaboration of less complex test mixtures used currently. The column test mixtures provided by the manufacturers can be analyzed with GC coupled with flame ionization (FID) or mass spectrometric (MS) detection. These mixtures usually include normal paraffin hydrocarbons as standard reference peaks, alcohols, acids, bases, and ketones, and they are widely used to check the column performance after the delivery and to control the performance during the usage. Hydrocarbon peaks should be sharp and symmetrical. They are used to indicate installation problems, characterize separation power of the column (Trennzahl number) and calculate Kovats retention indices for peak identification. Alcohols are particularly sensitive to active silanol groups on the column-tubing surface and to the other active sites that can form hydrogen bonds. Ketones give information about the presence of Lewis acid sites. Acids (phenols) and bases (anilines) show the alkaline or acid sites of the column by means of peak tailing and/or irreversible sorption resulting in reduced peak size. A tailing peak indicates activity somewhere in the system. For evaluating GC column

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performance the plate number (N_{eff}) and plate height (H) for some components, ratio of the peak heights of phenols and anilines to hydrocarbons, asymmetry factors for alcohols, phenols and anilines, and the Trennzahl number for two consecutive n-paraffins are calculated. Isothermal column temperature is recommended to generate the test chromatogram, as the temperature program results in artificially well-formed peaks and masks performance problems. However, a temperature program closely resembling the actual operating conditions of the column could be more informative, especially with specific detectors. It is also recommended that a column should be tested each time it is installed, to demonstrate proper installation and system performance.

Where routine analysis of stable compounds with similar properties is carried out, the injection of calibration solutions of these compounds or group representatives (e.g. polychlorinated biphenyls, PCBs) may serve the purpose of a test mixture. In pesticide residue analysis, where screening for over 150–200 compounds, with largely differing chromatographic properties, has to be performed on a daily basis, it is crucial to have a system suitability test (SST) mixture injected into the GC system that, with one injection, would indicate whether the GC system, including specific detection systems such as nitrogen–phosphorus (NPD) and electron-capture (ECD) detection, is fit for the purpose, or if any deterioration occurred during its previous use. Observation of the peak shapes of the substances of the properly selected test mixture reveals any malfunction and indicates the need for maintenance to be performed before the analyses of samples can be continued.

In case of specific detectors, the standard column test mixtures cannot be utilized to test system performance. Therefore, we developed and applied detection-specific SST mixtures to test the performance of the whole chromatographic system from the injector port to element-specific detectors.

The SST mixtures contain 8–10 compounds, which cover the expected retention time range and are suitable to monitor the performance of the GC coupled with ECD, NPD and pulse flame photometric detection (PFPD). They were used to establish characteristic GC parameters such as: resolution, number of effective theoretical plates, asymmetry, detection limit, and selectivity. Labile compounds, such as endrin, *p*,*p*′-DDT, and carbaryl, were added in order to control inertness and cleanness of the GC inserts, retention gaps, and columns [5,6]. These SST mixtures were used to control the performance of our chromatographic systems on both short and long-term basis over the last 3 years.

2. Experimental

2.1. Materials

Docosane ($C_{22}H_{46}$), tributylphosphate (TBP) and solvents of organic trace analysis grade were obtained from Merck. All pesticide analytical standards were purchased from Dr. Ehrenstorfer, Germany.

3. Equipment

GC systems: Hewlett-Packard (1) HP 5890 Series II operated with ECD and NPD under constant 12 psi head pressure (2.6 ml He/min flow rate at 70 °C; psi = 6894.76 Pa), and (2) Varian 3800 operated with NPD and PFPD, and constant 2 ml He/min carrier gas flow. Columns: CP-SIL 8 CB, 25 m, 0.25 mm i.d., 0.25 μm film thickness, or CP-SIL 8 CB 25 m, 0.32 mm i.d., 0.25 μm film thickness. Oven temperature program: 70 °C for 1 min, 20 °C/min to 160 °C, and 4 °C/min to 270 °C, isotherm for 10 min. Injector: deactivated glass liner with 4 mm i.d. was installed on the HP GC system. Splitless 2 mm i.d. or high linearity liners were used with the Varian GC. Hot splitless injectors with constant temperature of 250 °C, with split valve opened 2 min after injection, or temperature programming injection with initial temperature of 70 °C were used.

3.1. System suitability test mixtures

The compositions of SST mixtures for checking the performance of chromatographic system with NPD and PFPD, and ECD, and the functions of their components are given in Tables 1 and 2.

3.2. Calculation of performance parameters

Response factor (RF, mm s/pg), also called sensitivity:

$$\mathrm{RF} = \frac{\mathrm{Area}}{C_\mathrm{A}} = \frac{HW_\mathrm{h}}{C_\mathrm{A}}$$

where C_A is the amount of the injected hetero-atom or carbon in pg, H is the peak height in mm and W_h is the peak width at the half height in s.

$$C_\mathrm{A} = \frac{nA_\mathrm{w}C}{M_\mathrm{r}}$$

where n is the number of hetero atoms or carbon in the molecule, A_w is atomic mass of P, N, S or carbon, C is injected amount (pg) of molecule, M_r is molecular mass; detection limit (LD, pg/s):

$$\mathrm{LD} = \frac{fN}{\mathrm{RF}}$$

where N is the noise level in mm, and f is multiplication factor equal to 2 in our case.

Notes: There is a disagreement among chromatographers concerning the measurement of the noise level and the selection of multiplication factor. Whatever procedure is used it must be clearly described and applied consistently through the laboratory operation and to all equipment to ensure the comparability of the results. We have chosen a practical approach and use the amplitude of the observed noise (distance

Table 1
The composition of GC SST mixture for NPD, FPD, PFPD and MS, and the purpose of the use of its components

Name	Molecular formula	Concentration[#] (μg/ml)	Retention time (min)	Purpose of use
EPTC	$C_9H_{19}NOS$	5.023	4.75	N_{eff}, sensitivity, selectivity S to C (for PFPD)
Propoxur	$C_{11}H_{15}NO_3$	10.035	6.85	Inertness
Tributylphosphate (TBP)	$C_{12}H_{27}O_4P$	0.250	7.28	Sensitivity, selectivity P to C
Dimethoate	$C_5H_{12}NO_3PS_2$	0.502	8.36	Asymmetry
Pirimicarb	$C_{11}H_{18}N_4O_2$	5.036	9.71	Sensitivity, selectivity N to C
Chlorpyriphos methyl	$C_7H_7Cl_3NO_3PS$	0.249	10.29	Resolution with parathion methyl
Parathion methyl	$C_8H_{10}NO_5PS$	0.249	10.53	Resolution with chlorpyriphos methyl
Carbaryl	$C_{12}H_{11}NO_2$	9.998	10.77	Inertness
Chlorpyriphos ethyl	$C_9H_{11}Cl_3NO_3PS$	0.250	11.81	Reference for RRTs
Quinalphos	$C_{12}H_{15}N_2O_3PS$	0.250	13.55	Resolution with methidathion
Methidathion	$C_6H_{11}N_2O_4PS_3$	0.249	14.01	Resolution with quinalphos
Hydrocarbon	$C_{22}H_{46}$	100.250	17.10	Selectivity
Phosalone	$C_{12}H_{15}ClNO_4PS_2$	0.504	22.10	N_{eff}, RRT

Table 2
The composition of GC SST mixture for ECD and MS, and the purpose of the use of its components

Name	Molecular formula	Concentration (ng/ml)	Retention time (min)	Purpose of use
Lindane	$C_6H_6Cl_6$	100.2	10.81	N_{eff}
Chlorothalonil	$C_8Cl_4N_2$	100	11.33	Asymmetry
Chlorpyriphos Ethyl	$C_9H_{11}Cl_3NO_3PS$	99.8	14.35	Reference for RRTs
Diclobutrazole	$C_{15}H_{19}Cl_2N_3O$	1004.3	17.24	RRT
α-Endosulfan	$C_9H_6Cl_6O_3S$	100.4	18.60	Asymmetry and resolution with endrin
Endrin	$C_{12}H_8Cl_6O$	202.2	19.15	Inertness and resolution with α-Endosulfan
o,p′-DDT	$C_{14}H_9Cl_5$	100.1	20.00	Resolution with *p,p′*-DDD
p,p′-DDD	$C_{14}H_8Cl_4$	99.6	20.48	Resolution with *o,p′*-DDT
p,p′-DDT	$C_{14}H_9Cl_5$	100	21.53	Inertness
Fenpropathrin	$C_{22}H_{23}NO_3$	100	24.18	RRT
Deltamethrin	$C_{22}H_{19}Br_2NO_3$	100	33.76	N_{eff}, RRT

between the lower and the upper boundary of the observed noise as the noise level), which can be considered equivalent to 4 times standard deviation. We measure the noise for 10 times half peak width as close to the corresponding peak, as possible (Fig. 1).

The LD [pg/s] characterizes the sensitivity of the detector without the influence of the column (peak broadening, or tailing). It should be distinguished from the minimum detectable quantity or limit of detection (LOD) expressed in fractions of gram.

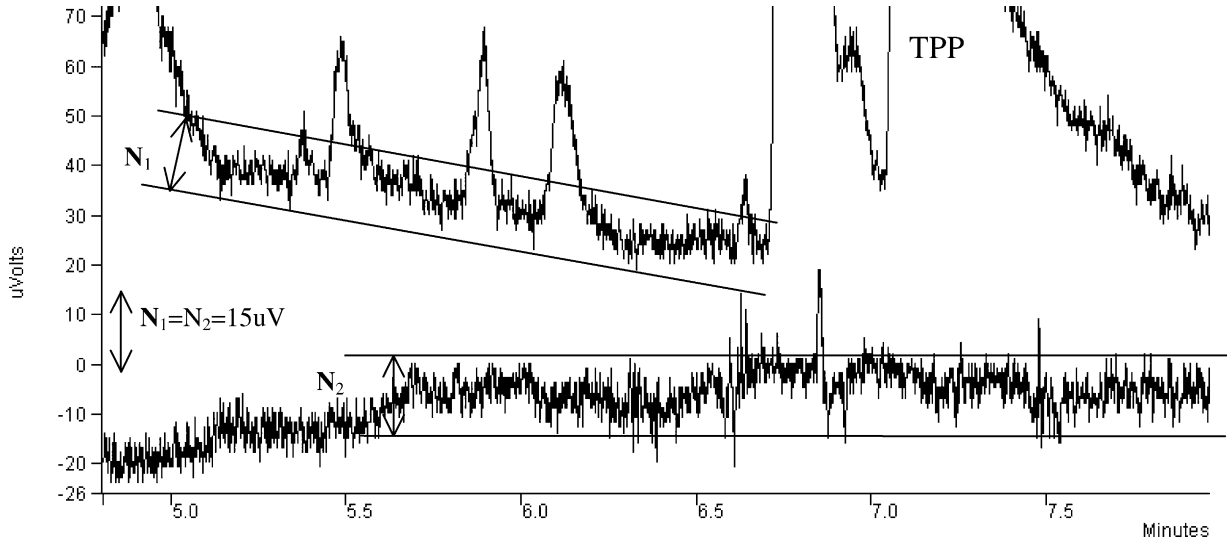

Fig. 1. Measurement of noise level at TPP peak. N_1 is measured in the vicinity of TBP peak in the SST chromatogram. N_2 is measured in the chromatogram of blank solvent injection.

Minimum detectable quantity (MDQ, pg) or Limit of detection (LOD, pg) of P, N and S is calculated as:

$$\mathrm{MDQ} = \mathrm{LD} \times W_{1/2}$$

where $W_{1/2}$ is peak width in seconds at half height; selectivity (Sl) of P, N and S to carbon:

$$\mathrm{Sl} = \frac{\mathrm{RF}}{\mathrm{RF_C}}$$

where RF is the response factor of P, N, or S, and $\mathrm{RF_C}$ is the response factor of carbon.

Asymmetry (A_s):

$$A_s = \frac{b}{a}$$

where a is a front part and b is a back part of the line parallel to the base line at the 10% of peak height.

Number of effective theoretical plates:

$$N_{\mathrm{eff}} = 5.545\left(\frac{t'_R}{W_h}\right)^2$$

where t'_R is the adjusted retention time, and W_h is the peak width at the half height. The t'_R and W_h are measured by the data evaluation software.

Relative retention time:

$$\mathrm{RRT} = \frac{t'_{R(i)}}{t'_{R(\mathrm{ref})}}$$

where $t'_{R(i)}$ and $t'_{R(\mathrm{ref})}$ are the adjusted retention times of component i and the reference compound (chlorpyrifos).

Adjusted retention time: $t'_R = t'_{R(i)} - t_0$. The dead time (t_0) was measured by injecting 5 μl of light hydrocarbon into the system.

Resolution:

$$R_S = \frac{1.18(t'_{R(2)} - t'_{R(1)})}{W_{h1} + W_{h2}}$$

where $t'_{R(1)}$ and $t'_{R(2)}$ are the adjusted retention times of closely eluted compounds, and W_{h1} and W_{h2} are their peak widths on the half heights.

4. Results and discussion

4.1. NPD and PFPD SST

Labile and "difficult" compounds, such as dimethoate, carbaryl, and imazalil, can only be reproducibly analysed with inert and properly installed injector and column. Since they are very sensitive to the operating conditions, they indicate even slight deterioration or malfunction of the system. Therefore, they can be included in a test mixture as indicators of wrong cut or installation of the column, presence of active sites on the surface of the liner and/or column, contamination of the system, and poor detector performance. Peak tailing and broadening and retention time shift are the first symptoms when the system becomes contaminated (Fig. 2A and B). The difference in peak shapes of S-ethyl dipropylthiocarbamate (EPTC), chlorpyrifos (relatively stabile compounds) and dimethoate due to system contamination is shown on Fig. 3. Since the sensitivity of the detector may

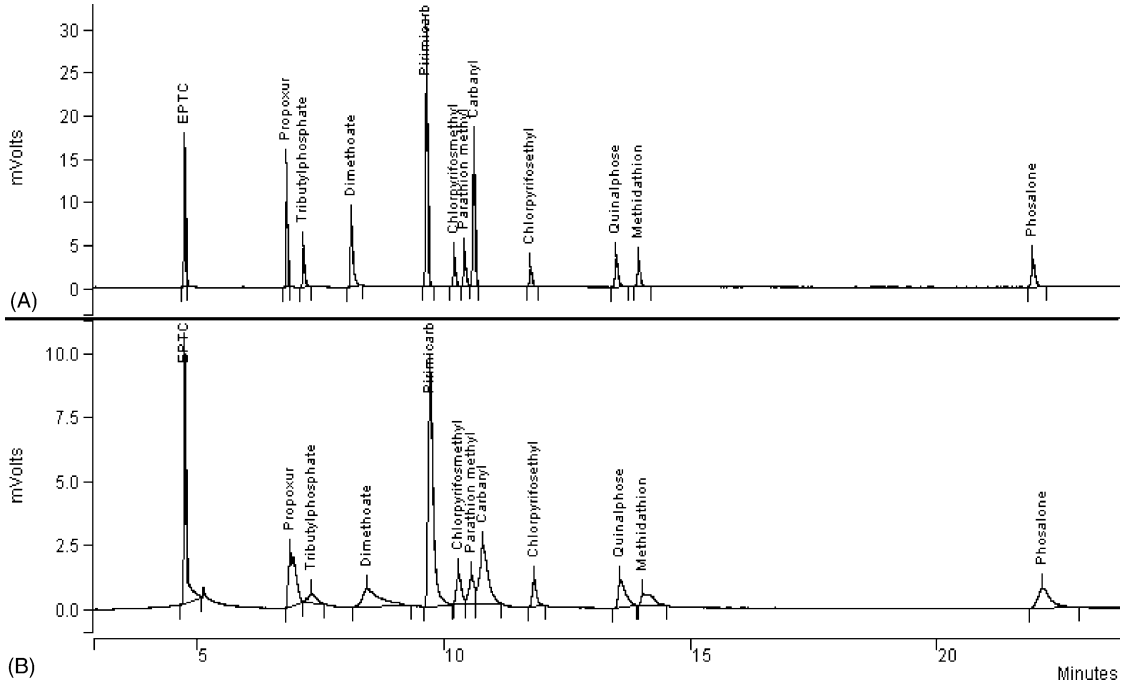

Fig. 2. Chromatogram of NPD SST: (A) injected into a clean system, (B) after injection of 20 lettuce extract containing 5 g/ml sample equivalent.

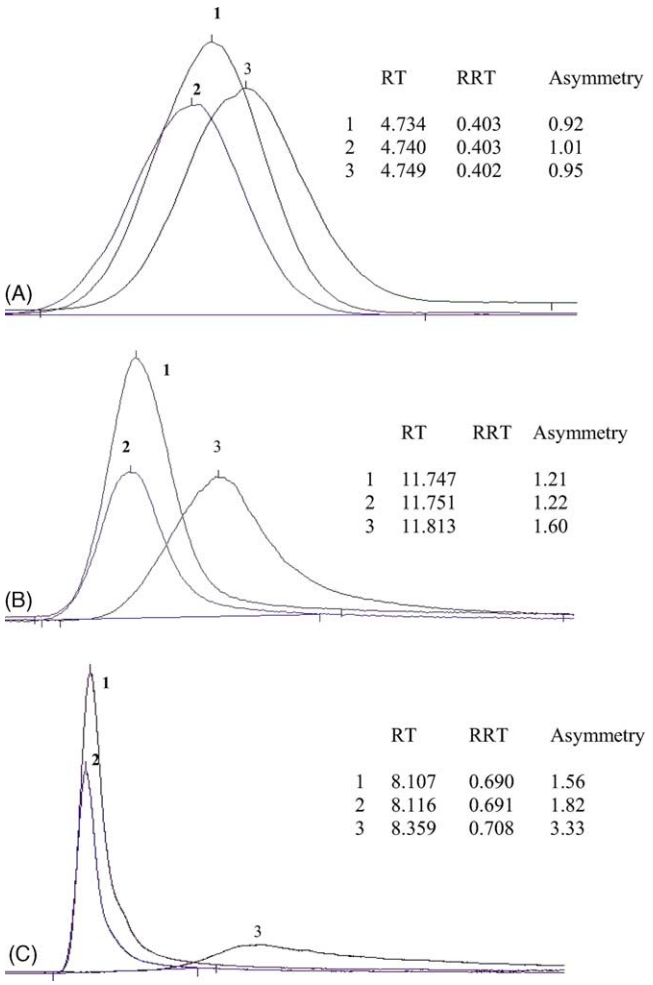

Fig. 3. Shapes of chromatographic peaks of EPTC (A), chlorpyrifos ethyl (B) and dimethoate (C): (1) SST mixture injected into a clean system, (2) after injection of 20 lettuce extracts containing 5 g/ml matrix equivalent, (3) after additional injection of 20 apple extract containing 5 g/ml sample equivalent.

also be changing in time, the peak areas obtained at different occasions are not necessarily comparable. Peak shapes, RRT values and asymmetry factors demonstrate that while EPTC peak remain unchanged and chlorpyriphos peak changes slightly after 20–40 injections of sample extract, dimethoate exhibits significant tailing and retention time shift.

The average, standard deviation (S.D.) and relative standard deviation (R.S.D.) of RRT of 6 consequent injections of SST mixture into the freshly maintained Varian GC system are given in Table 3. This table also includes the differences in the average RRTs of the components of SST mixture injected into the clean system and after 40 injections of sample extracts. The table shows that the change in GC system performance is best indicated with RRT shift of dimethoate, tributylphosphate and carbaryl.

Carbaryl was used to monitor the column condition and to check the inertness of the chromatographic system when nitrogen-specific detectors are used. Carbaryl is very sensitive to the surface effects and decomposes to alpha-naphthol. The decomposition in the injector port results in an α-naphthol peak, which can be detected with FID or MS, while decomposition in the column during elution is indicated by the increasing baseline. The degradation can be characterized by the signal ratios of labile carbaryl to stable pesticides, for example propoxur. Their peaks ratio serves as an indicator of the inertness of the GC system equipped with MS or NPD (Fig. 4).

High-boiling contaminants can cause shifts in retention time, elevated baseline, and peak broadening, which can lead to the loss of resolution power of the chromatographic column. The resolution of two critical peak pairs of chlorpyrifos methyl/parathion methyl and quinalphos/methidathion are used to illustrate the separation power of the column with different film thickness. Usually chlorpyriphos methyl and parathion methyl are well resolved in columns with 0.32 μm film thickness, but they co-elute when 0.25 μm film

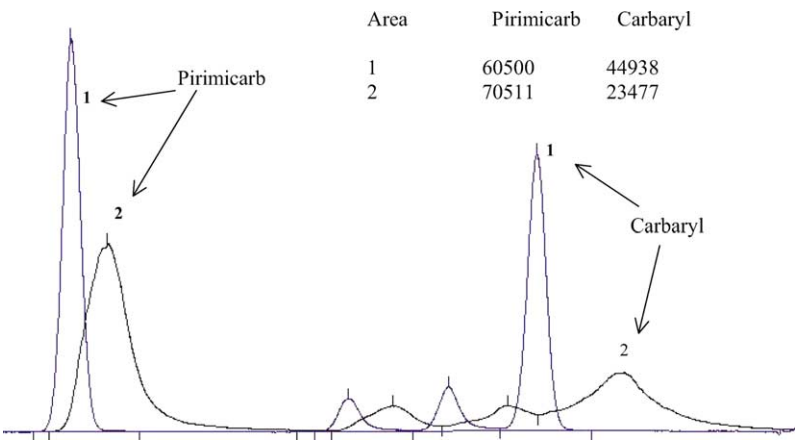

Fig. 4. Deterioration of chromatographic peak shape detected with NPD: (1) SST mixture injected into a clean system, (2) after injection of 40 sample extracts containing 5 g/ml matrix equivalent.

Table 3
Average, standard deviation (S.D.) and relative standard deviation (R.S.D., %, $n = 6$) of RRT of SST compounds in clean and used GC system

	Average RRT			Difference of RRTs		S.D.	R.S.D. (%)
	Initial	After 20	After 40	Initial-20	Initial-40		
EPTC	0.403	0.403	0.402	0.0004	−0.0010	0.0001	0.023
Propoxur	0.579	0.579	0.580	0.0002	0.0007	0.0001	0.012
Tributylphosphate	0.608	0.608	0.616	0.0001	0.0083	0.0001	0.010
Dimethoate	0.690	0.691	0.708	0.0005	0.0175	0.0002	0.027
Pirimicarb	0.820	0.821	0.822	0.0003	0.0017	0.0001	0.012
Chlorpyrifos methyl	0.868	0.869	0.871	0.0001	0.0029	0.0001	0.008
Parathion methyl	0.886	0.886	0.891	0.0003	0.0053	0.0001	0.009
Carbaryl	0.901	0.902	0.911	0.0009	0.0097	0.0001	0.007
Chlorpyrifos	1.000	1.000	1.000	0.0000	0.0000	0.0001	0.010
Quinalphos	1.147	1.148	1.148	0.0004	0.0003	0.0000	0.000
Methidathion	1.186	1.186	1.186	0.0004	−0.0004	0.0001	0.005
Phosalone	1.866	1.867	1.871	0.0007	0.0056	0.0002	0.013

Notes: Initial—injection in a GC system with new liner and clean column, after 20—SST injection following 20 injections of lettuce sample with 5 g/ml sample equivalent, after 40—SST injection following additional injection of 20 apple sample with 5 g/ml sample equivalent, (4) S.D.s and R.S.D.s are calculated from 6 replicate injections into a clean system.

thickness is used. In the latter case, quinalphos/methidathion can be used to characterize the resolution power of the column (Fig. 2).

The performance parameters of NPD generally occurring in our laboratory are given in Table 4.

4.2. ECD SST

The calculation and interpretation of performance parameters are the same as for NPD. Well-known sensitive indicators of bad GC performance, e.g. endrin and DDT, can be used with ECD. Breakdown of endrin and DDT is indicated by the reduced ratio of these compound areas to chlorpyriphos area or by appearance of the extra peaks corresponding to endrin aldehyde and endrin ketone, or DDE and DDD, respectively. The conversion is much faster in the presence of alkaline sites.

The breakdown of DDT generally indicates a dirty injection port caused by the introduction of oily or other non-volatile co-extracts. In this case, the liner and the retention gap have to be replaced or substantially cut to restore normal performance. The sample extracts causing DDT breakdown would usually need additional cleanup to reduce the amount of co-extracted materials.

Endrin breakdown generally indicates the chemical reactions, which are taking place in the injection port. Proper deactivation of inlet liner is essential for minimizing it. The breakdown can be caused by active sites on the glass surface, the impurities in the carrier gas and/or septa particles [5]. Therefore, endrin is a useful indicator of the system cleanness and the quality of the liner, especially when in-house deactivation procedure is used. Examples of SST values including number of effective plates, MDQ of chlorine, asymmetry, and peak ratios are given in Table 5.

Table 4
Example for the performance parameters observed with NPD SST

Name	c (ng/μl)	M_r	Specific atom	c_a (ng/μl)	Area	RF	LD (pg/s)	Sl to C	t'_R (s)	$W_{1/2}$ (s)	N_{eff}	MDQ (pg)	A_s	R_s	Ratio
EPTC	2.01	189	S	0.34	4486	13.21	1.51	390	249	1.0	360096	1.48			
Propoxur	4.01	209	N	0.27	4910	18.28	1.09	539	391	1.6		1.74			
TBP	0.10	266	P	0.01	9690	829.97	0.02	24476	410	1.8		0.04			
Dimethoate	0.20	229			5430				487	2.5			1.7		
Pirimicarb	2.01	238	N	0.47	9552	20.15	0.99	594	585	2.3		2.24			
Chlorpyrifos methyl	0.10	323	N, P, S		2357				625	2.5				4	
Parathion methyl	0.10	263	N, P, S		3060				642	2.6					
Carbaryl	4.00	201	N	0.28	5667	20.37	0.98	600	657	2.5		2.48			0.87
Chlorpyrifos	0.10	351			2217				724	2.9					
Quinalphos	0.10	298			2704				838	3.2				6	
Methidation	0.10	302	N, P, S		2455				870	3.2					
Docosane	40.10	310	C	39.84	1351	0.03			985	5.0					
Phosalone	0.20	368			2570				1362	4.0	637217				

Abbreviations: c_a is the concentration of specific atom; Sl the selectivity; t'_R the corrected retention time; A_s the asymmetry; R_s the resolution; ratio denotes peak area ratio of propoxur to carbaryl.

Table 5
Example for the performance parameters observed with ECD SST

Name of solvent	c (ng/μl)	M_r	Specific atom	c_a (ng/μl)	Area	RF	LD (pg/s)	t'_R (s)	$W_{1/2}$ (s)	N_{eff}	MDQ (pg)	A_s	R_s	Ratio
Lindane	100.2	291	Cl6	73.3	335269	4.57	175	577	2.8	239 407	8.1			
Chlorothalonil	100				267981				3.5			1.4		
Chlorpyriphos Ethyl	99.8				167767			789	3.9					
Diclobutrazole	1004.3				438028			963	3.8					
alfa-Endosulfan	100.4				1123251			1044	5.5			2.1	4	
Endrin	202.2	381	Cl6	113.0	290962	2.57	311	1077	4.0		20.6			0.58
o,p′-DDT	100.1				663665				5.9				0	
p,p′-DDD	99.6				NR				4.2					
p,p′-DDT	100	355	Cl5	50.1	1052489	2.55	314	1220	4.2		24.7			0.16
Fenpropathrin	100				127740			1379	4.7					
Deltamethrin	100	505	C, N, O		206129			1954	5.2	784 170				

Abbreviations: c_a is the concentration of specific atom; Sl the selectivity; t'_R the corrected retention time; A_s the asymmetry; R_s the resolution; ratio denotes area ratio of endrin and *p,p′*-DDT to chlorpyriphos.

4.3. NPD optimisation

Besides the regular characterization of the GC system, SST mixture can be conveniently used for the optimisation of NPD. Tailing of dimethoate and TBP peaks might indicate both column (liner) contamination/deterioration, as it was shown before, and poor NPD bead condition. The problem of bad NPD performance can be easily observed if the end of the column is connected to two detectors, e.g. NPD and ECD or NPD and PFPD. Observation of the peak shapes with both detectors helps to find the reason of tailing: if both detectors indicate tailing the column or liner can cause the problem, if no tailing is observed with ECD or PFPD but NPD gives tailing peak, the operating conditions of the detector may need to be optimised. Though the performance of NPD is the result of the complex interaction of gas flow rates and bead temperature, the selectivity and sensitivity of NPD depends mainly on hydrogen flow and the bead temperature, respectively. These two parameters need to be first adjusted [7]. The recommended optimisation procedure of NPD on Varian GC includes injection of SST mixture with hydrogen flow varied from 4.0 to 5.5 ml with 0.1 ml increments and constant bead current [8]. Selectivity to P is measured using ratio of the RF of phosphorous in TBP to carbon in docosane.

4.4. Long-term system performance

NPD SST parameters were measured with Varian NPD for over 3 years operation. Values of the dimethoate asymmetry and peak ratio of propoxur/carbaryl are presented in Fig. 5. The points when column was conditioned, cut or replaced are marked. Usually when the column was cut as a regular maintenance procedure, the liner was also replaced at the same time. It was found that generally the dimethoate asymmetry is a more sensitive indicator of system contamination than the propoxur/carbaryl peak ratio. However when on-column injection and high linearity injection, which operates very similarly as the on-column injection, were used increasing peak ratio of propoxur/carbaryl indicated rapid column deterioration. It is interesting to notice that the poor system condition indicated by the tailing of dimethoate peak can be easily rectified by cutting the column and replacing the liner. When column deterioration indicated by the large peak ratio of propoxur/carbaryl occurred then the column needed to be replaced in order to regain the parameters of the clean and inert system. Another important observation is that the asymmetry of dimethoate peak did not change significantly when propoxur/carbaryl ratio was dramatically increased. One explanation is that the shape of the column cut and position of the column, which might cause dimethoate peak tailing during split/splitless injection, did not contribute to the peak shape, when on-column injection was used. The results suggest that the two parameters indicate different problems and both of them have to be monitored.

Variation of NPD selectivity to phosphorous and MDQ of phosphorous are shown in Fig. 6. Replacement of the bead and it's optimisation always leads to increased selectivity of the NPD to phosphorous, which drops down shortly after replacement and/or optimisation. Large variation and rapid change of MDQ values can also be observed. The MDQ values often can be improved by regular maintenance procedure as indicated on the graph. The number of N_{eff} indicates significant changes depending on column flow and injector port configuration (Fig. 7).

4.5. Comparison of different GC system used in one laboratory

Based on the data collected during a certain period of time acceptable performance limits can be established for all parameters characterizing the operation of the GCs. For instance minimum values are required for selectivity of detection of OP compounds, or for the separation power of the column, while the MDQs and tailing of peaks should have a maximum acceptable limit. It was observed that some performance parameters of different instruments, even those produced by one company, were significantly different

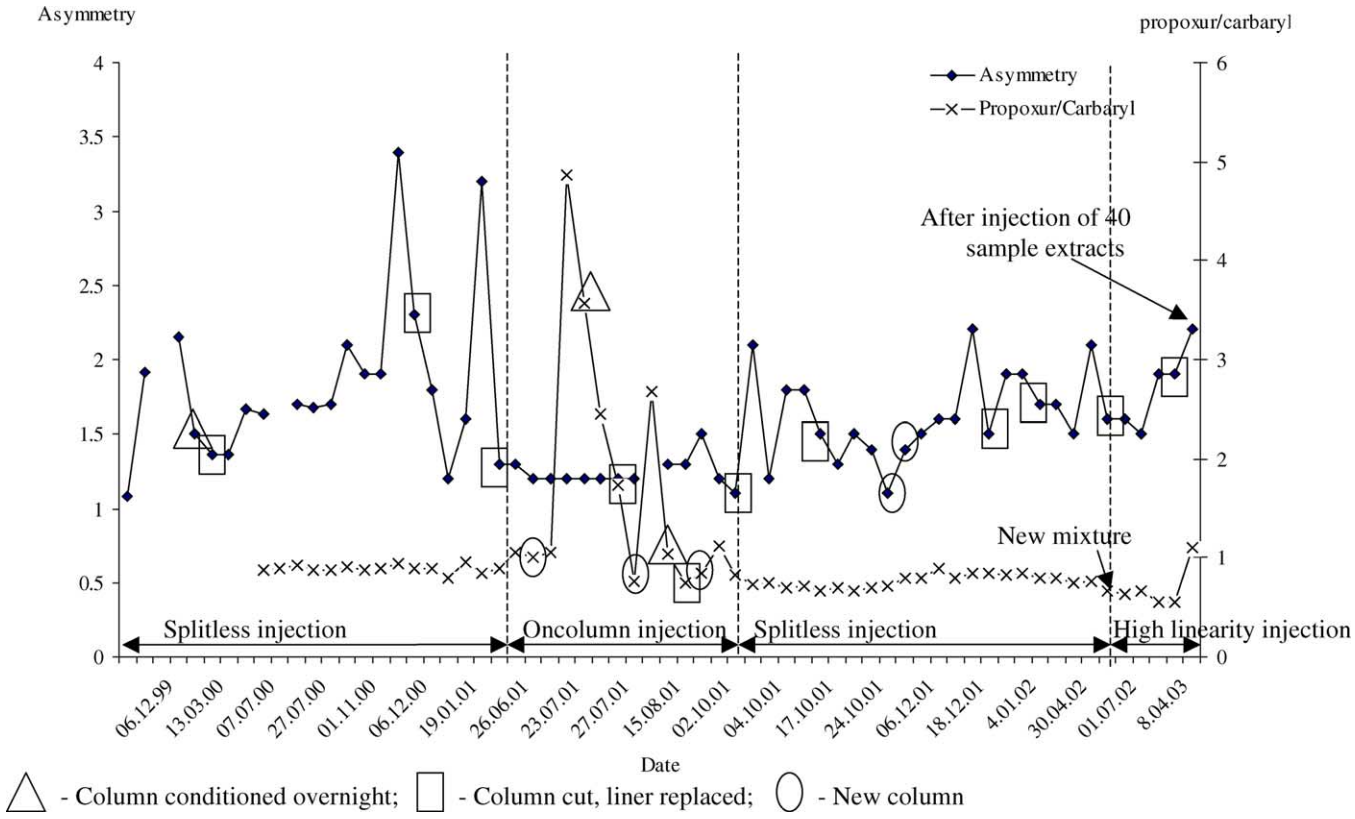

Fig. 5. Variation of asymmetry of dimethoate peak and the peak area ratio of propoxur/carbaryl.

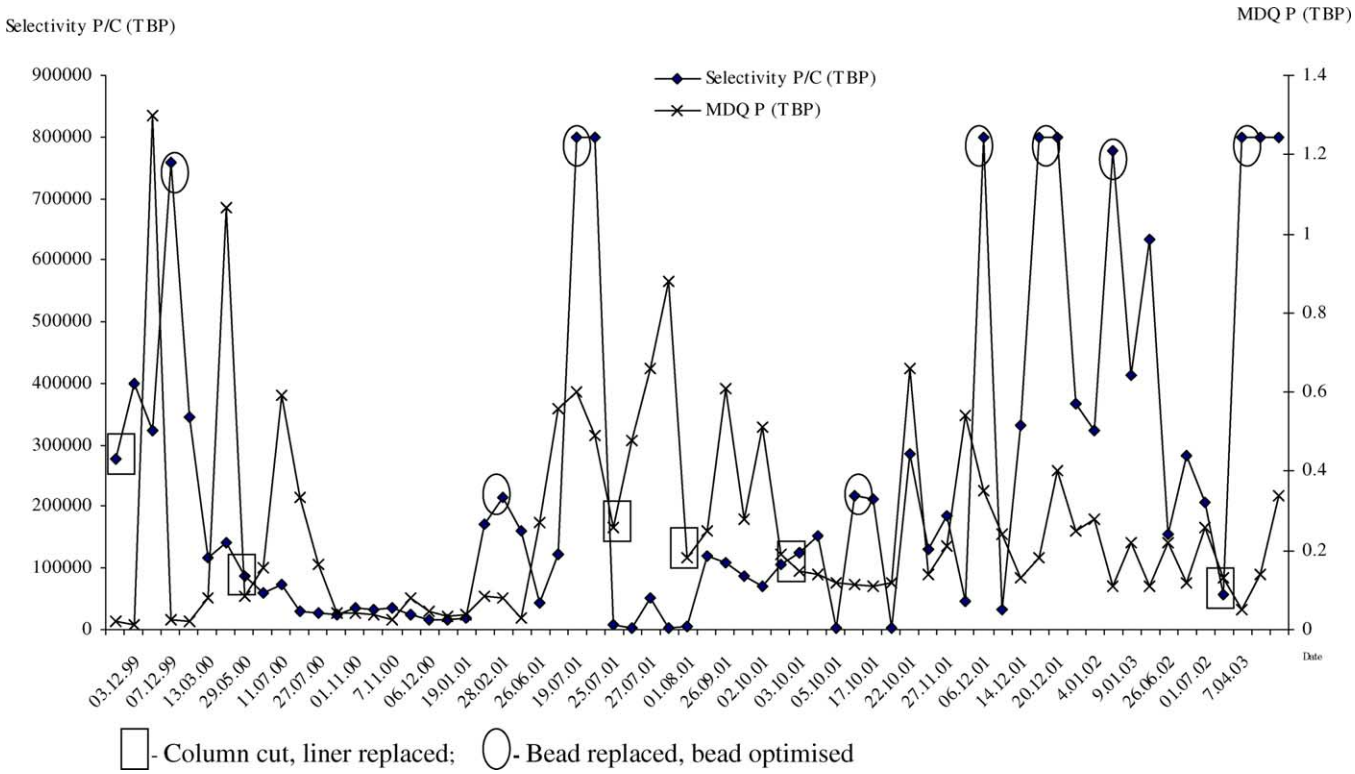

Fig. 6. Variation of selectivity P relative to carbon and MDQ of P in TBP during 3 years period.

Table 6
Examples of SST parameters measured with ECD, NPD and PFPD on different GCs

Value	Compound	ECD				Compound	NPD		PFPD	
		GC1	GC2	GC3	GC 4		GC 1	GC2	GC 1	GC 2
MDQ	Lindane	3.3	25.3	8.1	1.1	EPTC	0.6	1.4	77.5	17.3
	Endrin	14.1	90.1	20.6	1.7	Propoxur	0.7	1.7		
	p,*p*′-DDT	3.1	2.6	24.7	11.5	TBP	0.3	0.04	8.0	0.6
						Pirimicarb	0.8	2.2		
						Carbaryl	NR	2.48		
N_{eff}	Lindane	140922	108310	239408	364273	EPTC	353512	360096	272920	218908
	Deltamethrin	1769893	617325	784171	1052942	Phosalone	647606	637217	857188	693122
Assymettry	Chlorothalonyl	1.8	2.7	1.4	1.0	Dimethoate	1.5	1.7	1.3	1.5
	α-Endosulfan	1.7	2.2	2.1	1.2					
Resolution	α-Endosulfan/Endrin	2.0	1.4	4.1	4.8	Chlorpyriphos Methyl/parathion methyl		3.8	3.0	2.8
	o,*p*′-DDT/*p*,*p*′-DDD	3.0	3.7	NR	NR	Quinalphose/methidathion	5.0	6.0	5.6	5.2
Area ratio	Chlorpyriphos/endrin	0.84	0.75	0.58	0.19	Propoxur/carbaryl	NR	0.87		
	Chlorpyriphois/*p*,*p*′-DDT	0.41	0.43	0.16	0.64					
Selectivity						EPTC	2503	390	21 (P to S)	42 (P to S)
						Propoxur	3601	539		
						TBP	7874	24476		
						Pirimicarb	4119	594		
						Carbaryl	NR	601		

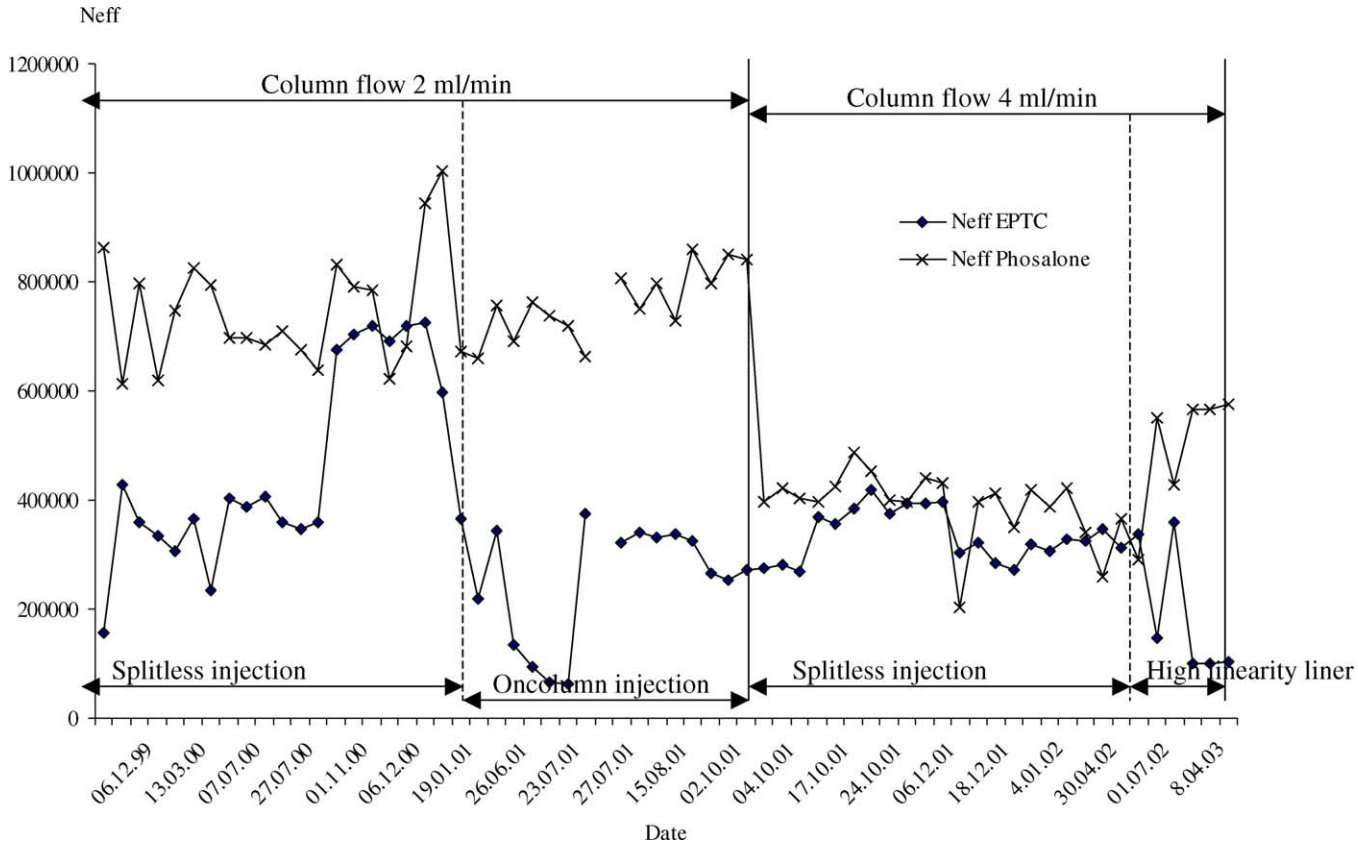

Fig. 7. Effect of column and injector port configuration on the N_{eff}.

(Table 6). Therefore, it might not be practical or might be simply impossible to define the same limits for all instruments in the laboratory, and specific characteristic limits have to be established for each instrument. The performance characteristics of different instruments may limit their use with a given method.

When a method is used for routine analysis the system performance recorded during its validation shall be compared with the actual operating characteristics of the GC. The characteristic parameters need not necessarily match, but special attention is required, for instance, when the actual P/C selectivity of the detection is 40 000 while it was 70 000 during the validation of the method. The analyst should verify in this case that the response is solely due to the analyte. Similarly, the GC may be used for the analysis of the samples if the actual MDQ is 10 pg in contrast to 4 pg reported during method validation if the lowest calibrated level is 20 pg.

5. Conclusions

The performance of gas chromatographs may continuously change during their regular use, which can affect the reliability of the results. The critical operation characteristic parameters–such as selectivity and sensitivity of detection, separation of critical peaks, inertness of the system–should be verified at each time before the start of an analytical batch. This can be most economically done with the injection of a properly selected SST mixture that gives information for all performance parameters with one injection.

In case of specific detectors, the standard column test mixtures cannot be utilized to test system performance. Therefore, we developed and applied detection-specific SST mixtures to test the performance of the whole chromatographic system from the injector port to element-specific detectors, such as NPD, PFPD, ECD, and MS systems. The SST mixture consists of several pesticides with largely differing chromatographic properties to enable analyst, with one injection, assess whether the GC system is fit for the purpose, or if any deterioration occurred during its previous use.

The critical performance parameters prevailed during the validation of the method should be recorded and reported together with the validation data. As a quality control measure, these parameters should be compared with the actual operation parameters of the GC system before its use for the analysis of samples. Where the actual parameters are less favourable than those prevailed during method validation, the analyst should verify the applicability of the method and record the performance parameters of the instrument together with the performance verification results. If the performance of the system is not suitable for the analysis, the

acceptable operation conditions have to be restored before the analysis can be started or continued.

During the regular use of the method the minimum performance requirements can be established and included in the standard operating procedures of the method.

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