CORRELATION ANALYSIS OF REACTIVITY IN THE OXIDATION OF SUBSTITUTED BENZALDEHYDES BY QUINOLINIUM FLUOROCHROMATE

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Oxidation of thirty six monosubstituted benzaldehydes by quinolinium fluorochromate (QFC) in dimethylsulphoxide (DMSO), leads to the formation of corresponding benzoic acids. The reaction is of first order with respect to QFC. A Michaelis-Menten type kinetics was observed with respect to the reactants. The reaction is promoted by hydrogen ions; the hydrogen-ion dependence has the form k_{obs}=a +b[H^+]. The oxidation of [^{2}H]benzaldehyde (PhCDO) exhibited a substantial primary kinetic isotope effect. The reaction was studied in nineteen different organic solvents and the effect of solvent was analysed using Taft's and Swain's multi-parametric equations. The rates of the oxidation of para- and meta-substituted benzaldehydes showed excellent correlation in terms of Charton's triparametric LDR equation, whereas the oxidation of ortho-substituted benzaldehydes were correlated well with tetraperametric LDRS equation. The oxidation of para-substituted benzaldehydes is more susceptible to the delocalized effect than is the oxidation of ortho- and meta-substituted compounds, which display a greater dependence on the field effect. The positive value of η suggests the presence of an electron-deficient reaction centre in the rate-determining step. The reaction is subjected to steric acceleration by the ortho-substituents. A suitable mechanism has been proposed.

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1. Introduction

Halochromates have been used as mild and selective oxidizing reagents in synthetic organic chemistry. [1] Quinolinium fluorochromate(QFC) is also one of such compounds used as mild and selective oxidizing agent in synthetic organic chemistry. [2] We have been interested in kinetics of oxidations by Cr(VI) species and have already published a few reports on oxidation by other pyridinium[3,4] and quinolinium halochromates. [5,6] In continuation of our earlier work, we report in the present article the kinetics of oxidation of some monosubstituted benzaldehydes by QFC in DMSO as solvent. The major objective of this investigation was to study the structure-reactivity correlation for the substrate undergoing oxidation.

2. Experimental Section

2.1 Materials

QFC was prepared by reported method[2] and its purity was checked by iodometric method. The aldehydes were commercial products. The liquid aldehydes were purified through their bisulfite addition compounds and distilling them, under nitrogen, just before use. [7] The solid aldehydes were recrystallized from ethanol. Deuteriated benzaldehyde (PhCDO) was also prepared by the reported method. [8]

Its isotopic purity, as ascertained by its NMR spectrum, was 96±5%. Due to non-aqueous nature of the solvent, toluene-*p*-sulphonic acid (TsOH) was used as a source of hydrogen ions. Solvents were purified by the usual methods.

2.2 Product analysis

The product analysis was carried out under kinetic conditions. In a typical experiment, benzaldehyde (5.25 g, 0.05 mol) and QFC (2.49 g, 0.01 mol) were made up to 50 cm^3 in DMSO and kept in the dark for *ca*. 15 h to ensure completion of the reaction. The solution was then treated with an excess (200 cm^3) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. The yields of DNP before and after recrystallization were 2.52 g (88%) and 2.32 g (81%) respectively. The DNP was found identical (m.p. and mixed m.p.) with the DNP of benzaldehyde. Similar experiments were performed with other aldehydes also. The oxidation state of chromium in completely reduced reaction mixtures, determined by an iodometric method was 3.90±0.10.

2.3 Kinetic Measurements:

The pseudo-first order conditions were attained by maintaining a large excess (× 15 or more) of the aldehyde over QFC. The solvent was DMSO, unless specified otherwise. The reactions were followed, at constant temperatures (±0.1 K), by monitoring the decrease in [QFC] spectrophotometrically at 354 nm. No other reactant or product has any significant absorption at this wavelength. The pseudo-first order rate constant, k_{obs}, was evaluated from the linear (r^2 =0.990-0.999) plots of log [QFC] against

time for up to 80% reaction. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3%. The second order rate constant, k_2, was obtained from the relation: $k_2=k_{obs}$/[aldehyde]. All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of p-$CH_3C_6H_4SO_3H$ (TsOH).

3. Results and discussion

The rates and other experimental data were obtained for all the aldehydes. Since the results are similar, only representative data are reproduced here.

3.1 Stoichiometry:

Oxidation of benzaldehydes by QFC results in the oxidation of corresponding benzaldehydes. Analysis of products and the stoichiometric determinations indicate the following overall reaction (1).

$$ArCHO + CrO_2FOQH + H_2O \longrightarrow ArCOOH + (HO)_2CrFOQH \quad (1)$$

Thus QFC undergoes a two electron change. This is in accord with the earlier observations with other halochromates. It has already been shown that both pyridinium fluorochromate (PFC) [9] and pyridinium chlorochromate (PCC)[10] act as two electron oxidants and are reduced to chromium (IV) species.

3.2 Rate laws

The reactions are of first order with respect to QFC. Figure 1 depicts a typical kinetic run. Further, the pseudo-first order rate constant, k_{obs} is independent of the initial concentration of QFC. The reaction rate increases with increase in the concentration of the aldehydes but not linearly (Table 1). A plot of $1/_{kobs}$ against 1/[Aldehydes] is linear ($r^2 > 0.995$) with an intercept on the rate-ordinate (Figure 2). Thus, Michaelis-Menten type kinetics are observed with respect to the aldehydes. This leads to the postulation of following overall mechanism (2) and (3) and rate law (4).

$$\text{Aldehydes} + \text{QFC} \overset{K}{\leftrightarrows} [\text{Complex}] \quad (2)$$

$$[\text{Complex}] \overset{k_2}{\rightarrow} \text{Products} \quad (3)$$

$$\text{Rate} = k_2K[\text{Aldehyde}][\text{QFC}]/(1+K[\text{Aldehyde}]) \quad (4)$$

The dependence of reaction rate on the reductant concentration was studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots. The thermodynamic parameters of the complex formation and activation parameters of the decomposition of the complexes were calculated from the values of K and k_2 respectively at different temperatures (Tables 3 and 4).

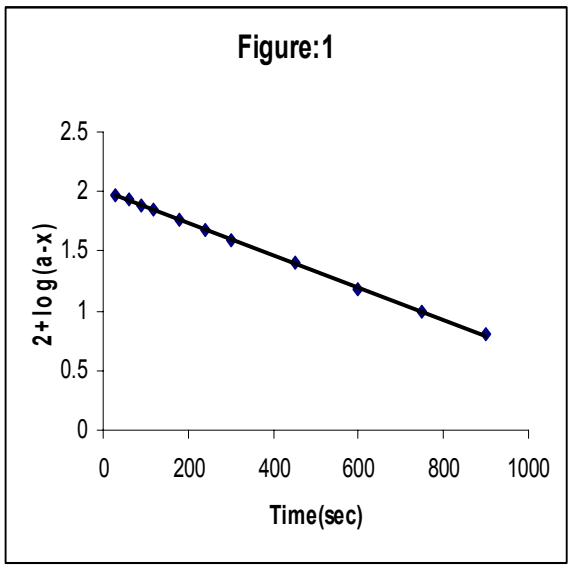


Figure 1. Oxidation of Benzaldehyde by QFC: A typical Kinetic Run

3.3 Test for free radicals

The oxidation of benzaldehyde by QFC, in an atmosphere of nitrogen failed to induce the polymerisation of acrylonitrile. Further, an addition of a radical scavenger, acrylonitrile, had no effect on the rate (Table 1). To further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol dm^{-3} of 2,6-di-t-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

Table 1. Rate constants for the oxidation of benzaldehyde by QFC at 298 K

10^3[QFC] (mol dm^{-3})	[Aldehyde] (mol dm^{-3})	[TsOH] (mol dm^{-3})	10^4 k_{obs} (s^{-1})
1.0	0.10	0.0	4.46
1.0	0.20	0.0	6.59
1.0	0.40	0.0	8.66
1.0	0.60	0.0	9.67
1.0	0.80	0.0	10.3
1.0	1.00	0.0	10.7
1.0	1.50	0.0	11.2
1.0	3.00	0.0	11.9
2.0	0.40	0.0	8.82
4.0	0.40	0.0	8.25
6.0	0.40	0.0	9.00
8.0	0.40	0.0	8.46
1.0	0.20	0.0	7.02*

*contained 0.001 mol dm^{-3} acrylonitrile

Table 2. Dependence of the reaction rate on hydrogen–ion concentration

[TsOH]/ mol dm^{-3}	0.10	0.20	0.40	0.60	0.80	1.00
10^4 k_{obs}/s^{-1}	5.22	6.12	7.79	8.64	10.8	12.6

[Benzaldehyde] 0.10 mol dm^{-3} ; [QFC] 0.001 mol dm^{-3};T=298 K

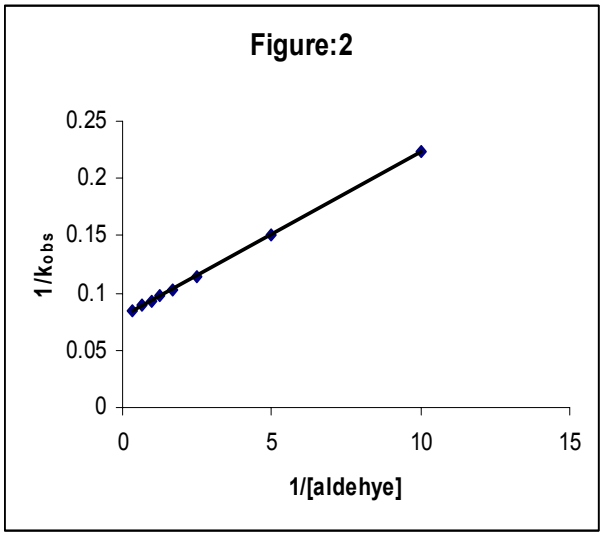


Figure 2. Oxidation of Benzaldehydes by QFC: A double reciprocal plot.

3.4 Effect of acidity

The reaction is catalysed by hydrogen ions. The hydrogen-ion dependence taking the form: $k_{obs} = a + b[H^+]$ (Table 2). The values for *a* and *b* for benzaldehyde are $4.41\pm0.25\times10^{-4}$ s^{-1} and $7.97\pm0.41\times10^{-4}$ mol^{-1} dm^3 s^{-1} respectively ($r^2 = 0.9897$)

3.5 Kinetic isotope effect

To ascertain the importance of the cleavage of the aldehydic C–H bond in the rate–determining step, oxidation of α,α-dideuterio-benzaldehyde (PhCDO) was studied. Results showed the presence of a substantial primary kinetic isotope effect (Table 3).

3.6 Effect of solvents

The oxidation of benzaldehyde was studied in 19 different organic solvents. The choice of solvents was limited by the solubility of QFC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. Kinetics is similar in all the solvents. The values of k_2 are recorded in Table 5.

The correlation between activation enthalpies and entropies of the oxidation of the thirty six benzaldehydes is linear (r^2=0.9428), indicating the operation of a compensation effect [11]. The value of the isokinetic temperature is 583±35 K. However, according to Exner[12], an isokinetic relationship between the calculated values of activation enthalpies and entropies is often vitiated by random experimental errors. Exner suggested an alternative method for establishing the isokinetic relationship. Exner's plot between log k_2 at 288 K and at 318 K was linear (r^2=0.9986; Figure 3). The value of isokinetic temperature evaluated from the Exner's plot is 730±55 K. The linear isokinetic correlation implies that all the alcohols are oxidized by the same mechanism and the changes in the rate are governed by changes in both the enthalpy and entropy of activation.

3.7 Reactivity oxidizing species

The observed hydrogen-ion dependence suggests that the reaction follows two mechanistic pathways, one acid-independent and another acid-dependent. The acid-catalysis may well be attributed to a protonation of QFC as equation (5) to yield a protonated Cr(VI) species which is a stronger oxidant and electrophile. Formation of a protonated Cr(VI) species has earlier been postulated in the reactions of structurally similar pyridinium chlorochromate (PCC).[13]

$$QHOCrO_2F + H^+ \leftrightarrows QHOCr^+(OH)OF \qquad (5)$$

The rate constants k_2, in eighteen solvents (CS_2 was not considered as the complete range of solvent parameters was not available) were correlated in terms of linear solvation energy relationship (6) of Kamlet et al.[14]

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \qquad (6)$$

In this equation, π^* represents the solvent polarity, β the hydrogen bond acceptor basicities and α is the hydrogen bond donor acidity. A_0 is the intercept term. It may be mentioned here that out of the 18 solvents, 13 has a value of zero for α. The results of correlation analyses terms of equation (6), a biparametric equation involving π^* and β, and separately with π^* and β are given below (7) - (10).

$$\log k_2 = -3.64+1.54(\pm0.18)\,\pi^* + 0.14\,(\pm0.15)\,\beta + 0.06\,(\pm0.14)\,\alpha \qquad (7)$$

$R^2 = 0.8656$; sd = 0.17; n = 18; $\psi = 0.40$

$$\log k_2 = -3.66 + 1.56\,(\pm0.17)\,\pi^* + 0.12\,(\pm0.14)\,\beta \qquad (8)$$

$R^2 = 0.8639$; sd = 0.16; n = 18; $\psi = 0.39$

$$\log k_2 = -3.63 + 1.59\,(\pm0.16)\,\pi^* \qquad (9)$$

$r^2 = 0.8576$; sd = 0.16; n = 18; $\psi = 0.39$

$$\log k_2 = -2.74 + 0.39\,(\pm0.34)\,\beta \qquad (10)$$

$r^2 = 0.0784$; sd = 0.41; n = 18; $\psi = 0.99$

Here n is the number of data points and ψ is Exner's statistical parameter[15].

Kamlet's[14] triparametric equation explain *ca*. 87% of the effect of solvent on the oxidation. However, by Exner's criterion the correlation is not even satisfactory [cf. (7)]. The major contribution is of solvent polarity. It alone accounted for *ca*. 86 % of the data. Both β and α play relatively minor roles.

The data on the solvent effect were also analysed in terms of Swain's equation[16] of cation- and anion-solvating concept of the solvents (11).

$$\log k_2 = aA + bB + C \qquad (11)$$

Table 3. Rate constants and activation parameters for the decomposition of QFC-Aldehyde complexes

Substance	10^4 k_2 (dm^3 mol^{-1} s^{-1})				ΔH^*	$-\Delta S^*$	ΔG^*
	288 K	298 K	308 K	318 K	kJ mol^{-1}	J mol^{-1} K^{-1}	kJ mol^{-1}
H	4.86	12.6	31.5	79.2	68.2±0.7	72±2	89.5±0.6
p-Me	10.8	27.0	64.8	153	64.7±0.5	78±1	87.6±0.4
p-OMe	26.1	63.9	150	351	63.3±0.6	75±2	85.5±0.4
p-F	5.67	15.3	38.7	98.1	69.6±0.5	66±2	89.1±0.4
p-Cl	3.33	8.89	23.1	60.3	70.9±0.9	66±3	90.4±0.7
p-NO_2	0.21	0.64	1.89	5.35	79.6±0.6	58±2	96.9±0.5
p-CF_3	0.63	1.83	5.04	13.6	75.2±0.4	65±1	94.3±0.3
p-COOMe	0.84	2.34	6.48	17.0	74.0±0.6	66±2	93.7±0.5
p-Br	3.21	8.66	22.5	56.9	70.3±0.4	68±1	90.5±0.4
p-NHAc	11.7	29.7	71.1	171	65.4±0.5	75±0	87.4±0.4
p-CN	0.38	1.14	3.24	9.27	78.4±0.7	58±2	95.5±0.6
p-SMe	13.3	35.1	84.6	207	66.9±0.5	68±2	87.0±0.4
p-NMe_2	117	270	576	1250	57.3±0.4	83±1	82.0±0.4
m-Me	8.64	21.7	52.2	126	65.3±0.7	77±2	88.2±0.5
m-OMe	8.91	21.6	50.4	117	62.7±0.6	86±2	88.2±0.4
m-Cl	1.48	3.99	10.3	27.0	71.0±0.8	72±3	92.4±0.7
m-Br	1.46	3.92	10.2	26.1	70.6±0.6	74±2	92.4±0.5
m-F	1.86	4.95	12.6	32.4	69.8±0.7	74±2	91.8±0.6
m-NO_2	0.15	0.46	1.35	3.96	80.4±0.8	59±2	97.7±0.6
m-CO_2Me	0.78	2.20	6.03	16.2	74.4±0.6	59±2	93.8±0.5
m-CF_3	0.54	1.53	4.32	11.5	75.2±0.6	66±2	94.7±0.5
m-CN	0.27	0.81	2.34	6.66	78.7±0.7	59±2	96.3±0.6
m-SMe	5.75	14.4	34.2	82.0	64.7±0.6	83±2	89.2±0.5
m-NHAc	5.31	13.5	32.4	78.3	65.6±0.6	80±2	89.4±0.5
o-Me	37.8	85.5	186	405	57.5±0.5	92±2	84.8±0.4
o-OMe	54.9	122	270	585	57.5±0.7	89±2	83.9±0.5
o-NO_2	0.46	1.31	3.60	9.81	75.0±0.7	68±2	95.1±0.6
o-COOMe	2.88	7.29	18.0	44.1	66.7±0.7	82±2	90.9±0.6
o-NHAc	61.2	132	280	576	54.4±0.4	99±1	83.7±0.3
o-Cl	11.2	26.1	62.1	137	61.3±0.6	89±2	87.7±0.5
o-Br	14.0	32.4	74.7	165	60.9±0.8	88±3	87.2±0.6
o-I	20.7	47.6	104	225	57.9±0.4	96±1	86.3±0.3
o-CN	0.95	2.61	6.84	18.0	72.0±0.7	72±2	93.4±0.6
o-SMe	62.1	135	283	594	54.7±0.5	98±2	83.7±0.4
o-F	9.02	22.5	54.0	126	64.4±0.4	80±1	88.1±0.3
o-CF_3	5.58	13.5	31.5	72.0	62.3±0.4	91±1	89.4±0.3
PhCDO	0.80	2.18	5.73	15.0	71.8±0.7	75±2	93.9±0.5
k_H/k_D	6.08	5.78	5.50	5.28			

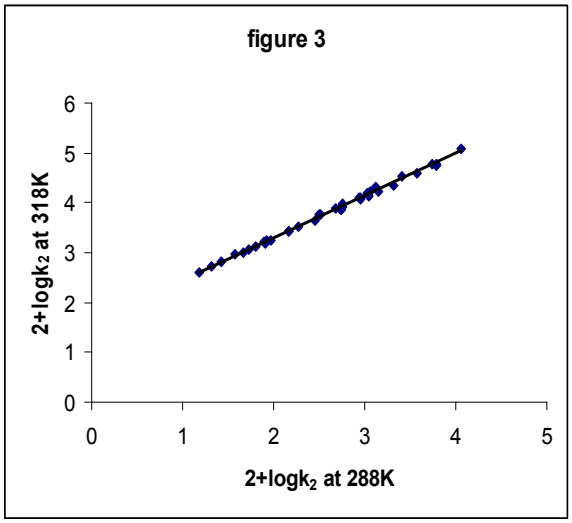


Figure 3. Exner's Isokinetic Relationship in the oxidation of benzaldehydes by QFC

Here *A* represents the anion-solvating power of the solvent and *B* the cation-solvating power. *C* is the intercept term. (*A* + *B*) is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of equation (8), separately with *A* and *B* and with (*A* + *B*).

$$\log k_2 = 0.70 + (\pm 0.05)\, A + 1.60\ (\pm 0.04)\, B - 3.87 \quad (12)$$

$R^2 = 0.9911$; sd = 0.04; $n = 19$; $\psi = 0.09$

$$\log k_2 = 0.48\ (\pm 0.53)\, A - 2.77 \quad (13)$$

$r^2 = 0.0456$; sd = 0.43; $n = 19$; $\psi = 1.00$

$$\log k_2 = 1.55\ (\pm 0.13)\, B - 3.64 \quad (14)$$

$r^2 = 0.8927$; sd = 0.14; $n = 19$; $\psi = 0.36$

$$\log k_2 = 1.30 \pm 0.12\ (A + B) - 3.84 \quad (15)$$

$r^2 = 0.8765$; sd = 0.16; $n = 19$; $\psi = 0.34$

The rates of oxidation of benzaldehyde in different solvents showed an excellent correlation in Swain's equation (cf. equation 12) with the cation-solvating power playing the major role. In fact, the cation-solvation alone account for *ca.* 88% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (*A* + *B*), also accounted for *ca.* 89% of the data. In view of the fact that solvent polarity is able to account for *ca.* 89% of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of log k_2 against the inverse of the relative permittivity is not linear ($r^2 = 0.5521$; sd = 0.29; $\psi = 0.69$).

3.8 Correlation analysis of reactivity

The effect of structure on reactivity has long been correlated in terms of the Hammett equation[17] or with dual substituent-parameter equations.[18, 19] In the late 1980s, Charton[20] introduced a triparametric LDR equation for the quantitative description of structural effects on chemical reactivities. This triparametric equation results from the fact that substituent types differ in their mode of electron delocalization.

Here, σ_l is a localized (field and/or inductive) effect parameter, σ_d is the intrinsic delocalized electrical effect parameter when active site electronic demand is minimal and σ_e represents the sensitivity of the substituent to changes in electronic demand by the active site. The latter two substituent parameters are related by equation (16).

$$\sigma_D = \eta\sigma_e + \sigma_d \quad (16)$$

Here η represents the electronic demand of the reaction site and is given by $\eta = R/D$, and σ_D represents the delocalized electrical parameter of the diparametric LD equation.

For *ortho*-substituted compounds, it is necessary to account for the possibility of steric effects and Charton,[21] therefore, modified the LDR equation to generate the LDRS equation (17).

$$\log k_2 = L\,\sigma_l + D\,\sigma_d + R\,\sigma_e + S\,\upsilon + h \quad (17)$$

where υ is the well known Charton's steric parameter based on Van der Waals radii.[22]

The rates of oxidation of *ortho*-, *meta*- and *para*-substituted benzaldehydes show an excellent correlation in terms of the LDR/LDRS equations (Table 6). We have used the standard deviation (sd), the coefficient of multiple determination (R^2), and Exner's[15] parameter, ψ, as the measures of goodness of fit.

The comparison of the *L* and *D* values for the substituted benzaldehydes showed that the oxidation of *para*-substituted benzaldehydes is more susceptible to the delocalization effect than to the localized effect. However, the oxidation of *ortho*- and *meta*-substituted compounds exhibited a greater dependence on the field effect. In all cases, the magnitude of the reaction constants decreases with an increase in the temperature, pointing to a decrease in selectivity with an increase in temperature.

All three regression coefficients, *L*, *D* and *R*, are negative indicating an electron-deficient carbon centre in the activated complex for the rate-determining step. The positive value of η adds a negative increment to σ_d, reflecting the electron-donating power of the substituent and its capacity to stabilise a cationic species. The positive value of S indicates that the reaction is subject to steric acceleration by an *ortho*-substituent.

To test the significance of localized, delocalized and steric effects in the ortho-substituted benzaldehydes, multiple regression analyses were carried out with (i) σ_l, σ_d and σ_e (ii) σ_d, σ_e and υ and (iii) σ_l , σ_e and υ. The absence of significant correlations showed that all the four substituent constants are significant.

$$\log k_2 = -1.42\ (\pm 0.36)\, \sigma_l - 1.95\ (\pm 0.29)\, \sigma_d - 3.17\ (\pm 1.64)\, \sigma_e - 2.57 \quad (18)$$

$R^2 = 0.8866$; sd = 0.25; $n = 12$; $\psi = 0.39$

Table 4. Formation constants for the decomposition of QFC–Aldehyde complexes and thermodynamic parameters

Substance	K / (dm^3 mol^{-1})				$-\Delta H$	$-\Delta S$	$-\Delta G$
	288K	298K	308K	318K	(kJ mol^{-1})	(J mol^{-1} K^{-1})	(kJ mol^{-1})
H	6.21	5.49	4.50	3.69	15.9±0.8	31±3	6.63±0.7
p-Me	5.89	5.17	4.41	3.78	13.8±0.4	25±1	6.53±0.3
p-OMe	5.44	4.72	4.05	3.24	15.4±0.9	31±3	6.30±0.7
p-F	5.81	5.06	4.38	3.69	13.9±0.4	25±1	6.49±0.3
p-Cl	6.15	5.40	4.70	3.99	13.4±0.4	23±1	6.65±0.3
p-NO_2	5.90	5.13	4.47	3.78	13.7±0.4	25±1	6.53±0.3
p-CF_3	5.46	4.77	4.05	3.33	15.0±0.7	30v2	6.32±0.5
p-COOMe	5.32	4.62	3.87	3.15	15.8±0.7	33±2	6.32±0.6
p-Br	5.56	4.86	4.14	3.42	14.8±0.6	29±2	6.37±0.5
p-NHAc	6.13	5.40	4.68	3.96	13.5±0.5	24±1	6.64±0.4
p-CN	5.85	5.13	4.40	3.72	14.0±0.5	26±1	6.51±0.4
p-SMe	6.02	5.49	4.76	4.03	12.7±0.7	21±2	6.65±0.6
p-NMe_2	5.99	5.27	4.59	3.87	13.0±0.5	24±2	6.56±0.4
m-Me	5.45	4.77	4.05	3.33	14.9±0.7	29±2	6.32±0.5
m-OMe	5.73	5.03	4.29	3.57	14.5±0.6	27±2	6.45±0.5
m-Cl	6.20	5.48	4.76	4.05	13.3±0.5	23±1	6.68±0.4
m-Br	6.02	5.31	4.58	3.87	13.6±0.5	24±1	6.57±0.4
m-F	5.66	4.95	4.23	3.51	14.6±0.6	28±2	6.42±0.5
m-NO_2	5.27	4.55	3.83	3.15	15.5±0.6	32±2	6.21±0.5
m-CO_2Me	5.30	4.59	3.87	3.17	15.6±0.7	32±2	6.22±0.5
m-CF_3	5.56	4.86	4.14	3.42	14.8±0.6	29±2	6.37±0.5
m-CN	5.48	4.76	4.05	3.32	15.1±0.6	30±2	6.32±0.5
m-SMe	6.05	5.33	4.61	3.88	13.7±0.5	24±2	6.61±0.4
m-NHAc	5.96	5.24	4.53	3.83	13.7±0.5	24±1	6.57±0.4
o-Me	5.98	5.26	4.54	3.82	13.8±0.5	25±2	6.57±0.4
o-Ome	5.92	5.22	4.50	3.75	14.0±0.6	26±2	6.55±0.5
o-NO_2	6.11	5.39	4.67	3.96	13.5±0.5	23±1	6.64±0.4
o-COOMe	6.18	5.47	4.77	4.03	13.3±0.5	23±2	6.67±0.4
o-NHAc	5.43	4.71	3.95	3.27	14.8±0.7	29±2	6.23±0.6
o-Cl	5.79	5.04	4.32	3.63	14.3±0.4	27±1	6.47±0.4
o-Br	5.36	4.68	3.90	3.20	15.6±0.7	32±2	6.26±0.5
o-I	5.61	4.89	4.17	3.45	14.8±0.6	29±2	6.39±0.5
o-CN	6.15	5.43	4.73	3.96	15.4±0.6	31±2	6.29±0.4
o-SMe	5.82	5.13	4.38	3.96	12.5±0.3	21±1	6.52±0.3
o-F	5.00	4.28	3.55	2.85	16.7±0.7	36±2	6.04±0.6
o-CF_3	5.88	5.16	4.41	3.76	13.9±0.4	25±1	6.52±0.3
PhCDO	6.10	5.40	4.68	3.90	13.8±0.6	24±2	6.63±0.5

Table 5. Solvent effect on the oxidation of benzaldehyde by QFC at 298 K

Solvents	K ($dm^{-3}mol^{-1}$)	10^4 k_2 (s^{-1})
Chloroform	5.77	41.7
Toluene	5.41	11.7
1,2-Dichloroethane	4.65	49.0
Acetophenone	6.15	50.1
Dichloromethane	4.68	45.7
THF	4.78	22.9
DMSO	5.49	126
t-Butylalcohol	4.46	18.6
Acetone	5.35	38.1
1,4-Dioxane	4.30	16.6
DMF	4.82	72.4
1,2-Dimethoxyethane	5.45	12.9
Butanone	5.89	28.2
CS_2	4.88	6.46
Nitrobenzene	4.45	56.2
Acetic acid	5.82	9.33
Benzene	6.03	14.5
Ethyl acetate	5.35	14.8
Cyclohexane	5.29	1.91

$$\log k_2 = -2.04\ (\pm 0.42)\ \sigma_d - 1.78\ (\pm 2.58)\ \sigma_e + 0.72\ (\pm 0.48)\ \upsilon - 3.40 \qquad (19)$$

$R^2 = 0.7562$; sd = 0.37; n = 12; $\psi = 0.57$

$$\log k_2 = -1.91\ (\pm 0.80)\ \sigma_I - 0.28\ (\pm 3.85)\ \sigma_e + 1.15\ (\pm 0.72)\ \upsilon - 2.22 \qquad (20)$$

$R^2 = 0.4551$; sd = 0.58; n = 12; $\psi = 0.85$

Similarly in the cases of the oxidation of para- and meta-subsituted benzaldehydes, multiple regression analyses indicated that both localization and delocalization effects are significant. There is no significant collinearity between the various substituents constants for the three series.

The percent contribution[23] of the delocalized effect, P_D, is given by following equation (21).

$$P_D = (|D| \times 100) / (|L| + |D|) \qquad (21)$$

Similarly, the percent contribution of the steric parameter[24] to the total effect of the substituent, P_S, was determined by using equation (21).

$$P_S = (|S| \times 100) / (|L| + |D| + |S|) \qquad (22)$$

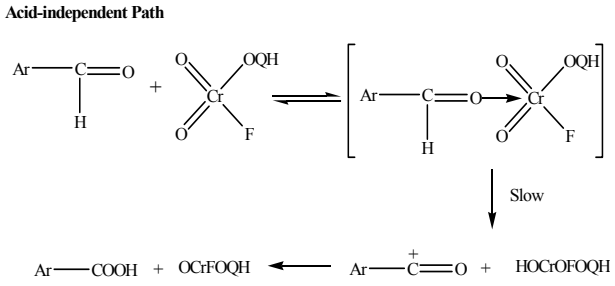
The values of P_D and P_S are also recorded in Table 6. The value of P_D for the oxidation of *para*-substituted benzaldehydes is *ca.* 42% whereas the corresponding values for the *meta*- and *ortho*-sobstituted aldehydes are *ca.* 34 and 38% respectively. This shows that the balance of localization and delocalization effects is different for differently substituted benzaldehydes. The less pronounced resonance effect from the *ortho*-position than from the *para*-position may be due to the twisting away ofthe alcoholic group from the plane of the benzene ring.

The magnitude of the P_S value shows that the steric effect is significant in this reaction.

The positive value of *S* showed a steric acceleration of the reaction. This may be explained on the basis high ground state energy of the sterically crowded alcohols. Since the crowding is relieved in the in the product aldehyde as well as the transition state leading to it, the transition state energy of the crowded and uncrowded alcohols do not differ much and steric acceleration, therefore results.

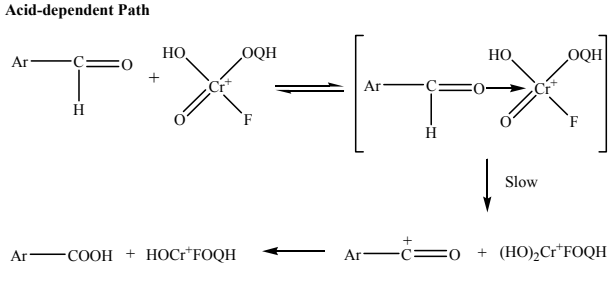
4. Mechanisms

A hydrogen abstraction mechanism leading to the formation of the free radicals is unlikely in view of the failure to induce polymerization of acrylonitrile and no effect of the radical scavenger on the reaction rate. The presence of a substantial kinetic isotope effect confirms the cleavage of a aldehydic C-H bond in the rate-determining step. The negative values of the localization and delocalization electrical effects i.e. of *L*, *D* and *R* points to an electron-deficient reaction centre in the rate-determining step. It is further supported by the positive value of η, which indicates that the substituent is better able to stabilize a cationic or electron- deficient reactive site. Therefore, a hydride-ion transfer in the rate-determining step is suggested. The hydride-ion transfer mechanism is also supported by the major role of cation-solvating power of the solvents.



Scheme - 1

The hydride ion transfer may take place either by a cyclic process via an ester intermediate or by an acyclic one-step bimolecular process. Kwart and Nickle[23] have shown that a dependence of kinetic isotope effect on temperature can be gainfully employed to determine whether the loss of hydrogen proceeds through a concerted cyclic process or by an acyclic one.



Scheme - 2

The data for protio- and deuterio-benzyl alcohols, fitted to the familiar expression: $k_H/k_D = A_H/A_D(-\Delta H^*/RT)$[21,25] show a direct correspondence of a symmetrical transition state in which activation energy difference for protio- and deuteriocompounds is equal to the difference in the

zero-point energy for the respective C–H and C–D bonds (≈4.5 kJ mol^{-1}) and the entropies of activation of the respective reactions are almost equal. Bordwell[24] has documented a very cogent evidence against the occurrence of concerted one-step bimolecular processes by hydrogen transfer and it is evident that in the present studies also the hydrogen transfer does not occur by an acyclic biomolecular process. It is well-established that intrinsically concerted sigmatropic reactions, characterized by transfer of hydrogen in a cyclic transition state, are the only truly symmetrical processes involving a linear hydrogen transfer[26].

Litller[27] has also shown that a cyclic hydride transfer, in the oxidation of alcohols by Cr(VI), involves six electrons and, being a Hueckel-type system, is an allowed process. Thus, a transition state having a planar, cyclic and symmetrical structure can be envisaged for the decomposition of the ester intermediate. Hence, the overall mechanism is proposed to involve the formation of a chromate ester in a fast pre-equilibrium step and then a decomposition of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product (Schemes 1 and 2).

Table 6. Temperature dependence for the reaction constants for the oxidation of substituted benzaldehydes by QFC

T/K	$-L$	$-D$	$-R$	S	η	R^2	sd	ψ	P_D	P_S
Para-substituted										
288	1.62	2.07	1.19	-	0.57	0.9999	0.007	0.01	42.4	-
298	1.53	1.99	1.15	-	0.58	0.9998	0.001	0.02	42.6	-
308	1.44	1.89	1.07	-	0.57	0.9989	0.001	0.04	42.9	-
318	1.35	1.82	0.99	-	0.54	0.9999	0.008	0.01	43.6	-
Meta-substituted										
288	1.98	1.44	0.95	-	0.66	0.9998	0.004	0.01	33.0	-
298	1.89	1.36	0.89	-	0.65	0.9997	0.004	0.02	32.9	-
308	1.80	1.26	0.78	-	0.62	0.9989	0.003	0.04	32.8	-
318	1.71	1.17	0.69	-	0.59	0.9998	0.008	0.02	32.8	-
Ortho-substituted										
288	1.71	1.99	1.34	1.08	0.67	0.9999	0.003	0.01	39.5	19.4
298	1.62	1.89	1.26	0.99	0.67	0.9998	0.004	0.02	39.6	17.2
308	1.53	1.80	1.17	0.90	0.65	0.9999	0.002	0.01	40.0	16.7
318	1.46	1.70	1.17	0.81	0.69	0.9989	0.005	0.04	39.3	15.8

The observed negative value of entropy of activation also supports the proposed mechanism. As the charge separation takes place in the transition state, the charged ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in the loss of entropy[28].

5. Conclusion

The reaction is proposed to proceed through a hydride-ion transfer from aldehyde to the oxidant in the rate-determining step. It has also been observed that an α-C-H bond is cleaved in the rate-determining step. Both deprotonated and protonated forms of QCC are the reactive oxidising species.

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CHROMATOGRAPHIC DETERMINATION OF PESTICIDES IN FOODS AND FOOD PRODUCTS

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Keywords: pesticides, gas chromatography, liquid chromatography, electrically driven systems.

The newest results in the chromatographic analysis of pesticides present in foods and food products are collected and the results are critically evaluated. Examples for the employment of preconcentration and prepurification technologies, gas chromatography using ECD, NPD, MS and MS/MS detection methods, liquid chromatographic methodologies such as thin-layer chromatography, high performance liquid chromatographic methods as well as electrically driven systems are presented. The advantages and disadvantages of the various chromatographic technologies are shortly discussed and the efficacies of the methodologies are compared. Pesticides included in the review are insecticides, herbicides, acaricides, organophosphorous and organochlorine compounds The application of the chromatographic methods for the determination of pesticides in a wide variety foods and food products is discussed in detail.

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INTRODUCTION

Chromatography has been developed as a powerful separation technique suitable for the quantitative analysis of compounds with very similar chemical structure. Various chromatographic techniques such as gas chromatography (GC), liquid chromatographic procedures (thin layer chromatography, TLC, high performance liquid chromatography, HPLC, ultra performance liquid chromatography, UPLC) and electrically driven systems found application in biology, medicine, chemical technology and in the analysis of natural products contributing to the isolation and identification of new molecules. These methodologies were successfully employed in analytical quality control and environmental sciences. Moreover, chromatography has been applied for the residue analysis of xenobiotics in air, ground and surface water, sludge, soil matrices, foods and food products and in human and veterinary health care.

The objectives of the recent review are the compilation and concise evaluation of the newest results obtained in the chromatographic analysis of pesticides in foods and food products, the brief enumeration of the techniques employed and the critical evaluation of the results.

GAS CHROMATOGRAPHY

Gas chromatographic (GC) methods are suitable for the separation and quantitative determination of compounds which are volatile or semi-volatile and thermally stable at the temperature of the measurement.

Unfortunately, the overwhelming majority of compounds are not volatile, consequently, the application of GC methods is limited.

Fruits, juices and vegetables

Gas chromatography coupled with mass spectrometry was employed for the determination of the residues of kresoxim-methyl and boscalid in fruits, vegetables and soil.

Both fungicides were successfully applied to control a considerable number of diseases caused by *Venturia inaequalis*, [1] powdery mildew, [2] *Sclerotinia blight* [3] and *Botritis cinerea*.[4] It was also established that the mixture of these two insecticides show good capacity to control strawberry grey mould disease.[5] Because of their considerable commercial importance these insecticides have been many times investigated by various chromatographic methods such as GC combined with electron capture detector (ECD),[6] liquid chromatography tandem mass spectrometry,[7] HPLC-DAD,[8] GC-ECD and GC-MS,[9] on column liquid-liquid extraction following liquid chromatography-tandem mass spectrometry,[10] *etc*. Samples of 10 g (melon, cucumber, tomato, apple, pear, pepper, eggplant and soil) were extracted with 50 mL of acetone or methanol, filtered, mixed with 50 mL of water, 50 g NaCl and 40 ml of *n*-hexane or dichloromethane or their mixture of 1:1, v/v ratio. The organic phase was dried with anhydrous Na_2SO_4. The extraction step was repeated three times, the combined extracts were evaporated to dryness and redissolved in 1 mL of *n*-hexane. Separations were performed on a capillary column (30 m x 0.25 mm i.d.; film thickness, 0.25 μm). The injector temperature was 250 ^{0}C. Temperature gradient initiated at 50 ^{0}C (1 min), ramped to 150 ^{0}C at 30 ^{0}C/min), then to 250 ^{0}C at 10 ^{0}C/min, final hold, 10 min. MS conditions were: electron ionization (EI) mode at 70 eV. The temperature of the ion source was 250 ^{0}C, the temperature of the transfer line was 25 ^{0}C. Helium was the carrier gas. Analytes were identified at full scan (*m/z* 50-400). Quantitative measurements were carried out at selected ion monitoring (SIM). The LODs were 0.006 and 0.015 mg/kg for kresoxim-methyl and boscalid and the

LOQs were 0.02 and 0.05 mg/kg, respectively. The RSD of the intra- and inter-day precision were lower than 13.8 and 14.5%, recoveries varied between 77.1 and 98.7% for kresoxim-methyl and 72.8-105.1% for boscalid. It was established that the good validation parameters of the method advocate its application for the analysis of kresoxim and boscalid in mixed formulations. [11] Five pesticide residues (gamma-HCH, clorothalonil, fenithrothion, chlorpyrifos and pocymidone) were determined in tomatoes. Analytes were extracted with ACN and a mixture of dichloromethane:petroleum ether (1:1, v/v). The suspension was centrifuged and the supernatant was filtered through Na_2SO_4. Analytes were separated and quntified by GC-ECD. The recoveries varied between 70% and 110%. LOD and LOQ were 0.04-0.06 ng/kg and 0.014-0.02 mg/kg.[12]

HS-SPME followed by GC-ECD was employed for the determination of organophosphorous (diazinon, malathion, chloropyrofos, quinalphos, profenofos) and organochlorine (chorothanoil, alpha-endosulfane, beta-endosulfan) pesticide residues in vegetable (cucumber) and fruit (strawberry) samples. GC-ECD measurements indicated that the washing with acetic acid, sodium carbonate, sodium chloride and tap water decreased the amount of pesticides, acetic acid being the most efficace. It was established that the efficacy of washing is correlated with the water solubility and, and vapour pressure of the washing solution (Chai et al., 2010).[13]

A fast, low-pressure GC-time-of-flight MS (LC-GC/TOFMS) was developed and applied for the identification and quantitative determination of of 150 pesticides in tomato, strawberry, potato, orangeand lettuce samples. Dispersive solid-phase extraction (d-SPE) and disposable pipette extraction (DPX) were employed for clean-up. The stationary phase for clean-up consisted of 150 mg $MgSO_4$, 50 mg primary secondary amine (PSA) 50 mg ODS, and 7.5 mg graphitized carbon black (GCB) per mL extract was applied. It was established that the method is suitable for the analysis of a wide rage of pesticide residues. [14] Insecticides (ethoprophos, diazinon, chlor-pyrophos-methyl, fenitrothion, malathion, chlorpyrophos, and fenamiphos) were extracted from banana leaves by applying a modified QuEChERS technique. Insecticides were separated and quantitated by GC followed with nitrogen phophorous detection (NPD). Recovery values of the method ranged from 89% to 104% with a RSD values of lower than 9.1%. LOD varied between 0.002–0.064 mg/kg.

The confirmation of the identity of target compounds was performed by GC tandem mass spectrometry [15] . A hyperspectral imaging system was applied for the determination of dichlorvos residues on the surface of navel orange. It was established that the method meet the requirements of online fast nondestructive detection.[16]

GC-MS technology was employed for the determination of organophosphate and pyrethroid insecticide residues in fruits, vegetables and fruit juices. The investigation revealed that 14% or 5% of the food samples consumed by children contain pesticide residues . [17] Seven strobilurin and six oxazole fungicides were determined in fruits and juices. Target compounds were preconcentrated by two procedures: ultrasound-assisted emulsification liquid-liquid micro-extraction and single-drop liquid-liquid microextraction. Analytes were separated by GC-MS used in the SIM mode. Enrichment factors were between 140-1140 and 80-1600 for the first and second extraction technique, respectively. It was established that LODs were below the MRLs t by the European Comission.[18] Organochlorine pesticides residues have also been determined in commercial fruits and baby food samples. Target compounds were extracted and prepurified by QuEChERS (quick, easy, cheap, effective rugged and safe) technique followed by GC-MS analysis. The recovery of the method varied from 70% to 120%, RSD was lower than 17% in the majority of cases. LOQ varied between 0.001-0.013 mg/kg.[19] Ultrasonic-assisted dispersive liquid-liquid microextraction (UA-DLLME) followed with GC-FID (flame ionization detection) was applied for the analysis of cypermethrin ans permethrin residues in pear juice. The enrichment factors for cypermethrin and permethrin residues were 344 and 351, respectively. LODs ranged from 3.1 to 2.2 µg/kg, recoveries were 92.1–107.1%. The intra-day and inter-day RSDs were less than 4.0%. The method was successfully employed for the measurement of these pesticide residues in pear juices.[20] Azole fungicide residues were determined in grape and wine using offline disperse solid phase extraction (DSPE) coupled with GC-positive chemical ionization mass spectrometry (GC-MS/PCI). Target comounds were extracted from grape and wine with ACN and ethyl acetate, respectively. Recoveries of the method varied between 71.2% and 102.2%, RSDs were less than 10.6%, LODs were lower than 10 µg/kg. It was stated that the method can be applied for the determination of azole fungicide residues in grape and wine.[21] A GC-MS procedure was applied for the detection and quantitation of 23 pesticides in 160 different vegetables marketed in Saudi Arabia. The pesticide residues were over the MRL in 53 samples. The most frequently occurring pesticides were carbaryl, biphenyl and carbofuran. Cabbage, carrot, green peper, cucumber and egg-plant were the most polluted vegetables. The monitoring of the environmental pollutants in vegetable has been advocated.[22] GC technology has been employed for the analysis of organophosphate pesticide residues in broccoliheads. The measurements indicated that malathion, diazinon, chlorphenvinphos, fenthion and ethion are the most freqeunt pollutants.[23]

A novel technique was developed for the simultaneous determination of 346 multiresidue pesticides in grapes. The method applied PSA matrix solid phase dispersion followed with GC-MS-SIM. Samples of 15 g were mixed with 6 g of anhydrous magnesium sulfate and 1.5 g of sodium chloride, then extracted with 15 mL of ACN and cleaned up with 0.3 g dispersive PSA. Four injections from one sample was enough to separate all the 352 pesticides. LOD varied between 0.0017-0.2667 mg/kg, recoveries ranged from 45% to 136%. RSD value of 95% of pesticides was equal or lower than 20%. The identification of pesticides was performed by the retention time, molecule ions, fragment ions, and the abundance ratio of the selected ions. It was stated that the technique suitable for the determination of 346 pesticide residues ing rapes.[24] Pesticide residues in grapes were detrmined by MSPD combined with GC-MS. Target compounds included in the measurements were vinclozolin, dichlofluanid, penconazol, captan, quinoxyfen, fluquinconazol, boscalid and pyraclostrobin. GC-MS analyses were performed in the SIM mode. The optimal MSDP method consisted of 0.5 g of grapes, 1.0 g of silica as clean-up sorbent, 1.5 g of ODS as bonded phase and 10 mL of dichloromethane/ethyl acetate (1:1, v/v) as eluting solvent. Recoveries were over 80% except for captan. LOQs ranges from 3.4 to 8.7 µg/kg being lower than MRLS. [25]

Organochlorine pesticide residues have also been determined in honey from various geographic regions. The concentration of hexachlorocyclohexanes (HCHs), dichlorodiphenyltrichloroethanes (DDTs), chlordane and hexachlorobenzene (HCB) in honey was measured after accelerated solvent extraction with GC-ion trap mass spectrometry. The measurements indicted that the amount of organochlorine pesticide residues ranged 0.21-8.70. 0.10-4.35, 0.02-3.75 and 0-1.16 ng/g for HCHs, DDTs, chlordanes and HCB, respectively. It was established that honey samples from developed countries show considerable differences in the concentration of organochlorine pesticide residues.[26] Chlorpyrifos, lamda-cyhalothrin, cypermethrin and deltamethrin residues were measured in honeys. The method employed liquid-liquid extraction (LLE) and low temperature purification (LTP). LTP cleanup used ACN-ethyl acetate mixture (6.5 mL:1.5 mL) as extracting agent. Final cleanup was performed with 2 g of florisil. Analytes were separated and quantitated by GC-ECD. LOD and LOQ were below 0.016 and 0.032 µg/g, respectively. The presence of target compounds was confirmed by GC-MS.[27] GC-ECD procedure was applied for the determination of 24 organochlorine pesticide residues in 109 honey samples. It was established that aldrin, cis-chlordane, trans-chlordane, oxy-chlordane, 2,4'-DDE and 4,4'-DDE was present in each samples. The concentration of pesticide residues was over the MRL values in 55 samples. A strict control of organochlorine pesticide residues in honey was proposed.[28] The acaricide residues in commercial beeswax were determined by GC using ECD, NPD and MS detection. The target compounds measured were chlorfenvinphos, fluvalinate, amitraz, bromopropylate, acrinathrin, flumethrin, coumaphos, chlorpyrophos, chlordimeform, endosulfan and malathion. Recoveries varied between 86-108%. LOQ ranged from 0.10 to 0.30 mg/kg for ECD and NPD detection and from12 to 85 µg/kg for MS detection.[29] Herbicides metribuzin and quizalofop-*p*-ethyl have been etermined in potato and soil by GC-ECD. Herbicides were extracted with acetone and methanol-water, the liquid phase was cleaned by SPE using florisil cartridges (500 mg, 3 mL). Target compounds were eluted with petroleum ether-acetic ether (9:1, v/v, 5 mL) and petroleum ether-acetic ether (8:2, v/v, 2 mL). LOQ was 0.01 mg/kg, recoveries varied between 72.9 – 109.5%. RSD ranged 0.7 – 9.2%. Identity of analytes was confirmed by GC-MS.[30]

Miscellaneous foods and food products

Beside of fruits, juices and vegetables various GC technologies have been frequently applied for the pesticide residue analysis of a wide variety of other foods and food products. Thus, the occurrence of pollutants in tea has been vigorously investigated. Single-walled carbon nanotube (SWCNTs) was employed as stationary phase for SPME preconcentration of pesticide residues in tea samples. Analytes were separated and quantified by GC-MS. LODs were 0.027-0.23 ng/mL. RSDs of measurements with single fiber, fiber-to-fiber, and day-to-day were 2.3-13.0, 8.2 – 14.6, and 4.1 – 12.5%, respectively. Recoveries were between 75.1 and 118.4%. The efficacy of SWCNTs was higher than the commerial poly(dimethylsiloxane) (PDMS) and plyacrylate (PA) fibers. The results indicated the presence of chlorfenapyr and lambda-cyhalothrin in some tea samples. It was stated that the method is simple, efficient and can be applied for the determination of pesticide residues in complicated accompanying matrices.[31] QeEChERS method followed by ion-trap GC/MS/MS was applied for the analysis of 22 pesticides in tea samples. Teas were homogenized with water and the analyted were extracted with ACN containing 1% of acetic acid. Initial cleanup was performed with dispersive dSPE, followed with solvent exchange and dSPE again. The recoveries ranged from 78 to 115% except for diazinon (130%) and malathion (122%). Average RSD was 8.7%, the LOD values except for terbufos were below the MRL limit set by EU and Japan.[32] Pyrethroid residues have also been determined in tea samples. Measurements were performed with GC and ion trap mass spectrometry.[33] Gas chromatography with micro-ECD was employed for the measurement of 21 organochlorine and 6 pyrethroid pesticides inhotpot condiment. Analytes were extracted with ACN, cleaned up with GPC, florisil SPE and PSA. LODS were 0.082-2.3 g/kg for organochlorine pesticides and 1.5-13.0 g/kg for pyrethroid pesticides. Recoveries ranged from 70.1% to 116.0% RSD being 0.2%-6.1%. It was stated that the method is rapid, sensitive and reliable, and can be applied for the simultaneous detection of multi-residues of pesticides in hotpot condiment[34]. Pesticides have also been investigated in milk and dairy poducts. The influence of lactic acid fermentation and heat treatment of bovine milk on the decomposition of seven organophosphorous pesticides (denthion, dimethoate, malathion, methyl-parathion, monocrotophos, phorate and trichlorphon) was studied in detail. Measurements were carried out by GC-MS. The results indicated that fermentation process and heat treatment accelerate the decomposition of pesticides.[35] GC-NPD was applied for the separation and quantitation of seven organophophorous pesticides (OPPs) in raw milk and infant formulas. Recoveries ranged from 62.2% to 97.25%.[36] GC-ECD technique was applied for the determination of organochlorine pesticides (DDT and derivatives, HCH, lindane, heptechlor and endosulfan) in raw and processed milk. LOD was 0.11 mg/kg. The measurements indicated that the concentration of organochlorine pesticides in the samples was below the MRL. It was further concluded from the data that the continuous monitoring and control of pesticides in milk is of paramount importance for public health.[37] GC was also applied for the determination of organochlorine pesticides OCPs in kaymak and butter marketed in Afyonkarahisar province of Turkey. It was found that the majority of samples was contaminated with organochlorine pesticide residues (672.46 ng/g .in kaymak and 308.95 ng/g in butter). It was further established that the concentration of OCPs such as β-HCH (90.01 ng/g), aldrin (528.04 ng/g, and endrin (7.31 ng/g) in kaymak was higher than the MRL value. The amount of β-HCH (214.18 ng/g), heptachlor (10.38 ng/g), aldrin (12.34 ng/g), dieldrin (12.69 ng/g), and endosulfan sulfate (8.08 ng/g) in butter was over the MRL. It was assumed that the consumption of contaminated products can be potential risk for public health.[38] Pyrethroid residues were also investigated in butter. Target compounds were concentrated with matrix solid phase dispersion methof followed with purification at low temperature. Analytes were separated and quantified by GC. LOD of cypermethrin and deltamethrin were 0.082 and 0.11 µg/g, LOQs were 0.28 and 0.32 µg/g. The recovery was about 90% with a RSD of less than 10%.[39] Simple and environmental friend GC-MS methodology was developed for the analysis of pesticide residues in cattle feed and soil samples. Investigation included 36 pesticides belonging to different classes. Measurements indicated that

organochlorine and organophosphorous pesticides were commonly detected, while the occurence of pyrethroid and chloroacetanilide pesticides was markedly lower. It was further established that residue levels were generally below the MRL.[40]

The pesticide content of various animal products has also been frequently investigated by using GC technolgies. Thus, OCPs (α-, β-, γ-HCH, heptachlor, heptachlor epoxide, aldrin, dieldrin, and eldrin) were determined in water and fishes by GC-MS. It was established that the amount of OCPs was higher in fish gonads than in the muscle tissue. Gonads of roach and bream contained mainly γ-HCH while muscle tissue concentrated β-HCH. The amount of OCPs in gonads varied between 0.385 - 0.554 ng/g wet weight (α-HCH) . 0.745 – 0.832 ng/g (γ-HCH), 0.479 – 0.576 ng/g (dieldrin), and 0.381 – 0.684 ng/g (eldrin). Water samples taken from the Odera River contained pesticides residues in the following order: endrin, γ-HCH, α-HCH, dieldrin, β-HCH, heptachlor, aldrin, heptachlor epoxide. It was assumed that the accumulation of OCPs in fish gonads may results in decreased reproduction of fish potentially leading to their extinction.[41] OCPs were also measured in fish feed. The first step of the analysis included the liquid-liquid extraction of fat. It was carried out on diatomaceous earth cartridge using *n*-hexane.ACN (80:20, *v/v*). Further purification was achieved by SPE employing silica gel cartridge. Analytes were identified and quantificated by GC-triple quadrupole tandem spectrometry. LODs of the method varied between 0.01 – 0.11 mg/L, LOQs ranged 0.02 – 0.35 mg/L. Repeatability were 3 – 15%, and the recoveries were 92 – 116%.[42] The accumulation of 18 current use and 8 OCPs in crab embrios was monitored by GC-MS. It was found that the level of contamination of crab embrios of site specific and can be used as an indicator of ecosystem health.[43] The accumulation of benzotriazole UV stabilizers (BUVs) in the blubbers of finless porpoises (*Neophocaena phocaenoides*) was studied by GC-high resolution mass spectrometry (GC-HRMS). The mean concentrations and standard deviations of two benzotriazole UV stabilizers (BUVs) were 38±28 ng/g and 19±19 ng/g, respectively. The bioconcentration factor (BCF) was 33 300 similar to that of persistent HCH. The strict monitoring of BUVBs was proposed to understand more in detail their potential risk to wildlife and human. [44] Microwave-assisted extraction followed with SPE and coupled to large-volume injection GC-MS/MS was employed for the determination of 17 pesticides in wild and aquaculture edible seaweeds. The optimal microwave conditions were 125^{0}C and 12 min, extraction solvent being 24 mL of *n*-hexane/ethyl acetate (80:20, *v/v*).SPE purification was performed on graphitized carbon and Florisil supports. Recoveries were near to 100%, RSD being lower than 13%. LODs varied between 0.3 – 23.1 pg/g, LOQs ranged from 2.3 to 76.9 pg/g below MRL. The method using microwave-assisted extraction was proposed for the routine analysis of pesticides in aquaculture and wild seaweed samples. [45] Pesticide residues were determined in four processed food (frozen Chinese dumpling, eel kabayaki, corned beef and retort curry) employing ion trap GC/MS technique. Target compounds were extracted with ethyl acetate-cyclohexane (1:1, *v/v*) in the presence of anhydrous sodium sulfate. The solvent was evaporated and the residue was redissolved in *n*-hexane. Lipids were removed from the solution by ACN-*n*-hexane partitioning. Pesticide residues in the ACN fraction was preconcentrated on ODS and graphite carbon/PSA silica mini-cartridge columns. LOQs were below 0.01 μg/g, recoveries ranged from 70% to 120%, and RSD was 15%. It was assumed that the technique can be applied for the multi-residue analysis of pesticides in processed foods prepared employing livestock and seafoods as main raw materials.[46] A GC method was applied for the detemination of carbofuran using broiler chickens as experimental model. The amount of carbofuran was measured in blood, muscle, liver and stomach contents. It was stated that carbofuran in the edible tissue of poisoned birds may result in the secondary poisoning of predators and may be harmful for humans.[47]

SIMULTANEOUS APPLICATION OF GC AND HPLC TECHNOLOGIES

The molecular base of separation is markedly different in GC and HPLC. As the separation in GC is mainly governed by the volatility of the analytes; the acidity or alkalinity, the adsorption capacity, the lipophilicity and polarity *etc.* of the target compounds play a considerable role in their HPLC retention behavior. Because of their diverse separation parameters the simultaneous application of GC and HPLC methodologies may facilitate and substantiate the analysis of target compounds present in complicated accompanying matrices. The application of GC and HPLC for the analysis of pesticides in bee and bee products has been previously reviewed.[48] The extraction by QueEChERS technology and the use of subsequent chromatographic methodology for the analysis of pesticide residues present in food matrices has also been reviewed.[49] The analytical methods employed for the determination of organophosphorous pesticide (OPP) residues in frutis and vegetables have also been compiled. The various extraction techniques and the chromatographic separation procedures were discussed and the results were compared.[50] The concentration of pesticide residues present in crushed grapes, cake, most, lees and wine was monitored by multiresidual GC-MS (71 pesticides) and multiresidual LC-MS-MS technology (45 pesticides). It was established that the amount of boscalid, cyprodynil, dimethomorph, fengexamid, metalaxyl and procymidone was the highest during the vinification process, their concentration was 0.01-0.02, 0.04, 0.01-0.08, 0.12-0.13, 0.09-0.11 and 0.07-0.13 mg/L, respectively.[51] A new technique has been developed for the determination of pestcide residues on processed tea leaves. The procedure includes extraction and dispersive d-SPE extraction followed with GC/NCI/tandem MS and UHPLC-MS/MS. LOD was below 1 μg/kg for GC and 10 μg/kg for UHPLC. The majority of recovery was over 70%. GC-NCI dected endosulfan sulfate and kelthane, while UHPLC detected imidacloprid and acetamiprid in the samples. It was established that the price of tea and the pesticide residue level did not correlated.[52]

LIQUID CHROMATOGRAPHYC TECHNOLOGIES

Oppositely to GC, liquid chromatographic (LC) methods can be used for the separation and quantitative determination of non-volatile target compounds in a very large range of molecular mass and surface acidity or alkalinity. Moreover, LC technologies can be easily applied for the analysis of both water-soluble and water-insoluble analytes.The analysis of 280 pesticides in food samples was

performed using QuEChERS extracts followed by liquid chromatography tandem mass spectrometry. Separation were carried out on an ODS stationary phase, analytes were identified with ion ratio calculation and mass spectral library searching.[53]

REVERSED-PHASE HIGH PERFOMANCE LIQUID CHROMATOGRAPHY

The overwhelming majority of LC analyses are performed in reversed-phase high performance liquid chromatographic (RPHPLC) separation mode. The advantages of this technique are the high variety of both stationary and mobile phases resulting in widely different separation characteristics, the reduced consumption of organic solvent, the increased safety of laboratory staff, and the lower environmental loading.

Fruits, juices and vegetables

A QuEChERS extraction method combined with LC-MS/MS measurements was applied for the determination of the residues of 150 pesticides in grapes. Pesticides were extracted with ACN. Phase separation was achieved by shaking the sample with a salt mixture containing magnesium sulfate, sodium chloride, disodium hydrogen citrate sesquihydrate, and trisodium citrate dihydrate. The mixture was centrifuged and an aliquot of the clear supernatant was dried with magnesium sulfate. After a new centrifugation step and aliquot of the supernatant was evaporated, redissolved in methanol-water buffer solution and used for LC analysis. Quantitation and identification were performed by using atmospheric pressure electrospray positive ionization in multiple reaction monitoring (MRM) mode. Recoveries ranged from 70% to 110%, the RSD varied between 1% and 25%.[54]

Some organophosphorous pesticides (fenitrothion, parathion, fenthion and foxim were determined in pear and water. A new ionic liquid, 1,3-dibutylimidazolium hexafluorophosphate was employed for the dispersive liquid-liquid microextraction of target compounds. Separation was carried out by HPLC. Recovery was over 75%, enrichment factor over 300-fold. LODs were 0.01-0.05 mg/L. RSD ranged from 1.3-2.7, 1.4-1.9, and 1.1-1.7, respectively[55]. A LC-MS/MS technique was applied for the analysis of 69 pesticides in fruits and vegetables (zucchini, melon, cucumber, watermelon, tomato, garlic eggplant, lettuce and pepper). Target compounds were extracted by QuEChERS. MS measurements were carried out in MRM mode. Two selected reaction monitoring (SRM) were employed for the quantitation and identification of target compounds in one run. Recoveries range from70% to 120% RSD being lower than 20%. It was stated that the method is rapid, simple and sensitive and can be employed in routine analytical laboratories[56]. A QuEChERS –HPLC-UV method was applied for the investigation of the dissipation of carbaryl on greenhouse cucumbers during the pre-harvest interval (PHI). It was established that the dissipation depends on the initial dose and follows first order kinetics. A waiting period of more than 14 days was proposed for the safe consumption of cucumber.[57] It was further established that washing, peeling and refrigeration storge markedly decreased the amount of carbaryl in cucumber samples.[58]

The concentration of propylenethiourea (PTU), 4-methyl-imidazoline-2-thione, the main degradation product of propylenebisdithiocarbamate (PBDC) was measured in tomatoes. Analytes were extracted with dispersive solid-phase clean up followed by high performance hydrophilic interaction liquid chromatography atmospheric pressure electrospray ionization mass spectrometry (HILIC-ESI-MS-MS).[59] LC-MS/MS technology was employed for the simultaneous determination of 54 pesticides. Samples of pepper, tomato, orange and lemon were extracted with ACN and liquid-liquid partitioned by salting out procedure applying NaCl. GC measurements were performed with the triple quadrupole in SRM mode. Recoveries ranged from 65.5% to 114.5%. RSD being 2.3 -8.3%. LOD varied between 0.03-14.9 µg/kg.[60] An enzyme-linked immuno-sorbent assay was developed and applied for the determination of fenhexamide residues in grape must, kiwifruit and strawberry. The results were compared with those obtained by HPLC. It was established that excellent correlation can be found between the data determined by HPLC and enzyme-linked immunosorbent assay.[61] An LC-MS/MS method was developed for the first screen of 300 pesticides in fruits and vegetables with a commercially enhanced product ion method. The probably positive extracts were further investigated using LC-MS/MS optimized for 55 pesticides. It was found that no false-negative and no-false postive were encountered during the analysis.[62] A chromatographic analitical method was developed for the determination of N-methyl carbamate pesticide residues in foods. The method was simple and rapid and makes possible the simultaneous determination of pesticide residues in foods.

It was stated that the method ensure safe products for consumers.[63] Benzimidazole fungicides and their degradation products were separated and identified in various raw agricultural commodities. Pretreatment of samples included the direct extraction and multifunctional adsorption cleanup (CHEMAC) involving salting out-partitioning /extraction with acetate-buffered ACN at low-temperature followed with sequential rapid solid-phasedispersive cleanup with a ternary sorbent mixture. Recoveries were between 70% and 92% , Intr-day and inter-day reproducibility ranged from 15% and 20%.[64]

A comprehensive and sensitive multi-residue LC-MS/MS method was developed and applied for the separation and quantitation of 73 pesticides and related products in edible oil, meat, egg, cheese, chocolate, coffe, rice, tree nuts, citric fruits, vegetables etc. Cleanup was performed by QuEChERS methodologyLC-MS/MS was operated in MRM mode. Recoveries varied between 70-120% RSD being lower than 20%. It was established that the method can be successfully applied for the analysis of organophosphorous pesticide and carbamate residues in various foods and food products.[65] Fungicides (metalexyl-M, azoxystrobin myclobutanil, fusilazole, penconazole, tebuconazole, propiconazole, diniconazole, and difenoconazole) were determined in wine. Target compounds were purified employing mixed-mode anion exchange and reversed-phase SPE cartridges. LC-MS/MS detection of analytes was performed applying atmospheric pressure electrospray ionization.

Optimal extraction condtions were: 10 mL of wine was diluted with 1 L of ultrapure water and passed through the

mixed-mode SPE cartridge at a flow-rate of 5 mL/min. Cartridge was washed with with 5 mL of aqueius NH_4OH (5% w/v). Target compounds were removed with 1 mL of methanol. RSDs were below 11%, LOQs ranged 0.01-0.79 ng/mL being below the MRLs for fungicides in grapes and wine. [66] Permethrin (3-phenoxybenzyl (1RS)-cis-trans-3-(2,2-dichlorovinyl)2,2-dimethyl-cyclopropanecarboxylate residues have also been investigated in wines using an isocratic HPLC technology. RP-HPLC measurements were performed on an ODS column (25 cm x 4 mm i.d.; particle size, µm). Isocratic mobile phase consisted of ACN-water (70:30, v/v). The flow rate was 2 mL/min, tartget compounds were detected at 215 nm and column was thermostated at 25^0C. Recoveried ranged from 93.95% to 86.58%. RSD varied between 0.89-3.69%. The method was proposed for the routine analysis of permethrin in wines because of the simple sample preparation technique, acceptable analysis time, and low cost.[67]

An octadecylsilica (ODS) column was employed for the determination of the residues of three acidic herbicides (2-4-dichlorophenoxyacetic acid, 2,4-D, Dicamba, 4-chlorophenoxyacetic acid, 4-CPA) in food crops. Because of their water solubility they can pollute soils, groundwater and air[68] causing serious environmental pollution[69] and organ damage in humans.[70] A considerable number of extraction procedures were developed and applied for the preconcentration and prepurification of acidic herbicides. Thus, the application of stir-bar sorptive extraction-liquid desorption [71], solid-phase microextraction (SPME) [72] and solid-phase extraction (SPE)-solid phase derivatization have been reported. [73] Liquid-liquid extraction (LLE) has been recently employed for the analysis of various target compounds such as Chinese cabbage *(Brassica rapa* spp. pekinensis), apple (*Malus pumila* Mill), pepper (*Capsicum annuum* L.), brown rice (*Oryza sativa* L.), and soybean (*Glycine max* L.) Target analytes were extracted from the samples of 2,4-D, Dicamba and 4-CPA by homogenization 25 g of samples with 100 mL of acetone. The suspension was filtered and evaporated to 20 – 25 mL than it was mixed with 15 g of sodiumchloride dissolved in 100 mL of deionized water. The aqueous phase was washed twice with 50 mL of *n*-hexane. The aqueous phase was acidified with 10 mL of 10% sulfuric acid. The acidic solution was extracted twice with 50 mL of dichloromethane. Anhydrous sodium sulfate was added to the organic phase. The solvent was evaporated to dryness, the residue was redissolved in 50% acetone and used for GC measurements. Because of their elevated fat content the extraction of brown rice and soybean was slightly modified. The powdered samples (25 g each) were moistened with 25 mL of deionized water for 30 min, then homogenized with 100 mL of 5 M HCl:ACN (10:90, v/v). The suspension was filtered, the liquid phase was evaporated to 20-25 mL and mixed with 10 g of NaCl The liquid phase was alkalinized and parted rwice with 50 mL of *n*-hexane. The aqueous fraction was acidified with sulfuric acid, then extracted twice with 50 mL of dichloromethane and dryied with anhydrous sodium sulfate. The extract was evaporated to dryness and dissolved in 10 mL of water:ACN (1:1, v/v). Cleanup step used a glass column (600 mm x 12 mm) filled with a slurry of 10 g of activated silica in dichloromethane. The slurry contained 2 g of anhydrous sodium sulfate. The extract was loaded on the column and washed with 50 mL of acetone-dichloromethane (1:1, v/v) followed by 50 mL (40 mL for brown rice and soybean samples) methanol-dichloromethaned methanol-dichloromethane (20:80, v/v). Target compounds were removed from the column by 80 mL of (100 mL for brown rice and soybean) methanol-dichloromethane (30:70, v/v). HPLC-UV measurements were performed on an ODS column (250 x 4.6 mm i.d., partivle size, 5 µm). Isocratic mobile phase for the separation of 2,4-D, Dicamba and 4-CPA consisted of aqueous 0.02% phosphoric acid (pH 2.5)-ACN (60:40, v/v). Chinese cabbage, apple and pepper were analysed by the following mobile phase: aqueous solution of 0.1% formic acid (pH 3.0)-ACN (60-40, v/v). The flow rate was 0.8 mL/min, analytes were detected at 230 nm. LC-MS/MS measurements were carried on an NH_2 column at 35^0C. The components of the mobile phase were ACN-methanol (3:7, v/v; solution A) and aqueous solution of 0.1% formic acid (solution B). The flow rate was 0.5 mL/min. It was established that average recoveries for Chinese cabbage ranged from 94.30 to 102.63%, for apple it was 94.67-108.47%; for pepper 97.52-102.27%. The recoveries were similar in the Scase of analytes with elevated fat content: brown-rice 76.19-101.90%; soybean 74.60-107.39%. It was concluded from the results that the method is suitable for the determination of 2,4-D, dicamba and 4-CPA in Chinese cabbage, apple, pepper, brown rice and soybean. The method was proposed for the routine analyses of these pesticide residues (Shin *et al.,* 2011).[74]

Insecticides are extensively applied to protect agricultural poducts against harmful insects, to improve quality and to enhance yield[75,76]. Acetampidrid, a neonicotinoid insecticide has also been frequently used in the up-to-date agricultural practice. Various chromatographic technologies have been frequently employed for the determination of the amount of acetamiprid residues in foods and food products such as in tea,[77] chilli,[78] and bovine milk.[79] Both GC (Zhang *et al*., 2008)[5] and HPLC**Hiba! A könyvjelző nem létezik.** techniques were employed for the separation and quantitative determination of the target compound. The behaviour of acetamiprid residues in zuccini has been investigated in detail. Samples of chopped zucchini (20 g) were mixed with 100 mL of water-methanol (50:50, v/v), the suspension was homogenized and filtered. The filtrate was partially evaporated and extracted with *n*-hexane and redissolved in dichloromethane. RP-HPLC-DAD measurements were performed on an ODS column (250 mm x 4.6 mm i.d.; particle size, 5 µm). The flow rate was 1.0 mL/min. The mobile phase for zucchini and zucchini leaves were water-ACN (7:3, v/v) and water-ACN (75:25, v/v), respectively. Analyte was detected at 248 nm. LC-ESI-MS/MS analyses were carried out on an octylsilica column (150 x 4.6 mm i.d.; particle size, µm). Components of the gradient elution were methanol, 10 mM ammonium acetate solution and water. The flow rate was 0.5 mL/min the column temperature was 40^0C. MS/MS conditions were: nebulizing gas and drying gas were nitrogen; ion spray voltage, 4000 V; source temperature, 350^0C. LOD and LOQ values were 0.01 and 0.03 µg/g and 0.02 and 0.06 µg/g for zucchini and zucchini leaves, respectively. Recoveries varied between 85.7 – 92.2% for zucchini and 90.5 – 101.9% for zucchini leaves. RSD was lower than 12%.[80]

Carbamate pesticides are frequently applied in plant protection. although, they are considered to be toxic for the environment and for human beings. A considerable number of chromatographic method was developed for the measurement of carbamate rersidues in various accompanying matrices. Because of the low amount of

carbamate pesticides in the samples, preconcentration and prepurification techniques are often employed before the chromatographic separation step. Single-drop microextraction followed by GC-MS was used for the measurement of carbamate pesticides in water,[81] hot water extraction coupled with LC-MS for the analysis of bovine milk,[82] and SPME for the determination of pesticides in fruit juices.[83] SPE followed by LC-MS was employed for the determination of pesticide residues in water. [84] Gel-permeation chromatography (GPC) has also been employed as prepurification and preconcentration step in the analysis of animal tissues [85] and oils. [86] Gel permeation chromatography (GPC) followed with ultra-performance liquid chromatography and tandem mass spectrometric detection (UPLC-MS-MS) has been applied for the determination of the residues of 18 carbamate pesticides in chestnut and pine nut. Target compounds were extracted from chestnut and pine nut by homogenizing 2.000 g sample with 20 mL of ACN. Liquid fraction was filtered trough a sodium sulfate bed, rehomogenized with 20 mL ACN. The combined extracts were evaporated to dryness. Mobile phase for GPC procedure was cyclohexane-ethyl acetate (1:1, v/v); the flow rate was 4.7 mL/min; injection volume 5 mL; collecting time started at 8.2 min and finished at 14.2 min. Fractions collected between 8.2 and 14.2 min were collected and evaporated to dryness. UPLC-MS-MS measurements were performed on a column of 50 mm x 2.1 mm the particle size being 1.8 µm. The flow rate was 0.3 mL/min. Analytes were separated by gradient elution started with 10% ACN and finished 100% 10 mM ammonium acetate. MS detection was carried out with an electrospray interface in the positive ionization mode. The capillary voltage was 3 kV, Source temperature and desolvation temperature were 110^0C and 350^0C, respectively. Nitrogen was employed as nebulizing, desolvation, and cone gas. Recoveries were between 70.21 and 89.56%, and the RSD values ranged from 2.26 to 4.07%.[87]

The endocrine-disrupting activity of nonylphenol isomers (NP), linea nonylphenol and short chain ethoxylated derivatives has been many time demonstrated. It has been established that NPs can occur in food-contact materials.[88] A considerable number of chromatographic techniques was developed for the separation and quantitative determination of endocrin-disrupting compounds in various matrices such as milk, [89] eggs, [90] and environmental samples. [91] Linear nonylphenol, nonylphenol isomers, short chain ethoxylated derivarives ($NPEO_1$ and $NPEO_2$) were determined in commercial powdered milk infant formula employing HPLC with fluorescence detection (FL). Analytes were determined by reconstituted milk-based method (method A) and powdered milk-based method (method B). Samples for method A were prepared by mixing 4.3 g milk powder with 30 mL of HPLC grade water. Saponification was performed by adding 6 mL of 0.4 M sodium hydroxy solution to 3 g of reconsituted milk.

NaOH was dissolved in ethanol-water (9:1, v/v). Saponification was carried out at 60^0C for 30 min. The solution wasa acidified by formic acid (pH = 4). SPE was carried out in ODS cartridges conditioned with two column volume of ACN, one column volume of methanol, 2 x 1 mL of methanol and 1 x 1 mL mL of ethanol-water 9:1 v/v. Target compounds were eluted with 2 x 1 mL of methanol followed with 2 x 1 mL of ACN. Samples were concentrated to 0.5 mL, redissolved and used for HPLC-FL measurements. Method B empolyed SPE columns. Columns were immersed in ultrasonic bath the extraction time being 15 min at ambient temperature. Separations were performed on an octylsilica column (150 x 4.6 mm i.d., particle size, 3 µm). Target compounds were eluted in isocratic separation mode using mobile phase ACN-water (65:35, v/v) at the flow rate of 1 mL/min. LC-MS-MS conditions were: nitrogen was used as drying gas (9 L/min) and nebulizer gas (40 psi); capillary voltage, 400 V; flow rate 1 mL/min. Isocratic mobile phase consisted of 0.04% aqueous acetic acid solution-ACN (35:65, v/v). Desolvation temperature was 200^0C. The recoveries were 96.8%, 94.0%, 92.7% and 89.2% for $NPEO_x$, $NPEO_{1+2}$, NP, and 4-*n*-NP, respectively. RSDs (%) were 8.4, 7.0, 6.7 and 8.5, respectively. LOD values (µg/g) were 0.89, 0.48, 0.51 and 0.047, respectively. It was established that the selectivity and sensitivity of the non-reconstructed milk-base method was higher than those of the other analytical procedure. It was further stated that the method can be applied by ruotine laboratories for the quality control of powdered milk infant formulas.[92]

Miscellaneous foods and food products

A considerable number of other foods and food products was analysed by RP-HPLC technologies. Although the stationary phases used for the measurements were markedly similar the differences in preconcentration and prepurification methods, in the type of mobile phases and in detecting system is responsible for the considerable differences among the RP-HPLC methodologies.

HPLC-DAD was employed for the simultaneous determination of eight pesticides frequently applied in rice cultivation (ponoxsulam tricycazole, propanil, azoxystrobin, molinate, profoxydim, cyhalofop-butyl, deltamethrin and 3,4-dichloroaniline, the main metabolite of propanil). Extraction and cleanup of samples was achieved by solid-phase dispersion (MSDP) on neutral alumina (5 g) ACN being the elution solvent. Components of gradient elution system consisted of ACN-water starting with 30% ACN ramped to 100% ACN in 14 min at a flow-rate of 0.8 mL/min.LOD and LOQ ranged from 0.002 to 0.200 mg/kg and 0.006-0.60 mg/kg. Recoveries were 74-127% with an RSD below 12%. It was established that the method is suitable for the analysis of the majority of rice pesticides in rice grains at levels below MRLs.[93] The separation of 1o4 pesticides was achieved by LC-MS-MS. Target compounds were purified by two different methods. Method 1 used liquid-liquid extraction ACN being the extracting agent. Following step was dispersive solid-phase extraction using GCB, PSA and ODS sorbents (QuEChERS method modified for for fatty vegetables). Method 2 employed MSDP and preconcentration on Florisil stationary phase. Analytes were separated on an ODS column (50 mm x 4.6 mm i.d.; particle size, 1.8 µm). LODs were lower than 10 µg/g for 89% of analytes using both preconcentratzion methods. Recoveries ranged form 70% to 120% for QuEChERS technique and 50-70% for MSPD.[94] Simazine and terbutylazine residues were determined in olive oil. The technolgy applies liquid-liqued partitioning extraction and low temperature precipitation followed by MSPD using aminopropyl as dispersant. Cleanup was performed with Florisil and graphitized carbon supports. (60:40, v/v). Separations were carried out bc HPLC followed with UV detection. The recoveries were over 91%, LODs and LOQs

0.0127 and 0.0540 µg/g for simazine and 0.027 and 0.14 µg/g for terbutylazine, respectively.[95] Ultra-performance liquid chromatography followed with tandem mass spectrometry (UPLC-MS/MS) was employed for the analysis of pyrethrins in tea. Pyrethrins included in the investigation were pyrethrin I and II, jasmolin I and II and cinerin I and II. Analytes were extracted with ACN and the extract was passed through a multilayer solid phase extraction cartridge. MS used an electrospray ionization source in posotive mode (ESI+). Recoveries ranged from 76.15% to 101.86% the RSDs being 2.71 – 12.93%. LODs were lower than 0.009 mg/kg and LOQs did not exceed 0.03 mg/kg. It was stated that the data may help to draw up MRLs for pyrethrins in teas.[96] A LC-MS/MS technology was applied for the separation and quantitation of phoxim and its degradation product, O,O-diethyl-alpha-cyanobenzylideneaminothio-phosphonate (DCTP) in chicken and quail eggs. Eggs (1 g) were mixed with 1 g of anhydrous magnesium sulfate and extracted with ACN. The extract was passed through a SPE silica cartridge deactivated with trimethylamine. After RP-HPLC separation target compounds was detected with tandem mass spectrometry in positive-ion electrospray ionization (ESI) modeRSDs of intra- and inter-day variations varied between 2.1% - 6.7% and 2.8% and 6.4%for phoxim and DCTP, respectively. Recoveries ranged from 81.3% to 93.6% for phoxim and from 83.3% to 90.1% for DCTP.[97] Thiosultap sodium, thiocyclam, and nereistoxin were determined in pepper. The optimal extraction procedure combined ACN extraction in acidic medium with ultrasonic extraction followed with a cleanup step with anhydrous $MgSO_4$. Separation and quantitative determination of target compounds was carried out on a linear ion trap quadrupole LC-MS/MS in negative mode for thiosultap sodium and in positive mode for thiocyclam and nereistoxin. Recoveries ranged from 58% to 87%, RSDs were lower than 20%. The method has been successfully applied for the investigation of the decomposition of thiosultap sodium.[98] Pesticide present in onion were analysed by LC-ESI-MS/MS. The optimal conditions of MSPD were: 0.5 g of sample mixed with 1.0 g reused ODS; interaction time, 1 h; dispersion time, 5 min, elution solvent, ACN. Recoveries varied between 78.3 – 120.4%, RSD was lower than 20%. LOD and LOQ ranged from 0.003 to 0.03 mg/kg, and from 0.01 to 0.1 mg/kg.[99] Pesticide residues in flesh of *Cirrhinius mrigala* were determined by HPLC. The method revealed the presence of endosulfan a, p,p'-DDT, methamidophos, carbofuran, diazinon, parathion methyl, dimethoate malathion, chlorpyriphos, cypermetryn, carbosulfan and isoproturon in the flesh of farmed fish. it was established that the amount of pesticide residues was higher in farmed than in wild species.[100] The concentration of acephate, methamidophos, and omethoate was determined in animal and fishery products, their processed foods, and honey. Samples were extracted with ethyl acetate in the presence of anhydrous Na_2SO_4 (diatomaceous earth in the case of honey). The extract was further purified on a PSA mini-column and the analytes were detected by LC-MS in the ESI-SIM mode. Recoveries of the method ranged from 71.4% to 98.4%. RSD of repeatability was $\leq$ 12.5%.[101] A multiresidue method was developed and applied for the analysis of 74 pesticides and metabolites in traditional Chinese herbal medicines (TCHMs). The amount of pesticides were assessed in Cortex Cinnamoni, Flos Carthami, Folium Gingko, Herba Pogostemonis, Radix Ginseng and Semen Gingko. Target compounds were preconcentrated with accelerated solvent extraction (ASE), further purified by gel permeation chromatography and graphitized carbon black/primary, secondary amine SPE. Pesticide residues and metabolites were separated by LC-MS using gradient elution. Recoveries varied between 70-110% RSD being below 15%. In the majority of cases the LOD was lower than 0.01 mg/kg.[102] Systemic insecticide residues (fipronil, imidacloprid and thiametoxam) and their metabolites (fipronil sulfon, fipronyl sulfide, fipronil desulfinyl, and fipronyl carboxamide) were determined in honey and pollen. Prior to the extraction the samples were centrifuged and 1 g of the lower phase was mixed with 3 mL of methanol-water (10:90, v/v). The extract was passed through an florisil cartridge, eluted with methanol and analysed by LC.MS/MS in selective reaction monitoring mode.[103]

ELECTRICALLY DRIVEN SEPARATION SYSTEMS

Electrically driven separation sytems (capillary electrophoresis, micellar electrokinetic capillary chromatography, capillary isoelectric focusing, capillary gel electrophoresis, capillary isotachophoresis) show marked advantageous characteristics such as high separation efficiency, short analysis time, high resolution power, low consumption of samples and reagents, etc. Interestingly, the number of studies dealing with the application of electrically driven separation technologies in the analysis of pesticides in foods and food products is surpridingly low. The sample preparation methods employed for the determination of pesticides in foods have been recently reviewed (Kumar et al., 2010).[104]

Abbreviations

ACN	acetonitrile;
ASE	accelerated solvent extraction;
BCF	bioconcentration factor;
BUVs	benzotriazole UV stabilizers;
DAD	diode array detector;
DDTs	dichlorodiphenyltrichloroethanes;
DPX	disposable pipette extraction;
DSPE	disperase solid phase extraction;
ECD	electron capture detector;
ESI	electrospray ionizaton;
FID	flame ionization detection;
FL	fluorescence detection;
GC	gas chromatography;
GCB	graphitized carbon black;
GPC	gel permeation chromatography;
HCB	hexachlorobenzene;
HCHs	hexachlorocyclohexanes;
HILIC	hydrophilic interaction liquid chromatography;
HPLC	high performance liquid chromatography;
HS-SPME	headspace solid-phase microextraction;
i.d.	internal diameter;
LLE	liquid-liquid extraction;
LOD	limit of detection;
LOQ	limit of quantitation;
LTP	low temperature purification;
MRL	maximum residue level;
MRM	multiple reaction monitoring;

NCI	negative chemical ionization;
NP	nonylphenol isomers;
NPD	nitrogen-phodphorous detector;
OCPs	organochlorine pesticides;
ODS	octadecyl silica;
OPP	organophosphorous pesticides;
PA	polyacrylate;
PBDC	propylenebisdithiocarbamate;
PCI	positive chemical ionization;
PDMS	poly(dimethylsiloxane);
PHI	pre-harvest interval;
PSA	primary secondary amine;
PTU	propylenethiourea, 4-methylimidazoline-2-thione;
QuEChERS	quick, easy, cheap, effective, rugged and safe;
RP-HPLC	reversed-phase high performance liquid chromatography;
RSD	relative standard deviation;
SPE	solid-phase extration;
SPME	solid-phase microextraction;
SRM	selected reaction monitoring;
SWCNTs	single-walled carbon nanotubes;
TCHMs	traditional Chinese herbal medicines;
TLC	thin layer chromatography;
UHPL	ultra high performance liquid chromatography;
UA-DLLME	ultrasonic-assisted dispersive liquid-liquid microextraction;
UPLC-MS-MS	ultra-performance liquid chromatography combined with tandem spectrometry.

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EVALUATION OF CHROMATOGRAPHIC RETENTION DATA BY CLUSTER ANALYSIS. NEW ACHIEVEMENTS

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Keywords: cluster analysis; dendograms; Euclidean distance; average linkage; 3-D diagram of clusters; food and food products; health care; plant materials

The newest results in the application of cluster analysis a multivariate mathematical-statistical technique for the evaluation of large retention data matrices are collected. The results are critically evaluated, and examples for the application in gas chromatography, liquid chromatographic techniques such as thin-layer chromatography and high-performance liquid chromatography, as well as in electrically driven systems are presented.

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Introduction

Chromatographic techniques have been developed and employed for the separation and quantitative determination of a considerable number of organic and inorganic molecules present in complicated accompanying matrices even in very low concentrations.

The development of new mathematical-statistical computation methods for the analysis of retention data matrices has been one of the major advances in the data evaluation in up-to-date chromatographic practice. The most outstanding characteristics of this rapidly developing domain are the high-speed automated chromatographic instruments and new mathematical-statistical technologies. The evaluation of large data sets (retention characteristics of a high number of analytes measured on various stationary phase using different mobile phases, etc) is practically impossible by the well known linear regression calculation method. The modern mathematical-statistical techniques allow the parallel determination of a practically unlimited number of variables (chromatographic parameters) making possible the optimal solution of both theoretical and practical problems. Various multivariate computation methods have been successfully employed in the chromatographic practice for the identification of basic parameters influencing significantly the solute-solvent and solute-stationary phase interactions and to investigate the similarities and dissimilarities among solutes, supports and solvents. As each mathematical-statistical method highlights only several aspects of the chromatographic problem and investigation, the simultaneous employment of more than one mathematical method is rather a rule than an exception.

Cluster analysis (CA) techniques have been developed and successfully applied for the easily visualization of complicate multidimensional data matrices by reducing dimensionality. Variables with similar characteristics are near to each other on the CA dendogram, while variables with different characteristics are far away from each other. The principles of CA have been previously discussed.[1]

Gas chromatography

Foods and food products

CA has been frequently employed for the comparison of the fingerprints of food samples measured by GC-MS. Thus, the average mass scan (AMS) data obtained from essential oils were employed as variable for agglomerative hierarchical cluster analysis and principal component analysis (PCA). It was established that AMS combined with multivariate mathematical-statistic methods can be used for the analysis of essential oils.[2] The composition of steam distilled volatile oil of dried Lippia multiflora Moldenke was investigated by GC-MS and the composition was compared with those of other essential oils originated from Nigeria using CA. The calculations indicated the marked chemical variation in the species.[3] Essential oil was separated from Turkish oregano (Origanum onites L.) and its composition was analyzed by GC. CA indicated the presence of two chemo types, cravacrol and thymol. The results proved that there is no correlation between genetic structure and essential oil composition. [4] GC-combustion-isotope ratio mass spectrometry (GC-C-IRMS) has been employed for the measurement of the isotope rations of fatty acid methyl esters (FAME). The data were evaluated by linear discriminant analysis (LDA) and hierarchical CA. It was stated that the method enables the differentiation of oils according to their geographic region.[5] The effect of the grape content of musts on the composition of volatile compound was investigated by using solid-phase micro extraction (SPME) followed by GC-MS. CA calculations indicated that the change of the composition of must influences wine flavor and aroma. [6] The FAME composition of Runner peanuts were determined by GC-flame ionization detector (FID) and evaluated by CA and

factorial analysis (FA). It was established that CA separates cultivars according to the composition of FAMEs into normal, mid-, and high-oleic groups. FA computation indicated that the distribution of cultivars depends on the composition of fatty acids [7]. The fingerprints of the headspace volatile compounds of honey samples were determined by GC/MS. The data were evaluated by orthogonal partial least squares-discriminant analysis (OPLC-DA) and orthogonal partial least squares-hierarchical cluster analysis (OPLC-HCA). It was stated that the method can be employed for the botanical classification of honey samples and for the study of their chemical composition. [8] The fingerprints of Porulaca oleracea a traditional Chinese food and medicine were measured by GC/MS. The similarities and the differences among the fingerprints of different origin were computed by HCA. Computations indicated that the technique is suitable for the differentiation among the origin of samples.[9] Pyrolysis (Py) coupled to GC/MS was employed for the evaluation of the differences among the commercial samples of Cymbopogon citratus Stapf. Poaceae sold as tea. The data matrices were evaluated by HCA and PCA. Calculation indicated that the method is suitable for the correct classification of samples. [10] Fragrance alkenyl benzenes (estragole, trans-anethol, safrole, eugenol, methyl eugenol, isoeugenol, eugenyl acetate, myristicin and alpha-asarone) were separated and quantitatively determined by GC. The similarity and differences among 22 samples of essential oils were evaluated by hierarchical cluster analysis.[11]

Other analytes

GC methods combined with CA and other multivariate mathematical statistical procedures have been applied not only for the investigation of foods and food products but also in environmental protection studies, health care and biomedical research. Thus, the concentration of polycyclic aromatic hydrocarbons (PAHs) were measured in various sediments and waters in Argentina, Mediterranean sea and China. HCA was employed for the elucidation of the relationship between the amount of PAHs measured at different sampling sites.[12] The application possibilities of various mathematical statistical methods such as t-test, PCA, HCA and correlation analysis for the GC/MS metabolomics datasets have been earlier discussed.[13]

Liquid chromatographic methodologies

Thin layer chromatography

Thin-layer chromatography (TLC) is an easy to use liquid chromatographic technique. The advantages of the method are possibility of parallel determination in one run, the application of a high variation of detecting agent, and the rapidity. The disadvantages of TLC are the relative low reproducibility and moderate sensitivity. Because of the drawbacks mentioned above TLC data sets have not been frequently analyzed by CA. Reversed-phase TLC performed on octadecylsilica (ODS) layers were employed for the determination of lipophilicity of 14 s-triazine derivatives. Acetone, methanol, 2-propanol, and tetrahydrofuran were used as organic modifiers of the aqueous mobile phase. The data matrix was evaluated by PCA, HCA, partial least square (PLS) and correlation analysis.[14]

High performance liquid chromatography

Health care

HPLC has been used for the separation of the components of Prunella extracts. The experiments were motivated by the efficacy of Prunella extract to prevent and treat lung cancer. The presence of caffeic acid, rosmarinic acid, rutin, quercetin, oleanolic acid and ursolic acid in the extract was verified. Prunella samples were classified by CA. Investigations established that the efficacy of Prunella against lung cancer is attributable to multiple component acting at an optimal ratio.[15]

The anaesthetical activity of alkoxyphenylcarbamic acid esters was correlated by the calculated lipophilicity, reversed-phase HPLC retention factor and other structural parameters. The data were evaluated by PCA, CA and discriminating analysis. It was further established that artificial neural network (ANN) successfully predicted the surface anaesthetical activity. [16] The anti-inflammatory activity of the medicinal plant huang-lian has been investigated in detail. The components of the extracts of huang-lian of different origin (CEXs) were separated by HPLC and the chromatographic profile of the extracts was compared by HCA. Computations indicated that the data can be a good indicator of the biological activities of medicinal plants. [17] LC-MS was employed for the measurements of the impurities in the nerve agent precursor methylphosphonic dichloride (dichlor). HCA and factor analysis (FA were applied for the determination of the origin of the samples according to their impurity profile.[18] Polyphenols in tobacco waste were separated and identified by HPLC-PDA-ESI/MS/MS, and the concentration of chlorogenic acid and routine in the samples was measured by HPLC-UV. The data matrices were evaluated by HCA and PCA. Computations indicated that the concentration of chlorogenic acid and routine is characteristic for the tobacco wastes. It was concluded from the measurements that tobacco wastes can be used for the production of chlorogenic acid and routine.[19]

Food and food products

Various chemometrical method combined with chromatographic technologies have been frequently employed for the investigation of foods and food products controlling authenticity and origin. The use of fingerprint profiles and chemometrics for the characterization of wines has been recently reviewed.[20] The unsaponifiable fraction of virgin oils were investigated by HPLC-APCI-tandem MS. The data matrices were evaluated by PCA and CA. It was established that the method is suitable for the separation of oil cultivars according to the composition of the oil. [21]. Reversed phase HPLC (RP-HPLC) was employed for the determination of the fingerprints of 12 lentil cultivars and the data matrix was evaluated by CA.

Calculations indicated that the classification of the extracts considerable depended on the extracting agent.[22] A HPLC method was employed for the measurement of the concentration of biogenic amines in traditional Chinese sausages. It was established that the concentration of cadaverine was the highest followed by tyramine and putrescine. Samples were classified according to the profile of biogenic amines using CA. It was further found that the sanitary quality of the raw material and the specific flora exert a marked influence on the formation of biogenic amines in traditional Chinese sausages.[23]

The concentration of free amino acids during germination and seedling growth of Cola acuminata and C. anomala was measured by HPLC. PCA and CA were employed for the differentiation between the species. The computations indicated that both C. acuminata and C. anomala as well as their germination and seedling growth phases can be differentiated by the composition of free amino acids.[24]

The effect of anaerobic and aerobic conditions on the growth of Shewanella oneidensis was studied by Fourier transform infrared (FT-IR) spectroscopy and HPLC analysis of flavin compounds. The results were evaluated by CA and partial least-squares regression (PLSR). The method was proposed for the rapid characterization of the Shewanella cell metabolome in various process environments.[25] Phenolic compounds were separated and quantitatively determined in wines produced in China. Measurements were performed by HPLC-MS and the composition of the various wines was compared by HCA. Calculations indicated that the geographical parameters influence considerably the composition of phenolic compounds in wines. It was further established that the flavonol profile can be successfully applied for the discrimination between cultivars.[26]

Flavonols (myricetin, quercetin, and kaempferol) were measured in various red and white grape varieties and the similarity and differences among the chromatographic retention data were computed by HCA. It was found that the flavonol profile is suitable for the differentiation among cultivars and can be applied for chemotaxonomic aims.[27] HPLC-MS methodology was employed for the determination of the phenolic compound profiles of berry skins of nine red Vitis vinifera cultivars. The fingerprints were compared by using CA. It was established that the phenolic profile depended markedly on the type of cultivar, while the year-to-year variations were negligible.[28]

Both HPLC and GC-MS were applied for the measurement of the alkaloidal profile of Solanum nigrum complex. The data were evaluated by CA. Computation revealed significant differences among the species investigated.[29] HPLC-diode array detection (HPLC-DAD) and UPLC-DAD-TQD (ultra performance liquid chromatography) have been employed for the analysis of stilbenes. The stilbene profiles were evaluated by CA. Computations indicated that the amount of stilbenes can be enhanced by post harvest UV treatment.[30]

HPLC-PDA-MS/MS investigations were performed for the study of the composition of the tropical fruits grown in Brazil and their free scavenger activities was also measured. The relationship between the scavenger activity and chemical composition of fruits was determined by various multivariate methods such as CA and PCA. The highest level of bioactive compounds was found in buriti, otaheite apple, egg-fruit, golden spoon, physalis, piqia and star nut palm. Calculations found significant correlations between free scavenger activity and concentration of total phenolic compounds, and flavonoids.[31] The physical and chemical characteristics of pomegranate (Punica granatum L.) were investigated by various analytical such as HPLC and the distribution of the samples according to their properties was determined by CA and PCA. The results indicated the considerable differences among the pomegranate cultivars.[32] HPLC-UV was employed for the quantitative analysis of cotyledon isoflavones (genistein, daidzein, and their glucosyl and malonyl forms) and the data were evaluated by CA. Calculations proved that soybean varieties show marked differences in the composition of isoflavones and can be classified in three groups depending on the amount of isoflavones and the concentration of proteins.[33]

Plant materials

Last years the composition of medicinal herbs, the separation, quantitative determination and identification of the bioactive components have been vigorously investigated. Various chromatographic techniques such as gas chromatography, liquid chromatographic methods and electrically driven separation technologies have been frequently used for the analysis of medicinal plants.

Thus, the alkaloids in the extract of Evodia rutaecarpa (Juss.) Benth were determined by LC-ESI-MSn and the fingerprints were differentiated by various multivariate methods such as CA and PCA. Calculations established that the combined HPLC and CA method is suitable for the evaluating and controlling the quality of the extracts of E. ruteocarpa.[34] RP-HPLC combined with HCA was applied for the evaluation of the chemical fingerprinting of wild germplasm resource of Ophopogon japonicus. Computations indicated that the samples can be devided in three groups and the method allows the selection of wild germ resources of enhanced activity.[35]

A HPLC technique was applied for the measurement of the fingerprints of Keishibukuryogan formulas and the composition of the samples was compared by CA. It was stated that the method is suitable for the discrimination among samples according to the pharmaceutical manufactures, combination of ratios of botanical raw materials and time course of deterioration. The method was proposed for the quality control of multiple component drugs.[36] The fingerprints of the seed of wild Peganum harmala Linn. P. multisectum (Maxim) Bobr., P. Nigellastrum Bunge and P. variety were determined by HPLC and the chromatographic profiles were compared by PCA, HCA and linear discriminant analysis (LDA). The computations indicated that the method is suitable for the differentiation between the seeds of the different Peganum species.[37] HPLC-DAD technique was applied for the separation and quantitative determination of flavonoids in the leaves of Passiflora incarnata L., Passiforaceae. The effect of soil characteristics, environmental factors and meteorological conditions of the flavonoid content was elucidated by PCA and HCA. Calculations proved that the composition of soil, the environmental factors exert no

marked impact on the flavonoid content while the concentration of Fe, B and Cu in the soil influence considerably decreased the concentration of total flavonoids in the leaves of P. incarnata.[38]

A simple HPLC-DAD techniques was applied for the measurement of the flavonoids of sea buckthorn (TFS) and in the extract of TFS berries. The retention data were evaluated by PCA, partial least square-discriminant analysis (PLS-DA) and HCA employing Ward's minimum method of the PLS-DA loading matrix. It was concluded from the measurements that the method can be applied for the analysis of herbal extracts.[39] UPLC-DAD-FOF-MS system was applied for the measurement of the fingerprints of Cortex magnoliae officinalis species and the data were evaluated by mathematical statistical methods such as HCA, and Da. It was stated that the technique is reliable and can be employed for the quality control and authenticity test of Wen-Hou-Po.[40]

New silica-based RP-HPLC stationary phases were prepared by thermal immobilization of poly(methyloctylsiloxane) using various concentration of ligand, different times and temperatures. The separation characteristics of these RP-HPLC stationary phases were evaluated and the differences among the retention data sets was computed by HCA and PLC. Calculations proved that the separation characteristics of the new RP-HPLC stationary phases differ considerably from the majority of commercial phases.[41] The metabolic profile of Dactylopius (Hemiptera dactylopiidae) species pigments was measured by HPLC-photodiode array detector (PDA). CA and PCA were simultaneously applied for the comparison of the metabolic profiling of Dactylopius (Hemiptera dactylopiidae) species pigments according to the geographical origin and host plants.[42] HPLC-MS and GC-MS were employed for the determination of the metabolic profile of Daphnia magna.

The similarities and dissimilarities among the metabolic profiles was evaluated by CA, PCA and PLS-DA. It was stated that the method increases the amount of information obtained from aquatic toxicology testing.[43] A LC-MS/MS method was developed and applied for the discrimination and classification of Bacillus anthracis-cereus-thuringiensis strains. The data were evaluated by HCA. It was stated that the technique can be applied as an alternative method to predict similarities among microbial germs of B. cereus species without the use of whole genom sequencing.[44]

The dissolved organic fraction of a lake sediment was investigated by high-performance size-exclusion chromatography (HPSEC) and spectroscopy. The concentration of Ca, Mn, Fe, Cu, Zn and Cd was also determined. The data matrix. The data set was evaluated by CA. It was established that the calculations make possible the identification of periods with similar parameters in the lake sediment.[45] Dissolved organic matter (DOM) and dissolved organic carbon (DOC) were determined in drinking waters. HPSEC was employed for the measurement of the chromatographic profile of the samples. The similarities and differences between the water samples were elucidated by CA. It was established that the method allows the differentiation between polluted and un-polluted waters. Furthermore, the technique was proposed for the determination of the removal efficacy of coagulants (Al_2SO_4), $FeCl_3$ and high performance poly aluminium chloride.[46] Another HPSEC technology was employed for the characterization and classification of aquatic fulvic acids present in clear-water rivers and lakes. Beside HPSEC elemental analysis, liquid-state C^{13} NMR spectroscopy, and isotopic analysis were applied for the study of fulvic acids. CA and PCA were used for the classification of fulvic acids. The computations separated two clear-water groups and one brown-water group. It was established that aryl-C and O-alkyl-C content play a considerable role in the discrimination of fulvic acid species.[47]

HPSEC followed by various multivariate mathematical-statistical computation methods was applied for the investigation of cooked rice texture in relation to starch fine structure and leaching characteristics. Amylopectin fine structure was elucidated by high-performance anion-exchange chromatography coupled with pulsed amperometric detection. Correlation and stickiness of cooked rice depends considerably on the amylose/amylopectin ratio. It was established that the apparent amylose characteristics of cultivars.[48]

Hydrophilic interaction chromatography (HILIC) and reversed-phase separation mode was applied for the determination of the fingerprint of the acetonitrile-water extract of Ganoderma species a traditional Chinese medicine. The fingerprints obtained on various columns were differentiated by HCA. It was concluded from the data that the simultaneous application of fingerprints measured in different chromatographic conditions increases considerably the reliability of the analysis.[49]

Electrically driven systems

The high separation power, and relatively simple instrumentation of capillary electrophoresis (CE) and related technologies facilitated their successful application in many fields of up-to-date scientific research such as health care, analysis of pharmaceutical, foods and food products, etc. Similarly to other chromatographic methodologies CA has also found application in the elucidation of CE migration time data. Thus, CE was employed for the determination of the nucleoside and modified nucleoside profiles of urogenic tract cancer patients and healthy controls. The data matrix was evaluated by various multivariate mathematical-statistical methods such a PCA, HCA, K-nearest neighbor method (kNN) and partial least squares-discriminant analysis (p-PLS-DA). Computations proved that the sensitivity and specificity of the method were 76.5% and 80.2%. It was stated that the fingerprints of urinary nucleosides can be used as a reliable and convenient tool for the diagnostic of urogenital cancer diseases.[50] Proteomic approaches were employed for the identification of altered proteins in endometrial carcinoma. The objectives of the measurements were the search for potential biomarkers or therapeutic targets. Proteins were extracted and separated by 2-dimensional electrophoresis. The method identified 99 proteins. CA established that the proteins are involved in various biochemical processes. It was concluded that the

measurements may promote the study of endometrial carcinogenesis, investigation of the spatial and genotypic clustering of Salmonella. Genetic similarities were evaluated by CA. Computation indicated the relative homogeneity of isolates.[51, 52] Capillary electrophoresis fragment sizing system was applied for the identification of the intra-varietal diversity within 'Askari' and 'Keshmesh' (Vitis vinifera L.). The similarity of samples were investigated by CA. It was stated that the method can be applied for the identification of intra-cultivar diversity.[53] Cellulose-acetate electrophoresis was used for the isozyme and protein separation from the mycelial extracts of 27 isolates of Trichoderma harzianum, 10 isolates of T. aureoviride, and 10 isolates of T. Longibrachiatum. The relationship among the isolates was revealed by CA. The results showed that the distance between T. harzianum and T. aureoviride is smaller then to T. longibrachiatum. It was further established that T. harzianum isolates show the highest genetic variation.[54]

Hydrophobic interaction chromatography (HIC) before 2-dimensional gel elecrophoresis (2DGE) was employed to remove highly abundant proteins of plasma which influence the detectability of low abundance proteins of biomedical interest. CA was applied for the classification of plasma proteins according to their hydrophobicity (low, medium and high). The depleting capacity of HIC was compared with that of immuno-affinity (IA) column. It was suggested that HIC can be applied as an alternative procedure to IA.[55] The effect of plant growth (Ryegrass, Lolium perenne) and microbial strains (Bacillus subtilis, Sphingobacterium multivolume, acinetobacter radioresistens, Rhodococcus erythropolis, and Pseudomonas fluorescence) on the soil petroleum remediation was investigated. Denaturing gradient gel electrophoresis (DGGE) measurements suggested that the best results can be achieved by the simultaneous application of plant growth and complex microbial community. The differences between the treatments were evaluated by CA.[56]Thin-layer chromatography, CE, FTIR spectroscopy, ICP-TOF-MS (inductively coupled plasma time-of flight mass spectrometry) with laser ablation were evaluated by CA and PCA. The method was proposed for the rapid comparative analysis of unknown samples.[57]

CA has also found application for the evaluation of micellar electrokinetic chromatography data. Samples were separated by an electrolyte consisting of 100 mM borate (pH 9.8) and 20 mM sodium dodecylsulfate. Tea infusions were injected for 5 s at 0.5 psi. The total length of the fused silica capillary was 60 cm, the internal diameter being 75 µm. Analytes were detected by a laser-induced fluorescence detector. Green teas were differentiated by CA.[58]

Abbrevations

AMS	average mass scan,
CA	cluster analysis,
FA	factorial analysis,
FAME	fatty acid methyl ester,
FID	flame ionization detector,
GC-C-IRMS	gas-chromatography-combustion-isotope ratio mass spectrometry,
HCA	hierarchical cluster analysis,
OPLC-DA	orthogonal partial least squares-discriminant analysis,
OPLC-HCA	orthogonal partial least squares-hierarchical cluster analysis,
PCA	principal component analysis,
SPME	solid-phase microextraction.

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OXIDATION OF ALIPHATIC PRIMARY ALCOHOLS BY TETRAKIS (PYRIDINE) SILVER DICHROMATE – A KINETIC AND MECHANISTIC APPROACH

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Keywords: Correlation analysis; alcohols; dichromate; kinetics; mechanism; oxidation.

The oxidation of nine aliphatic primary alcohols by tetrakis(pyridine) silver dichromate (TPSD) in dimethylsulfoxide leads to the formation of corresponding aldehydes. The reaction is first order with respect to TPSD. A Michaelis-Menten type kinetics is observed with respect to alcohols. The reaction is promoted by hydrogen ions; the hydrogen-ion dependence has the form $k_{obs} = a + b[H^+]$. The oxidation of [1,1-$^2H_2$]ethanol ($MeCD_2OH$) exhibits a substantial primary kinetic isotope effect (k_H/k_D = 5.85 at 298 K). The reaction has been studied in nineteen different organic solvents. The solvent effect was analysed using Taft's and Swain's multiparametric equations. The rate of oxidation is susceptible to both polar and steric effects of the substituents. A suitable mechanism has been proposed.

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Introduction

Inorganic chromate and dichromate salts have been used as oxidizing reagents in synthetic organic chemistry for long time. However, these salts are drastic and non-selective oxidants in nature and as ionic compounds generally insoluble in most of the organic solvents. In order to overcome these limitations, a large number of organic derivatives of Cr(VI) have been prepared and used in synthetic organic syntheses as mild and selective oxidants in non-aqueous solvents.[1]

One such compound is tetrakis(pyridine)silver dichromate (TPSD) reported by Firouzabadi and co-workers.[2] Only a few reports are available in literature regarding oxidation aspects of TPSD.[3] It is known that the mode of oxidation depends on the nature of the counter-ion attached to the chromium anion. Therefore, in continuation of our earlier work, we report here the kinetics and mechanism of oxidation of nine aliphatic primary alcohols by TPSD in dimethylsulphoxide (DMSO) as solvent. The mechanistic aspects are discussed.

The main aims of the present investigation are to (i) determine kinetic parameters and to evaluate the rate laws, (ii) to study the correlation analysis of effect of structure on (iii) and to postulate a suitable mechanism for the oxidation process.

Experimental Section

Materials

TPSD was prepared by the reported method[2] and its purity was checked by an iodometric method. The procedures used for the purification of alcohols have been described earlier.[4] [1,1-$^2H_2$]Ethanol ($MeCD_2OH$) was prepared by Kalpan's method.[5] Its isotopic purity, as ascertained by its NMR spectra, was 96±3%. Due to the non-aqueous nature of the medium, p-toluenesulphonic acid (TsOH) was used as a source of hydrogen ions. TsOH is a strong acid and in a polar medium like DMSO it is likely to be completely ionised. Solvents were purified by the usual method.[6]

Product analysis

The product analysis was carried out under kinetic conditions. In a typical experiment, ethanol (2.30 g, 0.05 mol) and TPSD (7.48 g, 0.01 mol) were made up to 50 cm^3 in DMSO and kept in dark for *ca.* 15 hr to ensure the completion of the reaction. The solution was then treated with an excess (200 cm^3) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenyl-hydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol and weighed again. The yield of DNP before and after recrystallization was 1.98 g (91%) and 1.84 g (81%), respectively. The DNP was found identical (m.p. and mixed m.p.) with the DNP of acetaldehyde. Similar experiments with other alcohols led to the formation of DNP of the corresponding carbonyl compounds in yields ranging from 72 to 87%, after recrystallization. Iodometric determinations of the oxidation state of chromium in completely reduced reaction mixtures indicated that the oxidation state of the reduced chromium species was 3.90±0.10.

Kinetic Measurements

The reactions were followed under pseudo-first-order conditions by keeping a large excess (× 15 or greater) of the alcohol over TPSD. The temperature was kept constant to ±0.1 K. The solvent was DMSO, unless specified otherwise. The reactions were followed by monitoring the decrease in the concentration of TPSD spectrophotometrically at 365 nm for 80% of the reaction. The pseudo-first-order rate constants, k_{obs}, were evaluated from the linear (r = 0.990 - 0.999) plots of log [TPSD] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3%. The second order rate constant, k_2, was evaluated from the relation $k_2 = k_{obs}/[alcohol]$. Simple and multivariate linear regression analyses were carried out by the least-squares method on a personal computer.

Results and Discussion

Stoichiometry

The oxidation of alcohols results in the formation of corresponding aldehydes. The overall reaction may be represented as equation (1).

$$3RCH_2OH + Cr_2O_7^{-2} + 8H^+ \rightarrow 3RCHO + 7H_2O + 2Cr^{+3} \quad (1)$$

Rate-laws

The reactions are of first order with respect to TPSD. Further, the pseudo-first order rate constant, k_{obs} is independent of the initial concentration of TPSD. The reaction rate increases with increase in the concentration of the alcohols but not linearly (Table 1).

Table 1. Rate constants for the oxidation of ethanol by TPSD at 288 K

10^3 [TPSD] mol dm^{-3}	[Alcohol] mol dm^{-3}	[TsOH] mol dm^{-3}	10^4 k_{obs} s^{-1}
1.00	0.10	0.00	18.9
1.00	0.20	0.00	27.6
1.00	0.40	0.00	35.9
1.00	0.60	0.00	39.9
1.00	0.80	0.00	42.3
1.00	1.00	0.00	43.8
1.00	1.50	0.00	46.0
1.00	3.00	0.00	48.5
2.00	0.20	0.00	29.7
4.00	0.20	0.00	26.1
6.00	0.20	0.00	30.6
8.00	0.20	0.00	27.0
1.00	0.40	0.00	37.8*

* contained 0.001 mol dm^{-3} acrylonitrile

FIGURE : 1

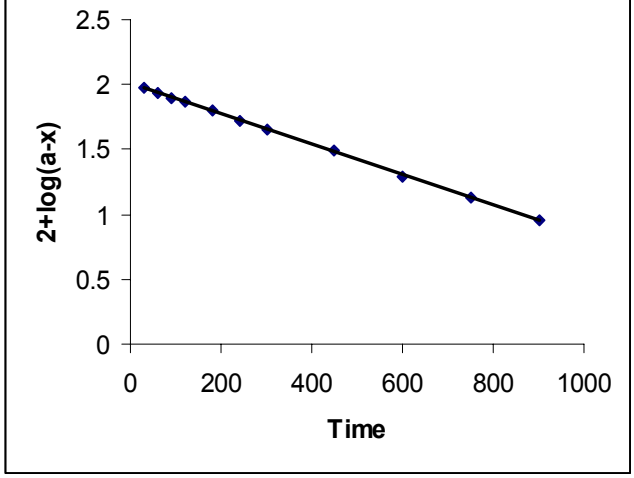


Figure 1. Oxidation of Ethyl alcohol by TPSD: A typical Kinetic Run

The Figure 1 depicts a typical kinetic run. A plot of $1/k_{obs}$ against 1/[Alcohol] is linear (r>0.995) with an intercept on the rate-ordinate. Thus, Michaelis-Menten type kinetics is observed with respect to alcohols. This leads to the postulation of following overall mechanism (2) and (3) and rate law (4).

$$\text{Alcohol} + \text{TPSD} \overset{K}{\leftrightarrows} [\text{complex}] \quad (2)$$

$$[\text{complex}] \overset{k_2}{\rightarrow} \text{Products} \quad (3)$$

$$\text{Rate} = k_2\, K[\text{Alcohol}][\text{TPSD}]/(1 + K\,[\text{Alcohol}]) \quad (4)$$

The dependence of reaction rate on the reductant concentration was studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots (Figure 2). The thermodynamic parameters of the complex formation and activation parameters of the decomposition of the complexes were calculated from the values of K and k_2 respectively at different temperatures (Tables 2 and 3).

Induced Polymerization of Acrylonitrile

The oxidation of alcohols, in an atmosphere of nitrogen, failed to induce polymerisation of acrylonitrile. Further, the addition of acrylonitrile did not affect the rate. This indicates that a one-electron oxidation, giving rise to free radicals, is unlikely in the present reaction (Table 1). To further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol dm^{-3} of 2,6-di-t-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

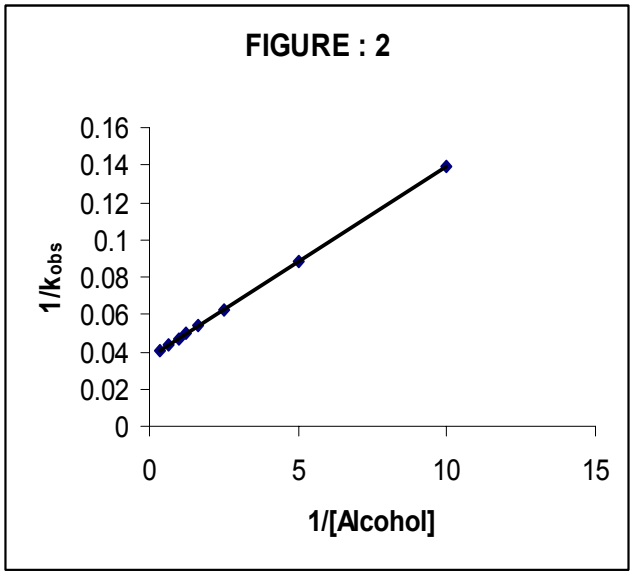


Figure 2. Oxidation of Alcohols by TPSD: A double reciprocal plot

Effect of Hydrogen Ions

The reaction is catalyzed by hydrogen ions (Table 4). The hydrogen-ion dependence has the following form equation (5). The values of *a* and *b*, for ethanol, are 18.6±0.07 × 10^{-4} s^{-1} and 31.8±0.12 ×10^{-4} mol^{-1} dm^3 s^{-1} respectively (r^2 = 0.9999).

$$k_{obs} = a + b\,[H^+] \qquad (5)$$

Kinetic Isotope Effect

To ascertain the importance of cleavage of the α–C–H bond in the rate-determining step, oxidation of [1,1-$^2H_2$]ethanol was studied. The results showed the presence of a substantial primary kinetic isotope effect (Table 3).

Effect of Solvents

The oxidation of ethanol was studied in 19 different organic solvents. The choice of solvent was limited due to the solubility of TPSD and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The kinetics were similar in all the solvents. The values of k_2 are recorded in Table 5.

A satisfactory linear correlation (r = 0.9824; temp. 449 ± 32) between the values the activation enthalpies and entropies of the oxidation of the nine aliphatic alcohols indicated the operation of compensation effect in this reaction. [7] The reaction also exhibited an excellent isokinetic effect, as determined by Exner's criterion.[8] An Exner's plot between log k_2 at 288K and at 318 K was linear (r = 0.9961; ψ = 0.07; slope = 0.7744 ± 0.0261) (Figure 3). The value of isokinetic temperature is 500±43 K. The linear isokinetic correlation implies that all the alcohols are oxidized by the same mechanism and the changes in rate are governed by the changes in both the enthalpy and entropy of the activation.

Solvent Effect

The rate constants of the oxidation, k_2, in eighteen solvents (CS_2 was not considered, as the complete range of solvent parameters was not available) did not yield any significant correlation in terms of the linear solvation energy relationship (LESR) of Kamlet and Taft[9] (6).

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \qquad (6)$$

$$\log k_2 = -4.24 + 1.59\ (\pm 0.20)\pi^* + 0.19(\pm 0.16)\ \beta + 0.14\ (\pm 0.16)\ \alpha \qquad (7)$$

R^2 = 0.8586; sd= 0.18; n= 18; ψ = 0.41

$$\log k_2 = -4.21 + 1.64(\pm 0.19)\pi^* + 0.15\ (\pm 0.15)\ \beta \qquad (8)$$

R^2 =0.8508; sd=0.18; n=18; ψ = 0.40

$$\log k_2 = -4.24 + 1.68\ (\pm 0.18)\ \pi^* \qquad (9)$$

r^2 = 0.8415; sd = 0.18; n = 18; ψ = 0.41

$$\log k_2 = -2.83 + 0.44\ (\pm 0.36)\ \beta \qquad (10)$$

r^2 = 0.0865; sd=0.43; n=18; ψ= 0.98

Here n is the number of data points and ψ is the Exner's statistical parameter. [10] Kamlet's[9] triparametric equation explains *ca.* 86% of the effect of solvent on the oxidation. However, by Exner's criterion[10] the correlation is not even satisfactory (cf. 7). The major contribution is of solvent polarity. It alone accounted for *ca.* 86% of the data. Both β and α play relatively minor roles.

The data on the solvent effect were analysed in terms of Swain's[11] equation (11) of cation- and anion-solvating concept of the solvents also.

$$\log k_2 = aA + bB + C \qquad (11)$$

Here A represents the anion solvating power of the solvent and B the cation-solvating power. C is the intercept term. $(A+B)$ is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of eq. (12), separately with A and B and with $(A + B)$.

$$\log k_2 = 0.63\ (\pm 0.04)\ A + 1.71\ (\pm 0.03)\ B - 3.98 \qquad (12)$$

R^2 = 0.9957; sd = 0.03; n = 19; ψ = 0.07

$$\log k_2 = 0.39\ (\pm 0.56)\ A - 2.81 \qquad (13)$$

r^2 = 0.0271; sd = 0.46; n = 19; ψ = 1.01

$$\log k_2 = 1.66\ (\pm 0.11)\ B - 3.77 \qquad (14)$$

r^2 = 0.9248; sd = 0.13; n = 19; ψ = 0.27

$$\log k_2 = 1.35 \pm 0.14\ (A + B) - 3.95 \qquad (15)$$

r^2 = 0.8463; sd = 0.18; n = 19; ψ = 0.40

Here n is the number of data points and ψ is the Exner's statistical parameter.[10]

Table 2. Formation constants and thermodynamic parameters for the Alcohol – TPSD complexes

Subst.	K (dm^3 mol^{-1})				$-\Delta H^{\#}$	$-\Delta S^{\#}$	$-\Delta G^{\#}$
	288 K	298 K	308 K	318 K	kJ mol^{-1}	J mol^{-1} K^{-1}	kJ mol^{-1}
H	6.03	5.25	4.40	3.62	15.5± 0.6	30 ± 2	6.55± 0.5
Me	5.85	5.02	4.25	3.45	15.8± 0.6	32 ± 2	6.46± 0.5
Et	5.40	4.61	3.75	3.00	17.4± 0.7	38 ± 2	6.22± 0.6
n-Pr	5.76	4.92	4.12	3.35	16.2± 0.6	33 ± 1	6.40± 0.5
n-Bu	6.12	5.30	4.52	3.67	15.3± 0.7	30 ± 2	6.59± 0.6
i-Pr	5.33	4.55	3.70	2.95	17.5± 0.8	39 ± 3	6.18± 0.6
$ClCH_2$	5.62	4.80	4.02	3.20	16.7± 0.8	35± 3	6.34± 0.6
$MeOCH_2$	6.15	5.35	4.50	3.72	15.3± 0.6	30 ± 1	6.60± 0.5
t-Bu	5.90	5.10	4.26	3.45	16.1 ±0.7	33 ± 2	6.48± 0.6
$MeCD_2OH$	5.98	4.18	4.35	3.56	15.6± 0.6	31 ± 2	6.52± 0.5

Table 3. Rate constants and activation parameters for the Alcohols – TPSD complexes

Alcohol	10^4 k_2 / dm^3 mol^{-1} s^{-1} at				ΔH	$-\Delta S$	ΔG
(R)	288 K	298 K	308 K	318 K	kJ mol^{-1}	J mol^{-1} K^{-1}	kJmol^{-1}
H	0.81	2.81	9.00	27.0	86.4 ± 0.1	23 ± 1	95.0 ± 0.6
Me	51.3	117	261	558	58.1 ± 0.3	87 ± 1	84.9 ± 0.4
Et	87.3	189	414	846	55.3 ± 0.5	93 ± 2	83.6 ± 0.7
n-Pr	153	315	621	1260	50.8 ± 0.7	104± 2	82.2 ± 0.2
n-Bu	162	342	693	1350	51.3 ± 0.1	101± 1	81.9 ± 0.3
i-Pr	243	477	954	1800	48.5 ± 0.5	108± 2	81.0 ± 0.3
$ClCH_2$	0.98	2.61	7.02	17.1	70.3 ± 0.5	78 ± 2	94.7 ± 0.5
$MeOCH_2$	8.10	19.8	47.7	108	63.3 ± 0.3	85 ± 1	89.4 ± 0.3
t-Bu	2250	3510	5400	7920	29.5 ± 0.1	155±1	75.5± 0.1
$MeCD_2OH$	8.29	20.0	46.6	105	61.9 ± 0.3	89 ± 1	89.2 ±0.4
k_H/k_D	6.19	5.85	5.60	5.31			

The rates of oxidation of ethanol in different solvents showed an excellent correlation in Swain's equation (cf. equation 12) with the cation-solvating power playing the major role. In fact, the cation-solvation alone account for *ca.* 92% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (A + B), also accounted for *ca.* 86% of the data. In view of the fact that solvent polarity is able to account for *ca.* 86% of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of log k_2 against the inverse of the relative permittivity is not linear (r^2 = 0.5313; sd = 0.32; ψ = 0.70).

Correlation Analysis of Reactivity

The rates of oxidation of the alcohols failed to yield any significant correlation separately with Taft's[12] σ^* and E_s values eqs. (16) and (17).

$$\log k_2 = -2.17(\pm 0.33)\,\Sigma\sigma^* - 1.73 \quad (16)$$

$r^2 = 0.8584$; sd = 0.42; $\psi = 0.40$; $n = 9$

$$\log k_2 = -1.13(\pm 0.36)\,\Sigma E_s - 2.28 \quad (17)$$

$r^2 = 0.5804$; sd = 0.73; $\psi = 0.69$; $n = 9$

The rates were, therefore, correlated in terms of Pavelich-Taft's [13] dual substituent-parameter (DSP) equation (19).

$$\log k_2 = \rho^* \sigma^* + \delta E_s + \log k_0 \quad (19)$$

The values of substituent constants were obtained from the compilation by Wiberg[12]. The correlations are excellent; the reaction constants being negative (Table 6). There is no significant collinearity (r^2 = 0.2322) between σ^* and E_s values of the nine substituents.

The negative polar reaction constant indicates an electron-deficient carbon centre in the transition state of the rate-determining step. The negative steric reaction constant shows a steric acceleration of the reaction. This may be explained on the basis of high ground state energy of the sterically crowded alcohols. Since the crowding is relieved in the product aldehyde as well as in the transition state leading to it, the transition state energies of the crowded and uncrowded alcohols do not differ much and steric acceleration, therefore, results.

Mechanism

The presence of a substantial primary kinetic isotope effect confirms the cleavage of an α-C-H bond in the rate-determining step. The large negative value of the polar reaction constant together with substantial deuterium isotope effect indicate that the transition state approaches a carbocation in character. Hence the transfer of hydride-ion from alcohol to the oxidant is suggested. The hydride-transfer mechanism is also supported by the major role of cation-solvating power of the solvents (Scheme 1).

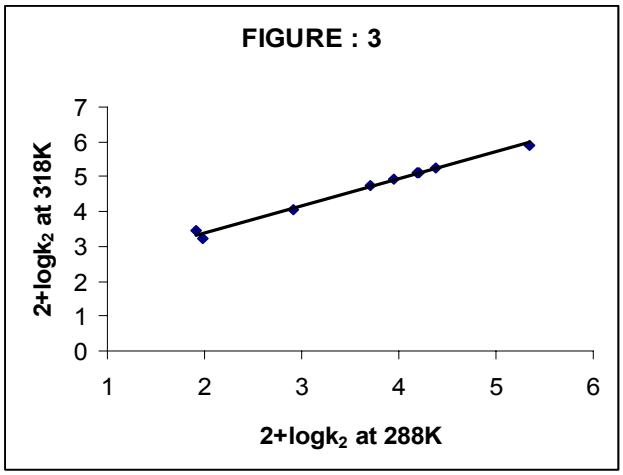


Figure 3. Exner's Isokinetic Relationship in the oxidation of Alcohols by TPSD

The hydride ion transfer may take place either by a cyclic process via an ester intermediate or by an acyclic one-step bimolecular process. This postulation is supported by an analysis of the temperature dependence of kinetic isotope effect. Kwart and Nickle[14] have shown that a study of the dependence of the kinetic isotope effect on temperature can be gainfully employed to resolve this problem.

Table 4. Dependence of the reaction rate on hydrogen–ion concentration,
[Alcohol]=0.10 mol dm^{-3} ; [TPSD]=0.001 mol dm^{-3} ; Temp. 298 K

[TsOH]/ mol dm^{-3}	0.10	0.20	0.40	0.60	0.80	1.00
$10^4\ k_{obs}/s^{-1}$	21.8	24.9	31.5	37.8	44.1	50.4

Table 5. Effect of solvents on the oxidation of alcohols by TPSD at 308 K

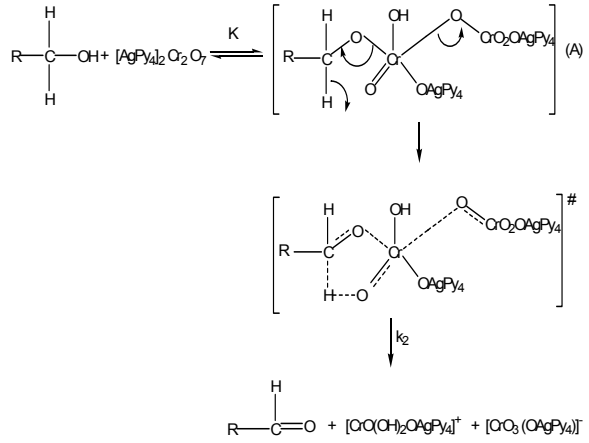
Solvents	K (dm^{-3} mol^{-1})	$10^5\ k_2$ (s^{-1})
Chloroform	6.11	36.3
Toluene	5.27	9.77
1,2-Dichloroethane	5.48	41.7
Acetophenone	4.48	56.2
Dichloromethane	4.63	38.9
THF	4.29	18.2
DMSO	5.02	117
t-butylalcohol	5.22	15.1
Acetone	4.81	32.4
1,4-Dioxane	4.36	17.4
DMF	5.58	63.1
1,2-Dimethoxyethane	5.55	11.0
Butanone	4.79	27.5
CS_2	4.78	5.25
Nitrobenzene	4.95	49.0
Acetic acid	5.43	6.46
Benzene	5.36	12.0
Ethyl acetate	4.76	15.8
Cyclohexane	5.18	1.45

Table 6. Temperature dependence of the reaction constant

T, K	$-\rho^*$	$-\delta$	r^2	sd	ψ
288	1.80±0.01	0.73±0.01	0.9999	0.010	0.01
298	1.71±0.02	0.63±0.01	0.9998	0.005	0.02
308	1.62±0.01	0.54±0.02	0.9989	0.002	0.04
318	1.55±0.02	0.45±0.02	0.9999	0.007	0.01

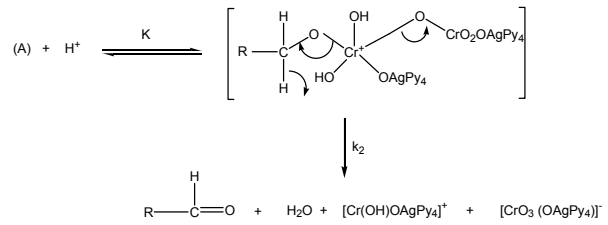
The data for protio- and deuterio-ethanols, fitted to the familiar expression $k_H/k_D = A_H/A_D \exp(E_a/RT)$ [15] show a direct correspondence with the properties of a symmetrical transition state in which the activation energy difference (ΔE_a) for k_H/k_D is equal to the zero-point energy difference for the respective C-H and C-D bonds (≈4.5 kJ/mol) and the frequency factors and the entropies of activation of the respective reactions are nearly equal.

Acid-independent Path (Scheme -1)



The similar phenomena have also been observed earlier in the reactions of halochromates. Bordwell [16] has documented a very cogent evidence against the occurrence of concerted one-step bimolecular processes by hydrogen transfer and it is evident that in the present studies also the hydrogen transfer does not occur by an acyclic bimolecular process. It is well established that intrinsically concerted sigmatropic reactions, characterized by transfer of hydrogen in a cyclic transition state, are the only truly symmetrical processes involving a linear hydrogen transfer[17]. Littler[18] has also shown that a cyclic hydride transfer, in the oxidation of alcohols by Cr(VI), involves six electrons and, being a Huckel-type system, is an allowed process. Thus the overall mechanism is proposed to involve the formation of a chromate ester in a fast pre-equilibrium step and then a disproportionation of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product (Scheme 1). The observed hydrogen-ion dependence can be explained by assuming a rapid reversible protonation of the chromate ester (A) with the protonated ester decomposing at a rate faster than (A) (Scheme 2).

Acid-dependent Path (Scheme - 2)



Conclusion

The reaction is proposed to proceed through a hydride-ion transfer from alcohol to the oxidant in the rate-determining step. It has also been observed that an α-C-H bond is cleaved in the rate-determining step. Both deprotonated and protonated forms of TPSD are the reactive oxidising species.

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CHROMATOGRAPHY OF XENOBIOTICS IN BIOLOGICAL AND ENVIRONMENTAL MATRICES

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Keywords: xenobiotics; gas chromatography; liquid chromatography; electrically driven systems; biological and environmental matrices

The newest results in the chromatographic analysis of xenobiotics present in biological and environmental matrices are compiled and the results are critically evaluated. Examples for the employment of preconcentration and prepurification technologies, gas chromatography using electron capture detection (ECD), nitrogen phosphor detector (NPD), various mass spectrometric detection methods (MS, MS/MS, etc), liquid chromatographic methodologies such as thin-layer chromatography (TLC), high performance liquid chromatographic methods (HPLC) as well as electrically driven systems are presented. The advantages and disadvantages of the various chromatographic technologies are shortly discussed and the efficacies of the methodologies are compared. Xenobiotics included in the review are volatile organic compounds (VOC), hydrocarbons and hydrocarbon-based pollutants, polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenols (PCB), other polyhalogenated compounds, pesticides, etc. The application of various chromatographic methods for the determination of xenobiotics in a wide variety of biological and environmental matrices is discussed in detail.

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Introduction

Chromatography has been developed as a powerful separation technique suitable for the separation and quantitative determination of organic and inorganic compounds with very similar chemical structure. Various chromatographic techniques such as gas chromatography (GC), liquid chromatographic procedures (thin layer chromatography (TLC), high performance liquid chromatography (HPLC), ultra performance liquid chromatography (UPLC) and electrically driven systems found application in biology, medicine, chemical technology and in the analysis of natural products contributing to the isolation and identification of new molecules. These methodologies were successfully employed in analytical quality control and environmental sciences. Moreover, chromatography has been applied for the residue analysis of xenobiotics in air, ground and surface water, sludge, soil matrices, foods and food products and in human and veterinary health care.

The objectives of the recent review are the compilation and concise evaluation of the newest results obtained in the chromatographic analysis of xenobiotics present in biological and environmental matrices and the critical evaluation of the results.

Prepurification and preconcentration methodologies

The application of magnetic nanomaterials for the preconcentration and prepurification of pollutants has been previously reviewed. It was stated that the advances of the use of magnetic nanomaterials are the high surface-to-volume ratio, easy surface modification and strong magnetism. The efficacy of the extraction is influenced by hydrophobic interactive forces, electrostatic attraction, and/or on the formation of covalent bonding between the analytes and the surface of nanomaterials. Pollutants can be desorbed by modifying ligands, changing pH, or adding organic solvent to the mobile phase. The desorbed pollutants can be separated and quantitatively determined by GC and/or HPLC.[1]

Gas chromatography

Gas chromatographic (GC) methods are suitable for the separation and quantitative determination of compounds which are volatile or semi-volatile and thermally stable at the temperature of the measurement. Unfortunately, the considerable numbers of xenobiotics are not volatile, consequently, the application of GC methods for the separation and quantitative determination of xenobiotics in biological and environmental matrices is limited.

Volatile organic compounds (VOC)

Because of their considerable impact on human health many analytical methods have been developed and successfully applied for the separation and quantitative determination of VOCs in atmospheric air.

The application of various on-line gas analyzers used for the monitoring of VOC in air has been earlier discussed in detail. [2] The newest methods employed for the determination of VOCs in atmospheric air, housing air, office air, occupational air and exhaled air have also been reviewed.[3]

The large volume injection-programmable temperature vaporization-GC-MS analysis (LVI-PTV-GC-MS) has been optimized for the determination of estrogenic compounds in environmental matrices. Analytes investigated included estrone, 17-β estradiol, 17-α-ethynyl estradiol, mestranol and estriol. The concentration of xenobiotics was analysed in estuarine water, wastewater, fish bile and fish homogenate. Optimized conditions of the measurements were: 45 µL volume of n-hexane extract injected at 60 ^{0}C, 6 µL/s with a went flow and vent pressure of 50 mL/min during 5 min. Limit of detection varied between 0.04 – 0.1n ng/L for water samples, 0.04 – 0.67 ng/g for fish bileang 0.1-0.75 ng for fish homogenate. It was established that the sensitivity of the method was higher than that of common split/splitless inlet.[4]

GC coupled with time-of-flight MS (GC-TOF-MS) was applied for the investigation of the composition of VOCs emitted from historical books. Contact head-space solid-phase extraction was employed for the preconcentration of target compounds. Linear hydrocarbons, linear aldehydes, 2-furfural and isopropyl were identified in the samples.[5]

Solid phase extraction of water samples was carried out by using C18 SPE column. Toluene, xylene, and cumene were extracted with dichloromethane and analyzed by GC/MS. It was found that the amount of target compounds varied between 2.34 and 52.12 ppm. It was established that the type of SPE stationary phase and that of the desorption sorbent influences markedly the efficacy of the prepurification.[6]

Solid-phase microextraction and GC/MS were employed for the measurement of the volatile compositions of mouse urine. The aim of the measurements was the elucidation of the relationship between the composition and concentration of VOCs and age, sex, social and reproductive status, physiologic state and genotype. Investigations indicated the presence of 49 new predictive compounds. Multivariate mathematical-statistical calculations proved that the data are suitable for the determination of the maturation state, stress level, and diet of mice. [7] Thermal desorption aerosol gas chromatography was employed for the study to determine gas-to-particle transitioning for polar and nonpolar VOCs found in the ambient atmosphere. It was suggested that the method is suitable for the study of the gas/particle-phase transitions for atmospheric semivolatile organic compounds.[8]

The volatile organic compound emissions from subarctic tundra was investigated by GC/MS. The measurements indicated that the emission of monoterpenes and sesquiterpenes increase markedly with increasing air temperature. [9] A new GC/MS was developed for the analysis of volatile organic compounds present in the urine of exposed volunteer workers. Samples were acidified, extracted by SPE, and derivatized with trimethylsilyl group. Accuracy was over 82.4%, precision was less than 28.4%. After the clean-up the level of mandelic acid and trans,trans-muconic acid considerably increased.[10]

GC/MS combined with solid-phase microextraction has been applied for the determination of the chromatographic profile of microbial volatile organic compounds in the headspace of cultures of filamentous fungi. Fungus (*Trichoderma atroviride*) was grown on a solid culture medium directly in headspace vials. GC/MS found various classes of compounds such as alcohols, ketones, alkanes, furanes, pyrones (mainly the bioactive 6-pentyl-α-pyrone), mono- and sesquiterpenes.[11]

A method based on thermal desorption followed by GC was developed for the measurement of five carbon compounds (acetaldehyde, propionaldehyde, butyraldehyde, isovaleraldehyde, and valeraldehyde). The results indicated that the mode of calibration exerts a considerable effect on the reliability of the analytical process.[12] The influence of the processing conditions on the VOC emission of larch particleboard has been investigated by GC/MS. The measurements indicated that the emission concentration and the amount of VOCs increased with increasing hot-pressing temperature and time. It was further established that the processing conditions influenced the composition of VOCs (variety of terpene, benzene, and derivatives). [13] A HS-GC-MS method was developed for the analysis of biogenic VOCs emitted by plants (monoterpenes, sesquiterpenes, and other related compounds). It was stated that the procedure is suitable for the simultaneous analysis of isoprene, and mono- and sesquiterpenes from plant emissions.[14]

Solid-phase microextraction followed by GC/MS and olfactometry were employed for the analysis of p-cresol, acetic, propionic, isobutyric, butyric, isovaleric, valeric and hexanoic acid in emissions at agricultural facilities. Samples were collected in polyvinyl fluoride bags. Recoveries of the target compounds ranged from 2 to 40% after 1 h and 0 to 14% after 7 d. The investigation indicated that the method of sampling exerts a marked influence of the concentration and composition of target compounds.[15]

An SPME method employing pencil-lead fibre was coupled with GC/MS. The concentration of organic volatile compounds of the roots, leaves and gum of *Astralagus compactus* was measured. Only one volatile organochlorine compound was detected in the samples (1-chlorotetradecane,). [16] Volatile organic compounds emitted from painting application and printing processes have been analyzed by GC/MS/FID. It was established that the toluene and C_8 aromatics were the most abundant compounds emitted from paint application while emissions from printing emission contained mainly heavier alkanes such as n-nonane, n-decane, n-undecane, toluene, and m/p xylene.[17]

An Y-tube experiment was employed for the investigation of house dust mite pheromones. American house dust mite (*Dermatophagoides farinae Hughes*) and

European house dust mite (*Dermatophagoides pteronyssinus Trouessart*) were included in the investigation. The experiments were motivated by the fact that mites can cause atopic diseases such as asthma, rhinitis, and dermatitis. The hexane extract of *D. farinae* was fractionated by microscale liquid chromatography using Florisil as stationary phase and the biological activity of the fractions was assessed. GC/MS measurements indicated that neryl or geranyl isomers are responsible for the biological activity. It was stated that neryl formate can be applied as a part of novel lure-and-kill system for house dust mite control.[18]

The efficacy of a novel in-tube extraction device for headspace sampling of waters was investigated by GC/MS. The method allowed the separation and quantitative determination of halogenated hydrocarbons, benzene, toluene, ethylbenzene, xylenes, fuel oxygenates, geosmin, and 2-methyl isoborneol. The measurements indicated that the highest extraction efficacy can be achieved by using mixed bed trap. The average relative standard deviations were lower than 10%. It was stated that the procedure can be employed for the analysis of tap, pond, and reservoir water and soft drinks.[19] GC/MS has also been employed for the separation and identification of the volatiles of *Streptomyces globisporus JK-1*. The measurements were motivated by the fact that some of the volatiles showed marked fumigant activity against *Penicillium italicum* on *Citrus microcarpa*. GC results indicated that the concentration of geosmin (trans-1,10-dimethyl-trans-9-decalol). It was further established that phenylethyl alcohol and caryophyllene showed weak inhibitory activity. Dimethyl disulfide and dimethyl trisulfide showed antifungal activity. It was concluded from the results that these class of volatiles have potential to control of blue mold of citrus species through fumigant activity.[20]

A GC method was employed for the study of the adsorption characteristics of the mesoporous silicate MCM 48 as enrichment medium. VOCs were applied as model compounds. The investigations indicated that the preconcentration efficacy of the sorbent markedly depended on the character of the enrichment medium and the conditions of desorption.[21] GC/MS technology was employed for the separation and quantitative determination of VOCs present in natural spoiled pork and *Salmonella typhimurium*-contaminated pork. The similarities and dissimilarities between the samples were elucidated by using multivariate mathematical-statistical methods such as principal component analysis (PCA) and multi-block PCA. The calculations proved that the method can be applied for the differentiation between natural spoiled pork and those contaminated with *S. typhimurium.*[22]

Hydrocarbons and hydrocarbon-based pollutants

Hydrocarbons were separated and quantitatively determined in geological chert samples. Analytes were extracted with focused ultrasound extraction (FUSE) and microwave-assisted extraction (MAE). Traditional Soxhlet extraction was employed as reference method. Both methods were optimized for solvent mixture composition (dichloromethane/hexane/acetone) and for process variables (sonication time and cycles and extraction temperature and time). The optimal conditions for FUSE were DCM/hexane 60:40, sonication time of 30 min and 9 cycles. The optimal extraction conditions for MAE were DCM/hexane/acetone 60:30:10, irradiation time of 15 min at 110 ^{0}C. Hydrocarbons C16-C40 were analysed by GC-MS.[23]

Another GC procedure was applied for the measurement of light hydrocarbons in Brazilian coal mines. It was established that the concentration of methane ranged from 3 ppm to 27% in the atmosphere of underground mines. Methane concentration in the air of surface mines varied between 3 and 470 pp.[24] GC/MS has been used for the investigation of the residual oil contamination of sediments. It was proposed that the method can be employed for the identification of oil in soils taking into consideration the transfer and weathering of oils in sediment.[25]

Aromatic and polyaromatic pollutants

A headspace-GC-MS method was developed for the analysis of monoaromatic volatile compounds (benzene, toluene, ethylbenzene, o-, m- and p-xylenes, and styrene) in olives and olive oil. Samples were put in the HS vial without any pretreatment and clean-up. Samples were automatically processed and injected in the GC column. Analytes were detected in SIM mode. The relative standard deviation (RDS, %) varied between 1.6-5.2% and 10.3-14.2% for olive oil and olives, respectively. The concentrations of the pollutants ranged between 23-332 μg/kg and 4.2-87 μg/kg for olive oil and olives, respectively.[26] Phenols and chlorophenols were separated and quantitatively determined in water using in situ derivatization headspace solid phase microextraction followed by GC/MS. It was established that fiber coating, extraction time and temperature, amount of derivatizating agent and ionic strength influenced markedly the efficacy of the extraction. The optimal conditions of the extraction were 4.0 g NaCl, 0.10 g of Na_2HPO_4 in 10 ml of sample solution, extraction temperature 60 ^{0}C, 600 r/min for 30 min. LOD values varied between 0.014 – 0.044 μg/L. Precision (RSD) was about 13.7%. Because of its precisity the method was proposed for the determination of phenols in wastewater samples.[27] The application parameters of silica gel modified with ketoimine groups was investigated as SPE stationary phase. It was established that the new sorbent is suitable for the preconcentration of benzene, phenol and o-chlorophenol before GC analysis.[28]

The oxidative degradation of chlorophenol derivatives was followed by GC/MS. Samples were treated power ultrasound (US), microwave (MW) irradiation It was established that these technologies promoted the decomposition of chlorophenol derivatives and can be successfully applied for the acceleration of the decomposition of chlorophenol derivatives.[29]

Polycyclic aromatic hydrocarbons

PAHs have been determined in surface waters using GC-MS. It was found that the PAH profiles were dominated by low molecular weight PAHs (two- and three ring

components). The data indicated that the PAH contamination has the origin in petrogenic input.[30] The concentration of polycyclic aromatic hydrocarbon (PAHs) in higher plants grown on an oil exploration site was measured by GC-MS. It was established that the amount of PAHs in the leaves ranged from 365 to 2870 µg/kg the average being 1430 µg/kg. Dibenzo[a,h]anthracene and 9,10-diphenylanthracene were not detected in the samples. It was further found that the concentration of 2- and 3-ring PAHs was higher than those of 4-, 5- and 6-ring PAHs.[31]

GC has been employed for the determination of 14 PCBs and 13 organochlorine pesticides in human plasma and the chromatographic data were correlated with plasma organochlorine levels. The calculations suggested that neither the amount of PCBs nor that of organochlorine pesticides are related to the occurrence of prostate cancer. It was further established that long-term low level exposure to organochlorine pesticides and PCBs in the general population does not contribute to increased prostate cancer risk.[32]

The occurrence and distribution of PAH in two soil size fractions have also been investigated by GC/MS. Particle size fractions included in the experiments were: < 250 µm (fraction A) and >250 µm to 2 mm (fraction B). Analytes were preconcentrated by pressurized fluid extraction (PFE) and analyzed by GC/MS. The concentration of PAHs varied from 9.0 to 1.404 mg/kg (soil fraction A) and from 6.6 to 872 mg/kg (soil fraction B). In the majority of cases significant differences were found between the concentration of PAHs in soil fractions A and B.[33] The occurrence of PAHs in dairy milk samples was assessed by using liquid-liquid extraction and solid-phase extraction followed by GC/MS. The results were evaluated by factor analysis. Calculations indicated that the main source of PAHs in milk may be the exhaust emitted from vehicles.[34]

The transport of semivolatile organic compound to the Tibetian Plateu was investigated in detail. The separation and quantification of the target compounds was achieved by GC/MS. The measurements indicated that the concentration of hexachlorobenzene was the highest followed by hexachlorocyclohexanes, DDT-related compounds and PCB congeners. It was further established that the amount of pollutants in the air was higher than in winter.[35]

Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) are extensively used in many up-to date technological processes. Besides of the manyfold benefits as adjuvants in a considerable number of modern industrial methods they show considerable undesirable toxicological effect. These side effects make necessary the development and application of reliable analytical methods for the separation and quantitation of PCB congeners. The application of GC methods employed for the analysis of PCB has been previously reviewed.[36]

Many investigations indicated that the low-level PCB exposures can be associated with immune system disfunction, cardiovascular disease, and impairement of the developing nervous system. The possible mechanism of PCB toxicity has been recently reviewed.[37]

Persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), PAHs, polybrominated diphenyl ethers (PBDEs), organochlorine pesticides (OCPs) and heavy metals were determined in adipose tissues of patients with *uterine leiomyomas* using GC/MS and inductively coupled plasma-optical emission spectrometry. It was assumed that the concentration of POPs can be correlated with the occurrence of *uterine leiomyomas*. [38] 145 PCB congeners and OCPs were determined in fur seal (*Callorhinus ursinus*) population (blubber, heart, liver, kidney, muscle, reproductive tissues, brain and lung were investigated). The concentration of POP sin various organs was measured by GC/ion trap mass spectrometry. It was concluded from the data that PCB can exert an effect on the fur seal population.[39]

The concentration of PAHs and PCBs were determined from the combustion of biomass pellets. It was established that the total concentration of PAHs varied between 6.4 and 154 µg/m^3 . Target compounds were analysed by GC/MS. Significant relationship was found between the amount of inorganic gases and the concentration of organic pollutants as well as between the concentration of PAHs and PCBs. It was suggested that the method can be employed for prediction purposes.[40]

Serum concentrations of PCBs were measured by high resolution gas chromatography using microelectron capture detection. It was established that PCBs can deteriorate the outer hair cells of the cochlea.[41] The enantiomeric composition of chiral PCB congeners and their biotransformation in a stream food web has also been investigated. The enantiomeric fractions of six PCB atropisomers (PCBs 84, 91, 95, 136, 149 and 174) were determined in fine benthic organic matter, coarse particulate organic matter, periphyton, Asian clam, mayflies, yellowfin shiner. The concentration and composition of PCBs were analyzed by GC-ECD. The measurements indicated that biotransformation of PCBs considerably depended on the type and composition of the microbial communities.[42] PCB levels in human adipose tissue was investigated by GC/tandem mass spectrometry (GC-MS/MS). The total mean PCB concentration were 27.2 µg/kg fat (Anhui Province) and 17.2 µg/kg fat (Jiangsu Province). A significant correlation was found between the age and PCB levels but the gender and PCB concentration was not correlated.[43]

GC/ECD measurements were applied for the determination of several PCB congeners in maternal, cord, and 6-month infant sera. The concentration of IG-specific anti-haemophilus influenzae type b, tetanus toxoid and diphteria toxoid were measured in 6-month infant sera using ELISA technologies. Multiple linear regression method was applied for the elucidation of the relationships between the measured biological and biochemical characteristics. It was concluded from the data that significant correlations cannot be assessed among parameters investigated.[44]

GC/MS measurements were performed for the study of the direct assessment of cumulative aryl hydrocarbon receptor agonist activity in sera from experimentally exposed mice and environmentally exposed humans.[45]

Solid-phase microextraction followed by GC-ECD was employed for the determination of PCBs in Brazilian breast milk samples. The relationship between detector response and analyte concentration was linear up till 16 µg/L (*r* over 0.9884). Precision (RSD) was <12%, (n = 5), recovery varied between 71 and 127%. The limit of quantitation varied from 0.45 to 2.42 µg/mL. The measurements indicated that there is a strong correlation between the level of contamination of the breast milk samples and the industrialization of the region.[46] GC-ECD and GC-MS negative chemical ionization detection (NCI) were employed for the determination of PCBs and polybrominated diphenyl ethers (PBDEs) in the tissues of the migrating salmon species *Oncorhynchus*, tshawytscha (Chinook salmon). It was established that the concentration of PCBs and PBDEs ranged from 78-25.5 ng/l wet weight and 272-1046 pg/gl wet weight, respectively.[47]

PCBs and OCPs were determined in biota and in sediments too. Ultrasonic extraction combined with silica gel with 45% sulphuric acid and florisil with 5% waster were employed for the preconcentration of analytes in biota. Samples of sediments were treated with metallic mercury and florisil column. Analytes were separated by GC/electron capture detection (ECD). The similarities and dissimilarities between the samples was assessed by principal component analysis (PCA).[48] The concentration of PCBs, p,p'-dichlorodiphenyldichloroethene (DDE) and methylmercury was assessed in human serum by using GC/ECD, cold vapor atomic absorption and atomic fluorescence spectroscopy. It was established that the total PCB concentration ranged from 8.7 to 3.091 ng/g. The amount of DDE varied between 0.3 to 7.083 ng/g. It was established that the serum concentrations of PCBs correlated linearly with fish consumption (r = 0.43, $p<0.0001$) but not with the DDDE concentration.[49] GC coupled with low-resolution mass spectrometry was employed for the analysis of PCBs and OCPs in serum samples. It was found that age and residence exert a significant influence on the amount of pollutants while the effect of gender was not significant. It was suggested that long-banned substances can occur in the general population.[50]

A new GC method was developed for the determination of polychlorinated and polybrominated dibenzo-p-dioxins (PCDDs/PBDDs), dibenzofurans (PCDFsPBDFs), biphenyls (PCBs/PBBs) and diphenyl ethers (PBDEs). The method applied various columns (silica, alumina and active carbon) and high resolution mass spectrometry. Samples were taken from the atmosphere near to a municipial solid waste incinerator.[51]

GC/MS has also been applied for the measurement of the concentration of PCDD/F and PCBs in food from animal origin. Samples of subcutaneous adipose tissue and blood as well as from muscle and liver after slaughtering. It was found that the results obtained in vivo and ex vivo samples showed good correlation. It was concluded from the measurements that the weakly invasive biopsy of subcutaneous adipose tissue performed on living animal can be used for the prediction of pollutants in muscle and liver.[52]

The efficacy of extraction technique suitable for the preconcentration of pollutants PCBs and OCBs has been compared. Extraction methods were Soxhlet extraction, accelerated solvent extraction (ASE) and supercritical fluid extraction (SFE). Ultrasonic extraction was applied for the determination of analytes in marine samples. Separation and quantitative analysis of target compounds was achieved by GC/ECD. It was established that the ultrasonic extraction was more efficient, more easily to carry out using smaller quantity of solvent and shorter analysis time.[53] The efficacy of various extraction technologies such as Soxhlet extraction (SE), accelerated solvent extraction (ASE), and microwave-assisted extraction (MAE) was compared using PCB and polybrominated diphenyl esters (PDBEs) as model compounds. Both soil and fish samples were investigated. It was established that the extraction efficacy of ASE and MAE was comparable with that of SE, and higher temperature and pressure increases the efficacy of the procedure.[54]

The fate of PCBs in soils amended with biosolids was investigated using incubation and leaching columns. Analytes were separated from the solid matrix by ultrasound-assisted pressurized solvent extraction (US-PSE). Samples were analysed by GC/MS. It was observed that the extractability of PCBs increased with increasing incubation time . It was further found that $CaCl_2$ cannot mobilize PCBs while linear alkylbenzene sulfonate (LAS) mobilized these target compounds.[55] The occurrence of inadvertent PCBs in commercial paint pigments were assessed by GC-tandem mass spectrometry (GC/MS/MS). The measurements revealed that PCB congeners can be detected in azo and phthalocyanine pigments, inks, textiles, paper, cosmetics, leather, plastics, food and other materials.[56]

GC followed by low-resolution tandem mass spectrometry (MS/MS) was employed for the measurement of co-eluting unlabeled and ^{13}C-labeled PCB congeners. It was concluded from the results that MS/MS can be applied for the determination of co-eluting unlabeled and ^{13}C-labeled PCBs.[57] A GC-ECD method was developed and applied for the determination of PCBs in the sediments. Target compounds were extracted by the Soxhlet method. Concentration of PCBs ranged from 15.3 to 997 ng/g (dry weight in < 2 mm fraction and from 29.9 to 952 ng/g in <200 µm fraction. The investigations indicated that the highest concentration of PCBs occurred below the discharge of municipal wastewater treatment plant.[58]

The efficacy of the serially coupled GC columns for the separation of PCBs has been investigated. The columns included in the experiments were a non-polar poly(5%-phenyl-95% methyl) siloxane column (40 m x 100 µm x 0.1 µm) and a polar 70%-cyanopropyl-polysilphenylene-siloxane column (4 m x 0.1 mm x 0.1 µm). The retention data were employed for the construction of the 2D and 3D images.[59]

GC followed with ECD detection was employed for the analysis of organochlorine compounds (OCs). The measurements were motivated by the supposition that diet and serum concentration of OCs may influence the K-ras

mutations in exocrine pancreatic cancer. The investigations suggested that dairy products may be source of OCPs.[60]

A GC technique was applied for the measurement of PCB congener profiles in clapper rails (*Rallus longirostris*) and the results were compared with those obtained by ELISA. It was concluded from the data the ELISA is more suitable for the qualitative exposure assessment while GC method is more reliable for detection.[61] The concentration of dioxins, furans and PCBs were measured in blood samples collected from 446 mothers in the city of Chapaevsk, Russia using high-resolution GC/MS. It was established that the concentration of target compounds increased with age, with the proximity to a local chemical plant, duration of local farming and consumption of local beef. Pollution decreased with longer breastfeeding, increase of body mass index and later blood draw date.[62]

The decomposition of PCBs in microcosm experiments was followed and the change of the composition of PCB congeners was followed by GC/MS. The measurements indicated that the biodegradation rates decreased with the degree of chlorination (from 75% to 22%). The bacterial abundance was also lower in soil microcosms exposed to the higher-chlorinated congeners. It was further established that the amount of biphenyl dioxygenase (BPH) genes increased in the presence of various PCB congeners.[63]

GC-ECD technology was employed for the analysis of PCBs, organochlorine pesticides (OCP), dichlorodiphenyltrichloroethane and its metabolites (DDTs), hexachlorobenzene (HCB), and hexachlorocyclohexane isomers (HCHs) in maternal serum. The results indicated that the concentration of DDTs is prevalent in the samples.[64] The concentration of PCBs was measured in butter available on the Polish retail market. Analytes were detected with a ion-trap mass spectrometer. The recoveries of the individual PCBs varied from 58% to 105%, RSDs were between 3-16%.[65] The effect of analytical artefacts on the determination of organochlorine pesticides and PCBs by GC/ECD and GC/MS was investigated in detail. The measurements indicated that artefacts can potentially render interferences difficult, confounded and erroneous. The use of an appropriate reference material considerably increases the reliability of the measurements.[66]

GC/MS has also been employed for the measurement of the amount of PCB 153, PCB 180 and PCB 138 in adult adipose tissue. PCB residues were found in 92% (PCB 153), 90% (PCB 180) and 86% (PCB 138) of the population. The mean concentration of the PCBs in the samples were 161.65±4.41. ng/g lipid for PCB 153, 111.62±6.27 ng/g lipid for PCB 180, and 38.41±8.61 ng/g lipid for PCB 138. Multivariate mathematical statistical methods indicated that age and body mass index correlated with PCB concentration. It was further established that occupation and diet predicted exposure in males while only dietary predictors influenced the exposure in females.[67]

GC method was employed for the determination of PAHs, PCBs, organochlorine pesticides and organotin compounds in the sediment of the Sava river. It was established that PAHs were present in moderate concentrations and their concentrations increased downstream. The concentrations of PCBs were low, the amount of hexachlorobenzene was relatively high. Organotin compounds were not detected.[68] GC/MS has also found application in the investigation of the fate of PCBs in a plant of high-temperature plasma melting of ash residues after municipal waste incineration. The results indicated the high the composition level of the incineration process [69] The relationship between the concentration of PCBs and the development of central-nervous system was investigated in detail. PCBs were separated by high-resolution GC. The measurements indicated that mono-ortho-substituted PCBs influenced unfavourably the psychomotor and mental development indices. It was further established that children with higher prenatal mono-ortho-substituted PCB exposures performed more poorly on the Bayley scale of infant development. It was further assumed that that dioxine-like PCBs may interfere with brain development in utero.[70]

Another GC/MS method was employed for the separation and identification of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated diphenyls (dl-PCBs). On the base of the results a new screening approach was developed. [71] GC/ECD analytical technique was also employed for the analysis of PCBs in the serum of pregnant women. The investigations suggested that higher PCB concentrations result in decrements of fetal and infant growth and development. [72] A GC-MS/MS technique was employed for the measurement of 83 PCBs, 23 OCPs and 19 PBDEs in the blood, eggs, and hatchling blood in the green sea turtle *Chelonia midas*. Significant correlations were found between the maternal transfer of persistent organic pollutants (POPs) and the amount of PCBs, PBDEs, gamma HCH, trans cordane and mirex. It was concluded from the data that POPs influence the development of *C. midas* eggs.[73]

Semi-empirical topological indexes was developed for the prediction of the relative retention time of of PCBs on 18 different high resolution GC columns. Calculations proved that the calculated molecular volume, molecular surface area, and the position and number of substituents are linearly correlated with the relative retention.[74]

A novel SPE-GC/MS method was developed for the analysis of 23 polychlorinated PCBs in sewage water using pyrenebutyric acid-bonded silica as sorbent. The recoveries of the method ranged from 69.44% to 111.91%. The results indicated that the novel sorbent can be successfully applied as SPE sorbent for the preconcentration of PCBs in sewage water. The LOD varied between 0.06-0.22 ng/L.[75] The separation capacity of three GC columns coupled in two series was investigated using PCBs as model compounds. A non-polar capillary column coated with poly(5%-phenyl-95%-methyl)siloxane was employed as the first column. The second columns were a polar capillary column coated with 70% cyanopropyl-polysilphenylene-siloxane and a

capillary column coated with ionic liquid 1,12-di(tripropylphosphonium)dodecane bis(trifluoromethane-sulfonyl)imide. The results indicated that the separation capacity of the apolar + ionic liquid column was better than that of non-polar – polar column coupling.[76] A GC-MS technology was applied for the measurement of POPs in adults from Guinea-Bassau. The following POPs were included in the investigation: 1,1,1-trichloro-2-2-bis(4-chlorophenyl)ethane and its metabolites, PCBs, PBDEs and HCHs. The investigations revealed that the concentration of 4,4'-DDE was the highest in the samples followed by other DDT metabolites, PCBs and HCHs and their concentrations decrease with time.[77]

Pyrethroids in apple juice were analysed by isotope dilution GC/MS method. The concentration of cypermethrin, permethrin, and bifentrin was determined. It was found that the intraday and interday reproducibilities of the method was lower then 0.5%. The expanded relative uncertainty was between 3 – 6%.

An other GC/ECD procedure was employed to control the validity of the data obtained by GC/MS.[78] The amount of PCBs, hexachlorobenzene (HCB), pentachlorobenzene (PeCB), hexachlorocyclohexane compounds (α–, β–, γ– and δ–HCH), and dichlorodiphenyltrichloroethane (DDT) derivatives (p,p'-DDE, p,p'-DDD, p,p'-DDT, o,p'-DDD, and o,p'-DDT) were determined in air and soil using passive sampling procedure followed GC/ECD analysis. The chromatographic retention data indicated the the pollution caused by the target compounds investigated was relatively low.[79]

Pesticides such as coumaphos, diazinon, amitraz or fluvalinate were introduced in bee hives and the pesticide concentration in bee workers, larvae and royal jelly was analysed by GC/ECD. Amitraz was determined by HPLC and GC-MS/MS was employed for the determination of diazinon. Amiraz and diazinon were not found in the samples while coumaphos and fluvalinate occurred in royal jelly and bee heads. The additional potential sub-lethal effects of the pesticides on the honey bees was discussed in detail.[80]

Another study employed HPLC-UV and HPLC-MS-MS for the determination of amitraz and its degradation product 2,4-dimethylaniline (2,4-DMA) in honey. Target compounds were purified by liquid-liquid extraction using hexane and isopropyl alcohol as solvents. Analytes were separated on a C-18 column using gradient elution. Acetonitrile and 0.02 M ammonium acetate were the components of the mobile phase. Recoveries varied between 83.4 and 103.4% for amitraz and 89.2 and 104.7% for 2,4-DMA. RSD values were lower than 11.6% for both HPLC-UV and LC-MS/MS measurements. LOD values were 6 μg/kg for amitraz and 8 μg/kg for 2,4-DMA. LOQ values were 20 μg/kg for amitraz and 25 μg/kg for 2,4-DMA. The validation parameters of LC-MS/MS method were: LOD, 1 μg/kg for amitraz; 2 μg/kg for 2,4-DMA; LOQ, 5 μg/kg for amitraz and 10 μg/kg for 2,4-DMA.[81]

The concentration of PAHs, PCBs and DDT adsorbed on microplastics was determined by GC/MS. Plastics were identified by Fourier transformed infra-red spectroscopy. The measurements indicated that the concentration of pyrene, phenanthrene, chrysene and fluoranthene, as well as those of PCB congeners 18, 31, 138, and 187 were the highest in the samples.[82]

Organic pollutants such as PAH, PCB, and OCP were analyzed in two different types of forest soil. The investigations were motivated by the strong adsorption of pollutants to soil organic matter. Cyclohexane, ethyl acetate and acetone were applied as extracting agents. Target compounds were preconcentrated with different techniques and the efficacy of various extraction procedures (pressurized liquid extraction, Soxhlet extraction, fluidized bed extraction, sonication, shaking and one-step extraction) was compared. Samples were further purified by gel permeation chromatography (GPC) and SPE. Concentrations of analytes in the samples were determined by GC/MS using two-different injection systems: split/splitless injection and programmable temperature vaporizer (PTV) injection. The measurements indicated that the highest extraction efficiency was achieved by using acetone/cyclohexane (2:1, v/v). It was further established that a two-step preconcentration procedure employing GPC followed by SPE can be successfully used for the separation of humic materials. It was found that the recovery rates varied between 89% and 106%. Because of the highest efficacy the application of PTV injection system was proposed. It was further stated that the method is suitable for the separation and quantitative determination of these classes of analytes in the trace level of 1-2 μg/kg humic soil.[83]

GC-MS-MS technology was employed for the determination of benzo[a]pyrene (BaP) on particulate matter less or equal to 10 μ (PM 10). The investigations were motivated by the carcinogenic character on BaP. Multivariate linear regression method was applied for the elucidation of the correlation between the concentration of BaP and the environmental conditions taking into consideration the various meteorological conditions such as solar radiation and wind speed.[84]

Similar GC-MS technique was employed for the analysis of particle-associated 16 PAHs near power plants. Samples PM10 and PM2,5 were collected on poly-tetra-fluorinated-ethylene (PTFE) filters. Target analytes were extracted by reflux followed by ultrasonication. GC-MS system used programmable temperature vaporizers (PTV) injector and large volume injection (LVI) method. It was foud that the average daily concentration of B[a]Py was 0.57 – 0.58 ng/m^3. It was assumed that the main sources of PAH pollution was oil and coal burning.[85]

Isotope dilution GC-MS was successfully applied for the analysis of 16 PAHs in edible oils. Target compounds were extracted by sonication using acetonitrile as solvent. Samples were further purificated using narrow gel permeation chromatography. LOQs were below 0.5 ng/g the recoveries being 81 – 96%. RSDs were lower than 20%. It was concluded from the results that the method can be employed for the measurement of PAHs in edible oils.[86]

Other pollutants

GC-ECD and GC-MS were simultaneously employed for the determination of the antiparasitic drug amitraz and its main metabolite, 2,4-dimethylaniline in food animal tissues. Analytes were preconcentrated by accelerated solvent extraction (ASE). Target compounds were extracted with n-hexane/methanol then further cleaned on a C18 silica bonded cartridge, hydrolyzed and derivatized to 2,4-dimethyl-7-F-butyramide for GC-ECD measurements. Samples were not hydrolyzed and derivatized before GC-MS analysis. Recoveries ranged from 72.4 to 101.3%, RSD being lower than 11.5% for GC-ECD. Recoveries for GC-MS measurements were between 77.4 and 107.1% RSD being lower than 11.6%. LOD and LOQ values were 5 and 10 µg/kg. For GC-MS LOD and LOQ were 2 and 5 µg/kg. It was stated that the method is rapid, reliable and can be used for the measurement of amitraz and 2,4-dimethylamine in liver and kidney of swine, sheep and bovine [2,4-dimethylamine in liver and kidney of swine, sheep and bovine.[87]

A highly sensitive GC-MS method was developed and successfully applied for the determination of dithiocarbamates (DTCs) and milneb in foods. Analytes were extracted with cysteine EDTA and methylated with methyl iodide. The methyl derivatives were cleaned-up on a neutral alumina mini column. The main recoveries were between 72 and 120% except for methiram. LOQ was 0.01 mg/kg. The procedure was successfully applied for the analysis of dimethyldithiocarbamates, ethylene-bisdithiocarbamates, polycarbamate, propineb and milneb. [88] GC-MS has also been employed for the determination of various pesticide residues in lettuce. Analytes were extracted with the matrix solid-phase dispersion technique. The optimal conditions were: 4.0 g of lettuce, 2 g of silica as dispersant sorbent, 0.1 g of activated carbon as clean up sorbent and acetonitrile as eluting sorbent. Pirimicarb, methyl parathion, procymidone, α-endosulfan, β-endosulfan were included in the experiments. Recoveries varied between 50 -120% RSD ranging from 0.6 to 8.0%. LOD and LOQ varied 0.01 to 0.02 mg/kg and 0.04 to 0.10 mg/kg.[89]

The relationship between the concentrations of persistent organochlorine pestides (OCPs) and endometriosis has been investigated in detail. The amount of target molecules (ng/g serum) was measured by GC-ECD. Calculations revealed a strong linear correlation between the concentration of OCPs and the occurrence of endometriosis.[90] The uptake, distribution and degradation of the fungicide propiconazole in red oaks (*Quercus rubra*) were assessed by GC-MS measurements. The data indicated the basipetal movement and degradation of the fungicide, and the survival of the pathogen *Ceratocytis fagaecearun* in roots. [91] The preconcentration method matrix solid-phase dispersion followed by GC-MS-SIM (selected ion monitoring) was applied for the determination of eight multi-class pesticides such as vinclozolin, dichlofuanid, penconazol, captan, quiboxyfen, fluquinconazol, boscalid and pyraclostrobin in grapes. The optimal conditions of preconcentration technology were: 0.5 g of grapes, 1.0 g of silica as clean-up sorbent, 1.50 g of C18 as bonded phase and 10 ml of dichloromethane/ethyl acetate (1:1, v/v). Because of the considerable matrix effects GC measurements used matrix-matched standards. Recoveries were better than 80% except captan. LOQ values ranged from 3.4 to 8.7 µg/kg. This values were lower than the maximum residue limit (MRLs) officially established.[92]

Liquid chromatographic technologies

Aromatic hydrocarbons

Not only GC methods but also HPLC technologies have been employed for the quantitative determination of phenols and related compounds in various accompanying matrices. The overwhelming majority of methods employ reversed phase stationary phases but other supports such as porous graphitized carbon has also found application in the HPLC analysis of xenobiotics.[93] Thus, the application of SPE followed with HPLC-UV for the quantitative determination of phenols in water was reported. Phenol and 10 phenol derivatives served as target compounds. The parameters of the method such as pH, solvent ratio, column temperature, sample volume, run time and flow rate were optimized. It was found that the run time was 20 min, the coefficient of determination (r^2) was over 0.99, the recovery ranged from between 67.9±7.28 and 99.6±4.26. LOD varied 0.51 – 13.79 µg/mL.[94]

Not only GC but also various high-performance liquid chromatographic technologies (HPLC) has also been employed for the separation and quantitative determination of PAHs in different matrices. Thus, the HPLC analysis of PAHs in water and soil has been reported. It was found that water, sediment and soil contain PAHs representing potential risk to human health.[95]

Ultrasonic abstraction followed by HPLC was employed for the investigation of the generation of PAHs during cooking. The measurements indicated that the majority of PAHs are generated during the first 1-4 h of cooking. [96] A new procedure was developed and successfully applied for the HPLC separation of nitrated-polycyclic aromatic hydrocarbons (nitro-PAHs) and PAHs. Analytes were analysed using normal-phase HPLC. The stationary phase was a phenyl column, mobile phase was hexane, the flow rate being very low (0.05 mL/min). It was established that pollutants were separated according to their polarity.[97]

SPE followed by HPLC and fluorimetric was applied for the separation and quntitative determination of PAHs in drinking water. Acenaphtene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]-anthracene, benzo[g,h,i]-perylene, indenol[1,2,3-c,d]pyrene were the target compounds. Some parameters of the SPE procedure such as solvent volume for cartridge conditioning, sample volume, and the methanol concentration in the sample were optimized. It was stated that the LOQ of the method ranged from 0.04 – 1 ng/L. It was further found the solvent consumption of the technique is low, the analysis time short, therefore, it can be applied for legislation purposes.[98]

HPLC has also been employed for the determination of PAHs (benzo[a]anthracene, chrysene, benzo[h]-fluoranthrene, benzo[h]fluoranthrene, benzo[a]pyrene, dibenzo[a]anthracene, benzo[g,h,i]perylene) in roasted coffee beans. Samples were saponified with potassium hydroxide then the pollutants were preconcentrated by liquid-liquid extraction (LLE) followed by solid-phase extraction (SPE). The regression coefficients of the linear correlation between the concentration of analytes and the detector response ranged form 0.9938 to 0.9995. The limit of detection (LOD) and limit of quantification (LOQ) varied between 0.016 and 0.497 and between 0.054 and 1.656 μg/kg, respectively.[99]

Polychlorinated biphenyls (PCBs)

PCBs were separated and quantitatively determined by HPLC technologies, too. The application of three types of RP sub-2-μm stationary phases has been previously reported. The correlations between the detector responses and the concentration of analytes were linear in the range of 0.5 – 50.0 μg/mL. LOD values varied from 0.1 to 5 ppm. It was concluded from the measurements that ultra high-performance liquid chromatography with UV detection can be applied for the analysis of various PCBs. The results were compared with those obtained by GC/MS. [100] The concentration of pollutants (mercury, methylmercury, and persistent organic compounds) was measured in marine fish oil; capsules; and canned cod liver. Analyses were carried out by vapour atomic absorption spectroscopy and GC/MS. The results indicated that the consumption of fish oil in capsules, and canned liver is safe, healthy and can be encouraged.[101]

A new extraction vessel was developed and successfully applied for the preconcentration of PCBs in avian blood. The method included pressurized solvent extraction (PSE). Florisil was employed for the elimination of lipids. Extraction volume was reduced from 30 to 10 cm^3. The recoveries achieved with the new method were between 70-130%. Target compounds were separated and determined by GC coupled with large volume injection ion-trap mass spectrometry (GC-LVI-ITMS-MS). LOD values ranged from 0.05 to 0.5 ng/g. RSD was in each case lower than 5%.[102]

The enantiomers of the organophosphorous insecticide O-ethyl O-4-nitrophenyl phenylphosphonothioate (EPN) were separated on two different chiral HPLC columns and the aquatic toxicity of the enantiomers was assessed using *Daphnia magna* and zebrafish (*Danio rerio*) embrio test . It was established that the separation capacity of the HPLC system was higher at lower temperature and at lower concentration of organic modifier in the mobile phase. The investigations indicated that the biological activity of enantiomers shows marked differences. [103] Although the majority of chromatographic technologies employs GC, HPLC methods have also found application in the chromatographic analysis of PCBs. The concentration of persistent organic pollutant (POP) in farmed Atlantic salmon was investigated in detail. The concentration of dioxin-like PCBs, non-dioxin-like PCBs, dioxins, polybrominated diphenyl ethers (PBDE), organochlorine pesticides, and very long chain marine ω-3 (VLC-n3) were determined in Atlantic salmon. Fish oils were decontaminated using active carbon and short path distillation. The measurements indicated that the decontamination process reduces by 68-85% the amount of POPs while the concentration of VLC-n3 was decreased only with 4-7%.[104]

Other pollutants

The concentration of acaricides frequently used in apiculture (fluvalinate, coumaphos, bromopropylate and its metabolite 4,4'-dibromobenzophenone) was determined in beeswax using HPLC followed by DAD detection. Samples were prepurified by SPE using Florisil cartridge. It was established that fluvalinate residues were present in 36.3% of samples, concentration ranging from 1.2 to 6.6 μg/g wax. Other acaricide residues were not detected.[105]

Malachite green (MG) has been frequently used in aquaculture as a parasiticide and fungicide. As MG shows marked carcinogenecity and mutagenicity the determination of its concentration in foods and food products is of paramount importance. The application of isotope dilution liquid chromatography/MS for the separation of MG and its principal metabolite leucomalachite green (LMG) has been previously reported. Fat content of the samples was removed by using an additional saponification step. This step increased considerably the efficacy of SPE columns. MS detection was carried out in selected ion monitoring (SIM) mode (m/z 329 and 334 for MG and d(5)-MG; 331 and 337 m/z for LMG and $^{13}C(6)$-LMG). It was established that the accuracy of the method was the same as other generally accepted methods.[106]

The ecotoxicologic effect of herbicides (oxadiazon, benzofenap, clomazone, and benzosulfuron-methyl) and fungicides (carbendazim, tricyclazole, and flusilazole) was monitored by various biological, microbiological and analytical (SPE-LC-electrospray-tandem MS). The measurements indicated that herbicides and fungicides exert a negative impact to planctonic organisms but the effect seem to be short lived.[107] A new enzyme-linked immunosorbent assay was developed for the determination of the fungicide fenhexamid and the results were compared with those obtained by HPLC. An excellent correlation was found between the methods.[108]

Both GC-MS and LC-Q-TOF were applied for the study of the degradation of the fungicide prochloraz by pathogen microorganisms. LC measurements indicated that the main degradation product of prochloraz was N-(2-(2,4,6-trichlorophenoxy)ethyl)propan-1-amine. [109] Ultra-sound-assisted emulsification (method A) and single-drop liquid-liquid microextraction (method B) were employed for the preconcentration of seven strobilurin and six oxazole fungicides in fruits and juice samples before GC-MS-SIM analysis. Enrichment factors ranged from 140 to 1140 for method A and from 80 to 1600 for method B. The procedure has been successfully applied for the determination of this class of fungicides in various fruit and juices.[110]

GC-MS and LC-MS-MS were employed for the investigation of the fate of pesticides in grapes and vinification process. It was found that multiresidue GC-

MS method was suitable for the detection of 71 pesticides, LC-MS-MS for the measurement of 45 pesticides, GC-MS was sued for the analysis of dithiocarbamates. It was established that boscalid and phosalone were the most persistent pesticides in grapes during ripening. The pesticides detected during the vinification process were: boscalid, cyprodinil, dimethomorph, fenhexamid, metalaxyl and procymidone their average concentration was 0.01-0.02; 0.04; 0.01-0.08; 0.12-0.13; 0.09-0.11 and 0.07-0.13 mg/L.[111]

LC-MS-MS procedure was applied for the analysis of methyldinocap in mango and soil. Target compound was extracted with acetone:methanol:4 N HCl (100:10:5, v/v/v) than hydrolyzed to 2,4-DNOPC. Analytes were cleaned up by liquid-liquid partition using ethyl acetate. LOQ of methyldinocap in soil and mango was 0.025 µg/g, RSDs ranged from 93 to 98%. The method has been employed for the study of the dissipation of methyldinocap in mango.[112]

The photocatalytic degradation of boscalid in aqueous titanium dioxide suspension was followed by using SPE prepurification step, HPLC-DAD and total organic carbon (TOC) analysis. The measurements indicated that the photodecomposition of boscalid follows pseudo-first-order reaction kinetics. This combined analytical technology allowed the separation and identification of 17 degradation products.[113]

HPLC-UV/Vis, fluorometric detection, ion chromatography and LC-MS were employed for the investigation of the radiolytic removal of carbendazim and chlorphenvinphos. It was concluded from the measurements that irradiation influences considerably the biological activity.[114]

A combined method employing GC and LC both hyphenated with tandem MS with quadruple-analyzer was used for the determination of organic contaminants in wastewater. GC-MS-MS technique applied C-18 cartridges for the prepurification of the target compounds. The method allows the detection of about 60 analytes (PAHs, octyl/nonylphenols, PCBs, organochlorine compounds, insecticides, herbicides and PBDEs. The UHPLC-MS-MS procedure made possible the analysis of 37 (more polar) pesticides. The most frequently detected pollutants were herbicides (simazine, terbutylazine, terbutryn, terbumeton, terbacyl, and diuron), fungicides (thiabendazole and carbendazim) and 4-t-octylphenol. The presence of insecticide diazinon, fungicide diphenylamide, UV filter benzophenone, N-butylbenzenesulfonamide, the insect repellent diethyltoluamide, caffeine, the pharmaceuticals erythromycin, benzenesulfonanilide, ibuprofen, atenolol, and paracetamol was also verified.[115]

Abbreviations

ASE	accelerated solvent extraction
BaP	benzo[a]pyrene
DCM	dichloromethane
DDTs	dichlorodiphenyltrichloroethane and its metabolites
ECD	electron capture detection
FID	flame ionisation detector
FUSE	focused ultrasound extraction
GC-MS	gas chromatography-mass spectrometry
GPC	gel permeation chromatography;
HCB	hexachlorobenzene;
HCHs	hexachlorocyclohexane isomers;
HS	head-space
LLE	liquid-liquid extraction;
LOD	limit of detection;
LOQ	limit of quantification;
LVI	large volume injection;
MAE	microwave-assisted extraction;
MSDP	matrix solid-phase dispersion;
MW	microwave;
NCI	negative chemical ionization;
OCPs	organochlorine pesticides;
PAHs	polycylic aromatic hydrocarbons;
PBBs	polybrominated biphenyls;
PBDDs	polybrominated dibenzo-p-dioxins;
PBDEs	polybrominated diphenyl ethers;
PBDFs	polybrominated dibenzofurans;
PCA	principal component analysis;
PCBs	polychlorinated biphenyls;
DL	dioxin-like polychlorinated biphenyls
PCDD/Fs	polychlorinated dibenzofurans
PFE	pressurized fluid extraction
PLE	pressurized liquid extraction
POPs	persistent organic pollutants
PSE	pressurized solvent extraction
PTFE	poly-tetra-fluorinated-ethylene
PTV	programmable temperature vaporizer
SIM	selected ion monitoring
SPE	solid-phase extraction
SPME	solid phase microextraction
SFE	supercritical fluid extraction
UPLC	ultra high-performance liquid chromatography
TEQ	toxic equivalent quotient
US	ultrasound
US-PSE	ultrasound-assisted pressurized solvent extraction

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1,3,5-TRICYANOBENZENE –A MUTAGENIC BY-PRODUCT OF CARBON FIBER PRODUCTION IN PYROLYSIS OF POLY(ACRYLONITRILE-CO-METHYL METHACRYLATE)

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Keywords: 1,3,5-tricyanobenzene; acrylonitril-co-methyl methyacrylate fiber; carbonization; mutagenic effect.

A solid by-product formed as deposits in the pyrolysis process of poly(acrylonitrile-co-methyl methacrylate) was analyzed. Two main components, namely ammonium sulphate and 1,3,5-tricyanobenzene were identified by IR, GC-IR, TG-MS and XRD techniques. The major organic components, 1,3,5-tricyanobenzene was crystallized from acetone extract as colourless needles. 1,3,5-Tricyanobenzene proved to be a mutagenic active agent by bacterial (*Salmonella typhimurium TA98* and *TA1537*) reverse mutation assay.

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Introduction

Pyrolysis of poly(acrylonitrile-co-methyl methacrylate) derivatives is the most common/simple method for carbon fibre manufacture[1]. A sponge-like pale yellow compound with unknown composition and beneficial effect, deposited on ceiling of the polymer pyrolysis industry, has been analyzed to get an insight about its chemical composition and biological effects.

Experimentals

The samples were collected from the ceiling of a industry where pyrolysis of the poly(acryl nitrile)-co-poly(methyl methacrylate) fibres were performed. The yellow coloured solid has polyurethane-foam like characteristics were collected and extracted with various solvents, and the evaporation residues were analyzed with TG-MS, IR and XRD techniques.

10 g of each sample was extracted with 200 ml of solvent (water, methanol, ethanol, toluene, dichloromethane, chloroform, acetone and acetonitrile) with rigorous stirring at room temperature for 2 h followed with a reflux for 10 min. The extracts were evaporated and the residue was studied by IR and XRD techniques. The evaporation residue was recrystallized with acetone. The nest-like aggregates of long needles were formed. The organic residue was dissolved in acetone and GC-IR and GC-MS studies were done on this solution.

X-ray powder diffraction measurements were performed by means of a Philips PW-1050 Bragg-Brentano parafocusing goniometer, equipped with a secondary beam graphite monochromator and proportional counter; scans were recorded in step mode by using CuK_a radiation at 40 kV and 35 mA tube power. Evaluation of the diffraction patterns have been obtained by full profile fitting techniques.

Solid state IR spectra have been obtained by a Biorad-Digilab FTS-45 FT IR spectrometer in the 4000-400 cm^{-1} region in KBr pellet at room temperature. GC-IR measurements were performed on a Thermo Finnigan TRACE GC combined with a Nicolet Magna 750 FTIR instrument supplied with a liq. N_2 cooled MCT-A ($Hg_xCd_{1-x}Te$) detector. The measurements were performed under isotherm conditions (200 °C) or with temperature programmed mode (40-200 °C with 40°C min^{-1} heating rate) on an RTX-5 crossbond Restek (30 m, 0.32 mm, 1 μm, 5% diphenyl-95% dimethylpolysiloxane) column.

TG-MS measurements were accomplished by a STD 2960 Simultaneous DTA/TGA (TA Instruments) + Thermostar GSD 200 Q-MS (Balzers) device with 10 °C heating rate in Ar or Ar-10%O_2 flow. Ammonium content was determined with standard method[2] after treatment with sodium sulphide (Na_2S).

GC-MS measurements were performed on a VG ZAB2-SEQ Tandem mass spectrometer (VG Analytical, UK) coupled with a HP 5890A gas chromatograph. Column parameters: Restek Rtx-5Am (low polarity phase; crossbond 174; 5% diphenyl/95% dimethyl polysiloxane), 30mx0.25 mm with 0.25 μm film thickness. The measurements were done under isothermal conditions (200 °C) or with a 65–220 °C temperature range with 10 °C min^{-1} heating rate, using He as carrier gas with 2 ml min^{-1} flow rate. Mass spectra were scanned with 1.5 sec cycle time in mass range of m/z 25-520. Electron impact (70 eV) ionization was used. The samples were analyzed in acetone solution.

Mutation tests were performed by a standard plate incorporation procedure as an initial mutation test. The experiments were carried out using aqueous as well as DMSO extracts and histidine requiring auxotroph strains of *Salmonella typhimurium TA98, TA100, TA1535, TA1537* and tryptophan-requiring auxotroph strain of *Escherichia coli WP2 uvrA*. Bacteria were exposed to the test item both in the presence or absence of an appropriate metabolic activation system. Molten top agar was prepared and kept at 45 °C. 2 ml of top agar was aliquoted into individual test tubes (3 tubes per control or concentration level). The equivalent number of minimal glucose agar plates was properly labelled. The test item and other components were prepared fresh and added to the overlay (45 °C). Each tube contained top agar (2000 µL, solvent or dilution of test item extracts or positive controls 50 µL, overnight culture of testers train 100 µL, phosphate buffer (pH=7.4) or S9 mix (post mitochondrial supernatant) 511 µL. This solution was mixed and poured on the surface of minimal agar plates. For activation studies, instead of phosphate buffer, 0.5 ml of the S9 mix was added to each overlay tube. The entire test consisted of non-activated and activated test conditions and each of them with the addition of negative and positive controls. The plates were incubated at 37 °C for 48 h. The colony numbers on the control, positive control and the test plates were determined. The mean number of revertants per plate, the standard deviation and the mutation factor values were calculated for each dilution "concentration" level of the test item and also for the controls[3] .

Discussion

The pale yellow coloured sponge-like, light-weight material so collected was non-uniform in character. The deposit showed porous structure with holes of different sizes (small and large) and distribution of well-defined heterogeneity could be observed in the tissue structure.

Identification of chemical nature

The IR spectroscopic results of the powdered deposit sample showed characteristics bands belong to ammonium ion (ν_{as}(NH) 3232 cm^{-1}; δ(NH) 1415 cm^{-1}, ρ(NH) 616), sulphate ion (ν_{as}(SO) 1092), aromatic CH groups ($\nu(CH_{aromatic})$ 3083 and covalently bound cyano groups (ν(CN) 2249 cm^{-1}). The bands of expected triazines and nitrates could not be detected at all. Extraction experiments were carried out with a series of solvents and the results of leaching can be seen in Table 1.

Table 1. Leaching results of homogenized deposit samples in various solvents at room temperature

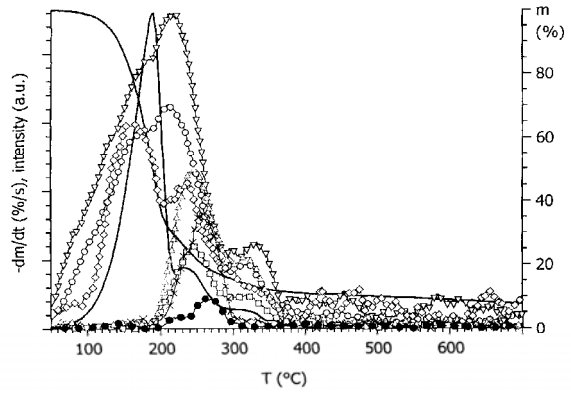
Solvent	Residue, wt.%	Dissolved part, wt. %
Water	38	62
Methanol	42	58
Ethanol	49	51
Toluene	59	41
Dichloromethane	44	56
Chloroform	45	55
Acetone	34	66
Acetonitrile	32	68

TG-MS studies on homogenized deposit sample were performed in Ar-10% O_2 (oxidative) and in pure argon (inert) atmosphere and the results can be seen in Fig.1. and summarized in Table 2.

Table 2. Mass changes during thermal decomposition of homogenized deposited sample in inert (Ar) or oxidative (Ar-10 vol.% O_2) atmosphere between 25 and 900 °C.

Conditions	$\Delta m_{25\text{-}400\ °C}$	$\Delta m_{25\text{-}700\ °C}$
Inert	89 %	92 %
Oxidative	90 %	99 %

Three peak pairs were occurred with *m/z*=17 and 16 fragment masses (NH_3 and NH_2 or OH and O, respectively) at TG-MS curve (Fig.1) in inert atmosphere. Two un-separated sharp peaks and a separated one were observed with maximums between 160-170 °C, 220-250 °C and 330-340 °C, respectively. The appearance of *m/z*=17 and 16 peaks were almost simultaneously with the appearance of *m/z*=44 (N_2O or CO_2) peak both in the 160-170 and 220-250 °C temperature range. The peak with *m/z*=64 (SO_2) could be detected between 220 and 250 °C and 340-360 °C. Fragments with *m/z*=75 ($C_3H_3^+$) and *m/z*=100 ($C_6H_2(CN)_2^+$) appeared in the second decomposition step (220-250 °C) unambiguously showed that the organic component(s) decomposed in this temperature range.



G_0= 0.576 mg (0.587 mg), 10 °C/min, Ar: 140 ml/min

Curve	Maximum	Scale
G [%]	100.1	100.1
DTG [%/s]	0.2298	0.2321
m/z 16 (NH_2)[/mg]	65.01	92
m/z 17 (NH_3)[/mg]	91.93	92
m/z 44 (CO_2)[/mg]	28.87	45
m/z 48 (SO)[/mg]	7.710	30
m/z 64 (SO_2)[/mg]	14.94	30
m/z 75 [/mg]	2.169	6
m/z100 [/mg]	0.6321	6

Fig.1. TG-MS curves of yellow sponge-like deposit material in Ar

In oxidative atmosphere, the organic component(s) were almost completely ignited whereas the inorganic component(s) were decomposed without the formation of important amount residues. The XRD study on the 1% residue observed, showed the presence of CaO, $CaSO_4$ (anhydride), and two modifications of SiO_2 (quartz and cristobalite) which probably derived from the upper layer of the ceiling deposits.

Evaporation of the aqueous extract resulted a colourless crystalline mass identified unambiguously as ammonium sulphate by IR and XRD. The ammonium sulphate content of various deposit samples collected was varied between 20-34 %. Ammonium sulphate decomposition proceeds in a complicated reaction route via consecutive decomposition steps [4] without formation of any solid residue: The formal summarized equation is:

$$(NH_4)_2SO_4 = 2NH_3 + H_2O + SO_2 + \text{'O'} \qquad (1)$$

Considering the available data about thermal decomposition of $(NH_4)_2SO_4$, the *m/z*=17 and 16 fragment pairs appeared in the first two decomposition steps (160-170 °C and 220-250 °C) belong to NH_3 and NH_2 fragments, however, the m/z=17 and 16 signals occurred at 350 °C probably belong to OH and O fragments. The first decomposition step is a simple NH_3 loss with formation of NH_4HSO_4, and the second step together with NH_3, SO_2 and oxygen formation belongs to further decomposition of NH_4HSO_4. Sulphonation by-reaction of the aromatic ring by SO_3 formed in situ by decomposition of ammonium pyrosulphate intermediate [5] may also be occurred. This could explain the presence of HO and O fragments without H_2O peaks at 330-340 °C due to desulphonation of the C-SO_2-OH fragment. Since no decomposition of organic compound(s) occurred at 160-170 °C, the *m/z*=44 band probably origined from ammonium sulphate decomposition, thus it had to be belonged to N_2O formation. The *m/z*=44 peak at 220-250 °C, however, probably belong to CO_2 because the oxidation of the organic component(s) can be occurred by the oxygen formed (Eqn. (1)) from the decomposition of ammonium sulphate, furthermore, other organic fragments can also be occurred in this temperature range.

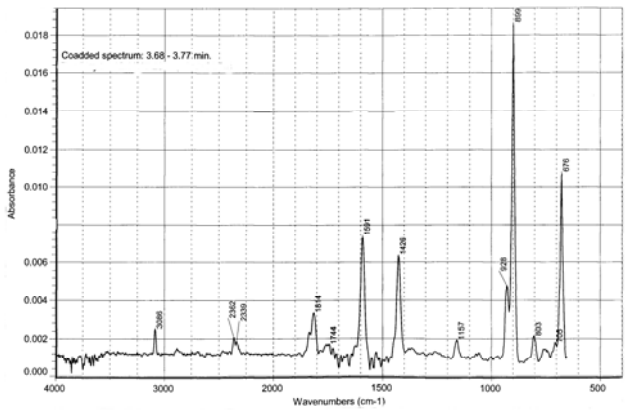


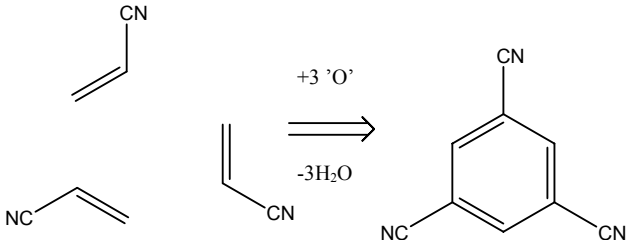
Fig.2 GC-IR of organic component found in the analyzed deposit material

Although acetonitrile proved to be the best solvent to remove the organic components, however, in order to avoid of interferences between the spectroscopic signals of nitrile group in MeCN and nitrile group of the unknown organic component, in the next experiments acetone was used. Surprisingly only one peak could be observed on the GC-MS chromatogram of the acetone extract at 2.51 min retention time (isothermal study), or at 13.7 min in the temperature programmed measurement. Similarly, only one peak was appeared in the GC-IR around 3.7 min (isothermal measurement) retention time.

Table 3. IR spectral data of organic component found in deposit material and 1,3,5-tricyanobenzene

Sample			
Solid	Gas phase	Authentic	Assignation
459	-	461	CC,CN
674	676	674	CC, CN
910	899	910	CH
931	928	931	CN, CC
1430	1426	1429	CN
2249	2250	2250	CN
3083	3086	3086	CH

The vibrational bands found in the IR spectrum of the only component separated by GC, was unambiguously show the presence of an aromatic ring and cyano groups. The residue formed by evaporation of the extract was recrystallized with acetone when a nest-like mass of colourless needles were formed. The IR spectrum of this compound completely agree/match with the IR spectrum of authentic 1,3,5-tricyanobenzene. The amount of this compound was varied between 64-78 % in each sample. The main characteristic bands of the isolated crystalline compound and its gaseous form can be seen in Table 3.



The agreement between the authentic sample and the spectrum of the needle like crystals unambiguously showed the identity of the questionable monomer compound, which could be formed by oxidative cyclotrimerization of acrylnitrile monomers. Another possible method to synthesise this compound is a cyclotrimerization reaction of cyanoacetylene formed during the pyrolysis of the acrylnitrile containing polymers. Cyclotrimerization of cyanoacetylene, however, always led exclusively to 1,2,3 and 1,2,4- isomers, because these were formed from 1,2-dicyanocyclobutadiene di-radical intermediate, and 1,3,5-isomer could have been formed only from 1,3-dicyanobutadiene di-radical. The formation of 1,2-dicyanocyclobutadiene di-radical is more favoured and the di-radical formed more stable in its tautomer forms, in which the nitrile moieties are in vicinal and not in 1,3-positions, therefore the formation of the 1,3,5-tricyanobenzene in this reaction cannot be expected[6].

Ammonium sulphate is formed as a decomposition product of the ammonium peroxodisulphate used as an oxidant in iron(III) catalyzed surface oxidation of poly(acrylonitrile-co-methylmethacrylate) fibers. The presence of decomposition product together with the cyclotrimerization product of the assumed reducing agent (acrylonitrile) confirms our postulation about the presence of an oxidative chemical reaction between acrylonitrile and ammonium peroxodisulphate by the formation of ammonium sulphate and 1,3,5-tricyanobenzene.

Results of mutagenecity studies

Mutation tests carried out with DMSO (1,3,5-tricyanobenzene) extracts of the deposit material using histidine-requiring auxotroph strains of *Salmonella typhimurium TA98* and *TA1537* exhibited mutagenic effect. The DMSO extracts contained 1,3,5-tricyanobenzene induced gene mutations by frameshifts in the genome of the used *Salmonella typhimurium TA98* and *TA1537*.

Conclusion

Based on IR, XRD, GC-MS, GC-IR and TG-MS methods the deposited material formed during pyrolysis of poly(acrylonitrile-co-methyl methacrylate) proved to be a mixture of ammonium sulphate 20-34 % and 1,3,5-tricyanobenzene 64-78 %. 1,3,5-Tricyanobenzene probably formed in the redox reaction of the liberated acrylonitrile and ammonium peroxodisulphate as a result of an oxidative cyclotrimerization reaction. 1,3,5-tricyanobenzene shows mutagenic activity on the growth of *Salmonella typhimurium TA98* and *TA1537* strains.

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STRUCTURE AND SPECTROSCOPY OF 3-CHLORO-4-FLUORO-1,2,5-THIADIAZOLE

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Keywords: thiadiazoles, ionization energy, infrared spectroscopy, photoelectron spectroscopy, IR, UPS, DFT, ab initio.

3-Chloro-4-fluoro-1,2,5-thiadiazole has been synthesized and investigated in the gas phase by IR spectroscopy and UV photoelectron spectroscopy. The ground-state geometry of the neutral molecule has been obtained from quantum-chemical calculations using the B3LYP/aug-cc-pV(T+d)Z method. Ionization potentials have been determined and the electronic structure has been discussed within the frame of molecular orbital theory. IR and photoelectron spectroscopies, supported by quantum-chemical calculations at the B3LYP and SAC-CI/aug-cc-pV(T+d)Z levels, provide a detailed investigation into the vibrational and electronic character of the molecule.

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1. Introduction

1,2,5-Thiadiazoles are important compounds in various fields of chemistry and biology due to their potential use as synthetic precursors, drugs in human medicine, agricultural protectors, organic conductors, and components of solar cells.[1,2] In addition, small derivatives received attention recently as precursors of reactive nitrile sulfide intermediates in photochemical processes.[3] The physical and chemical properties of the thiadiazole moiety can be finely modified by substituents attached to the thiadiazole ring, thus studying substituent effects is important in context of novel applications.

Small 1,2,5-thiadiazoles, mainly the symmetrically substituted derivatives ($X_2C_2N_2S$, where X= H, halogen, cyano, or alkyl), have been studied earlier.[4–9] The geometry of the dihydrogen and dichloro derivatives have been determined experimentally by microwave spectroscopy[4] and electron diffraction,[5,6] and the equilibrium geometries of the dihydrogen, difluoro, dichloro, dimethyl, and dicyano derivatives have been calculated by quantum chemical methods.[6,7,8,9] The structures of ionic states, considering the three lowest energy cationic states, have also been computed.[7] According to experiments and theory, the neutral thiadiazoles and the investigated radical cations have planar equilibrium structures. The vibrational and electronic properties of small 1,2,5-thiadiazoles have been studied by IR and Raman spectroscopies,[9, 10] and UV photoelectron spectroscopy.[7] Studies on unsymmetrically substituted thiadiazoles (XYC_2N_2S, where X≠Y) are relatively rare. The chloro and methyl derivatives (XHC_2N_2S, where X= Cl or CH_3) are known and the chloro derivative has been studied by IR/Raman[11] and photoelectron[12] spectroscopies. 3-Bromo-4-chloro-1,2,5-thiadiazole,[13] 3-iodo-4-chloro-1,2,5-thiadiazole,[13] and 3-chloro-4-fluoro-1,2,5-thiadiazole[14] have been synthesized, but their structures have not been thoroughly investigated by any experimental or theoretical means to date. The NMR data and IR band positions, supplementing the synthesis, have been published.[13,14]

In this work we present the gas-phase characterization of 3-chloro-4-fluoro-1,2,5-thiadiazole molecule and an investigation of its electronic and geometric structure by quantum-chemical methods and gas-phase spectroscopy. The latter includes He I and He II ultraviolet photoelectron spectroscopy (UPS) and mid-infrared (IR) spectroscopy.

2. Experimental section

3-Chloro-4-fluoro-1,2,5-thiadiazole was synthesized by modifying a known literature procedure[14] as follows. 10 g (64.5 mmol) 3,4-dichloro-1,2,5-thiadiazole and 4.5 g (77.6 mmol) anhydrous KF were suspended in 20 ml sulfolane and the mixture was refluxed overnight using an oil bath temperature of 180 ºC. Volatiles were then removed by distillation using vigorous stirring and an oil bath temperature of 200 ºC. 4.6 g raw product was obtained, which contained only small amounts of the side product difluoro and dichloro derivatives. Pure 3-chloro-4-fluoro-1,2,5-thiadiazole was obtained by distillation using a short Vigreoux column. The product (3.6 g, yield 40 %) is a colourless liquid with a boiling point of 109 °C at atmospheric pressure. ^{13}C-NMR ($CDCl_3$, 301 K): 133 ppm (C(Cl), d, $^2J_{CF}$ 163 Hz), 157 ppm (C(F), d, $^1J_{CF}$ 1106 Hz). ^{19}F-NMR ($CDCl_3$): –99 ppm.

NMR spectra of 3-chloro-4-fluoro-1,2,5-thiadiazole were recorded on a Bruker Avance 250 spectrometer using TMS and $CFCl_3$ as internal references.

The IR spectrum (resolution 1.0 cm^{-1}) of gaseous 3-chloro-4-fluoro-1,2,5-thiadiazole was recorded at room temperature on a Bruker IFS 28 FT-IR spectrometer equipped with a 22 cm single-pass glass cell. The cell, with

KBr windows, gave a spectral range from 4000 to 400 cm^{-1}. The effluent from the sample container was pumped continuously through the cell using a rotary vacuum pump while maintaining the pressure at 0.8 mbar.

The He I and He II ultraviolet photoelectron spectra (UPS) of the gaseous thiadiazole derivative were recorded using an Atomki ESA-32 photoelectron spectrometer described in detail elsewhere.[15] Photoelectron spectra were recorded using the constant transmission energy mode of the electron energy analyzer and were calibrated with the $Ar^+(^2P_{3/2,1/2})$ spin-orbit doublet. The resolution of the analyzer was 30 meV in He I measurements (fwhm for the Ar $^2P_{3/2}$ line). During the He II measurements the resolution of the electron energy analyzer was lowered to 80 meV (fwhm for the Ar $^2P_{3/2}$ line) in order to gain higher electron count rates.

3. Computational methods

The geometry of the ground state neutral molecule was calculated using the B3LYP method and harmonic vibrational frequencies were obtained to identify the structure as real minimum (zero imaginary frequencies) on the potential energy surface. The stability of B3LYP wave function was checked, and B3LYP wave function was found to be stable. Infrared intensities were calculated using the harmonic force field. Anharmonic vibrational wavenumbers were calculated at the B3LYP level within the framework of second-order vibrational perturbational theory. Vertical ionization energies (IEs) were calculated using the Symmetry Adapted Cluster/Configuration Interaction (SAC-CI) method using the geometry obtained at the B3LYP level. Calculations were done using the aug-cc-pVTZ basis set on C, F, N, and O atoms and aug-cc-pV(T+d)Z on Cl and S. Only valence electrons were correlated in SAC-CI calculation. All calculations were performed with the GAUSSIAN-09 quantum chemistry package.[16] References to original theoretical methods are listed in the program package manual.[17] For characterization of the normal vibrational modes of 3-chloro-4-fluoro-1,2,5-thiadiazole, the total energy distribution (TED), which provides a measure of the internal coordinate contributions, was determined.[18]

4. Results and discussion

4.1. Calculated equilibrium structure

Calculated structural data of 3-chloro-4-fluoro-1,2,5-thiadiazole is presented in Table 1 and the structure and numbering of atoms are shown in Figure 1. According to calculation, the molecule is planar and has C_S symmetry. The local C_{2v} symmetry of the thiadiazole ring is distorted due to unsymmetrical substitution by fluorine and chlorine atoms. The CN bond on the fluorine side is shorter than the CN bond connected to the chlorine atom. This is in agreement with the calculated structure of the difluoro and dichloro derivatives.[7] In general, bond lengths of the chloro-fluoro-derivative are between those of difluoro and dichloro derivatives. Bond orders can be calculated using the Gordy's rule[19] and by comparing the calculated bond lengths of the 3-chloro-4-fluoro-1,2,5-thiadiazole with those of molecules having typical single/double CC, CN, and NS bonds (H_3C–CH_3(1.527 Å)/H_2C=CH_2(1.325 Å), H_3C–NH_2(1.464 Å)/ H_2C=NH(1.264 Å), and H_2N–SH(1.721 Å)/HN=S(1.563 Å), calculated at the B3LYP/aug-cc-pV(T+d)Z level). C–N bonds, nominally double bonds, are between a single and a double bonds (bond order 1.76–1.81), and C–C and N–S bonds, nominally single bonds, are shorter than a C–C or N–S single bond (bond order 1.43 and 1.46, respectively). This tendency to bond order equalization is in agreement with the aromaticity of thiadiazoles.

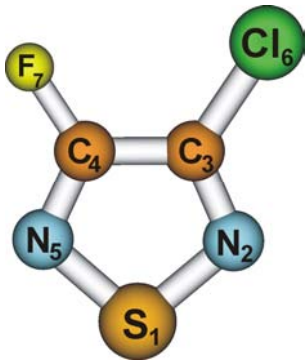

Figure 1. Structure of 3-chloro-4-fluoro-1,2,5-thiadiazole and numbering of atoms

Table 1. Calculated[a] equilibrium structure of 3-chloro-4-fluoro-1,2,5-thiadiazole

bond lengths / Å		bond angles /°	
S_1–N_2	1.642	$S_1N_2C_3$	107.0
N_2–C_3	1.305	$N_2C_3C_4$	113.1
C_3–C_4	1.430	$C_3C_4N_5$	115.1
C_4–N_5	1.296	$C_4N_5S_1$	106.2
N_5–S_1	1.643	$N_5S_1N_2$	98.6
C_3–Cl_6	1.714	$C_4C_3Cl_6$	123.9
C_4–F_7	1.321	$C_3C_4F_7$	123.1

[a]Calculated at the B3LYP/aug-cc-pV(T+d)Z level. See Figure 1 for numbering of atoms.

4.2. Gas-phase IR spectrum

The IR spectrum of gaseous 3-chloro-4-fluoro-1,2,5-thiadiazole is shown in Figure 2 with calculated and experimental vibrational wavenumbers listed in Table 2. IR bands of the molecule have been noted before[14] and are in general accord with the data given here. The calculated wavenumbers and IR intensities are in good agreement with experiment and support the band assignments. The calculated values indicate that twelve of the fundamentals should give rise to infrared bands above the 400 cm^{-1} cutoff of the instrument used in this experiment, however, two of them are not observed due to low IR intensity.

Using the calculated B3LYP/aug-cc-pV(T+d)Z rotational constants of 3-chloro-4-fluoro-1,2,5-thiadiazole, the asymmetry parameter κ is –0.52 and thus the molecule is a prolate asymmetric rotor (ρ^*= 1.36 and β= 1.03). The nonlinear planar structure, belonging to the C_S molecular point group, results in the species having fifteen normal modes of vibration, eleven of which are in the molecular plane (a') and four which are out-of-plane (a"). All vibrational modes are infrared active. The experimental fundamentals of a' symmetry are of A-type, B-type, or A/B-hybrid type, while those of a" symmetry modes are C-type bands with pronounced Q-branches. Using the equations of Seth-Paul[20] and the calculated rotational constants, the calculated PR separations for pure A, B, and C-type bands are 11, 8, and

16 cm^{-1}, respectively. In the gas-phase IR spectrum the PQR structure is clearly observed on many bands. The experimental PR separations for all A, B, and A/B type bands are in the range of 8–11 cm^{-1}, in good agreement with the predicted separations, and C-type bands are easily identified by their strong Q branch, notably at 713 and 531 cm^{-1}. The other two fundamentals of a" symmetry are not observed due to their low wavenumbers (below our detection limit of 400 cm^{-1}). Total energy distribution (TED) of the normal vibrational modes indicates that vibrations are strongly mixed. Detailed assignment is given in Table 2, and the simplified assignment below is based on the major internal coordinate contribution.

The highest energy fundamental of 3-chloro-4-fluoro-1,2,5-thiadiazole is observed at 1527 cm^{-1}. The corresponding IR band shows a B-type band structure with PR separation of 8 cm^{-1} and is assigned to one of the CN stretches. The second CN stretch, according to the calculation, must be assigned to the strong A/B type band at 1422 cm^{-1}. The weak B type band at 1334 cm^{-1} and the medium and weak A/B type bands at 873 and 813 cm^{-1} can be unambiguously assigned to thiadiazole-ring stretches. The band at 1334 cm^{-1} has significant CC character and the bands at 873 and 813 cm^{-1}, especially the latter, have dominant NS contribution. Molecules containing C–F bonds provide, in general, strong IR absorptions in the 1100 – 1300 cm^{-1} region due to CF stretches.[21] In the case of 3-chloro-4-fluoro-1,2,5-thiadiazole, a strong A/B type band is observed in the IR spectrum at 1121 cm^{-1}. Although the corresponding normal mode is strongly mixed (see TED), we assign this band to the CF stretch. The remaining four bands from very weak to weak at 768, 713, 599, and 531 cm^{-1} originate from in-plane and out-of-plane ring deformations.

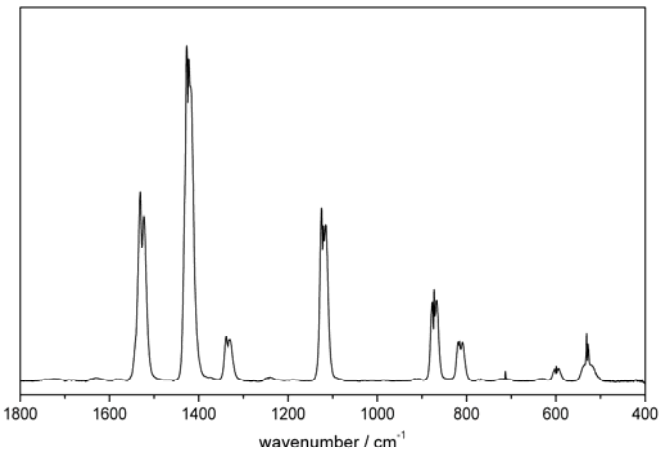

Figure 2. Gas-phase IR spectrum of 3-chloro-4-fluoro-1,2,5-thiadiazole

Table 2. Experimental and calculated vibrational wavenumbers (cm^{-1}) of 3-chloro-4-fluoro-1,2,5-thiadiazole

Experimental[a]	Calculated[b,c]	Intensity[b,d]	Assignment and description	TED[e]
1527 s	1517 (1551) a'	80	ν_1 C=N ring st	C_4N_5 st(60), N_2C_3 st(13), CF st(17)
1422 vs	1405 (1433) a'	210	ν_2 C=N ring st	N_2C_3 st(51), CF st(22), CC st(16)
1334 w	1327 (1356) a'	39	ν_3 C–C ring st	CC st(37), N_2C_3 st(28), C_4N_5 st(21)
1121 Q, s	1105 (1123) a'	96	ν_4 ip vibr (CF st)	r.b.(32), CF(23), CCl(19), C_4N_5(11), CC(11)
873 Q, m	860 (874) a'	48	ν_5 N–S ring st	N_5S_1 st(59), ring bend(15), CF ip rock(11)
813 w	804 (819) a'	22	ν_6 N–S ring st	S_1N_2 st(83)
768 Q (?), vw	765 (776) a'	0.3	ν_7 ip ring bend	ring bend(50), CC st(24)
713 Q, vw	726 (737) a"	2	ν_{12} oop ring def	r.t.(45), CF oop wag(36), CCl oop wag(19)
599 Q, vw	597 (608) a'	9	ν_8 ip ring bend	r.b.(57), CF st(20), N_5S_1 st(15)
531 Q, w	536 (543) a"	16	ν_{13} oop ring def	r.t.(75), CF oop wag(12), CCl oop wag(12)
n.o.	503 (509) a'	3	ν_9 ip CF bend	CF ip bend(45), CCl st(19)
n.o.	411 (414) a'	1	ν_{10} C–Cl st	CCl(39), CF ip bend(14), r.b.(12), S_1N_2(11)
n.o.	312 (316) a"	0.02	ν_{14} oop CF wag	CF oop wag(45), r.t.(24), CCl oop wag(22)
n.o.	215 (215) a'	0.2	ν_{11} ip CCl bend	CCl ip bend(67), CF ip bend(21)
n.o.	197 (201) a"	0.1	ν_{15} oop CCl wag	CCl oop wag(48), r.t.(45)

[a] Gas phase. Position of the most intense Q-band or the band centre is given. Abbreviations: s (strong), m (medium), w (weak), v (very). Additional very weak bands at 2648, 1244(Q) and 912 may belong to combination or overtone bands. [b] Calculated at the B3LYP/aug-cc-pV(T+d)Z level. Isotopes: ^{12}C, ^{14}N, ^{19}F, ^{35}Cl, ^{32}S. Asymmetric top parameters: $\kappa = -0.5165$, $\sigma = 7.2723$. [c] Anharmonic vibrational wavenumbers. Harmonic wavenumbers are in parenthesis. [d] In km mol^{-1}. Calculated using the harmonic force field. [e] Total vibrational energy distribution from force field analysis based on harmonic force constants. Contributions larger than 10% are provided. Abbreviations: st (stretching), r.b. (ring bend), r.t. (ring torsion), wag (wagging), oop (out-of-plane), ip (in-plane), def (deformation).

4.3. He I and He II photoelectron spectra

The He I and He II photoelectron spectra of 3-chloro-4-fluoro-1,2,5-thiadiazole are shown in Figure 3, and experimental and calculated ionization energies are listed in Table 3. SAC-CI calculations for vertical IEs give good agreement with experiment. From the calculated IEs, from the comparison of the He I and He II spectra utilizing relative ratios of photoionization cross sections, and from the comparison of the spectra of difluoro and dichloro derivatives,[7] the assignment is relatively straightforward.

The ground state electronic structure of 3-chloro-4-fluoro-1,2,5-thiadiazole is $^1A_1$. The sequence of molecular orbitals (MOs) deduced are

…..$(8a')^2(1a")^2(9a')^2(10a')^2(2a")^2(11a')^2(12a')^2(3a")^2(13a')^2(14a')^2(4a")^2(5a")^2$.

Molecular orbital plots are shown in Figure 3. A possible starting point to describe the electronic structure is to consider the MOs of a five-membered aromatic ring, modified with the two exocyclic fluorine and chlorine atoms. Three π orbitals, two nitrogen 'lone pair' orbitals (n_N), one on each N atom, and one sulfur 'lone pair' orbital (n_S) can be deduced from the thiadiazole moiety as low IE MOs, as well as five σ orbitals corresponding to five σ bonds of the ring. Ionization from some of these σ orbitals will produce photoelectron bands in the investigated IE region. These MOs are augmented, and mix to some extent, with MOs of substituents attached to the thiadiazole frame. The two nitrogen 'lone pairs' are best described as linear combinations, n_N^- and n_N^+. MO plots show that n_N^- is largely localised on N atoms, and hence it is well described as 'nitrogen lone pair', but n_N^+ strongly mixes with n_S. MOs in general are far from localised (see Figure 3), but in order to keep discussion simple we use the notations above.

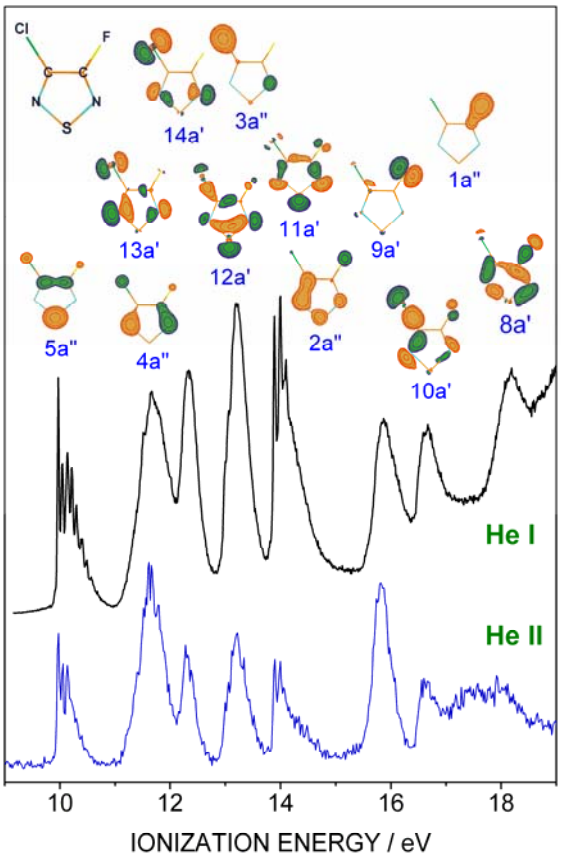

Figure 3. He I and He II photoelectron spectra of 3-chloro-4-fluoro-1,2,5-thiadiazole and schematics of the corresponding MOs

According to calculations, the first band in spectra at 9.97 eV can be unambiguously assigned to the π_3 MO. This PE band shows vibrational fine structure with a strong adiabatic transition. The band shape thus indicates a relatively small geometrical change due to ionization. The vibrational fine structure is not entirely resolved, but our best estimates indicate ionic vibrational wavenumbers of 1350±50 and 590±50 cm^{-1}. These values, comparing to the wavenumbers of the neutral molecule (see above), can be assigned to one of the ring stretches and one of the ring deformations of the ground state radical cation, respectively. The ionization energy of 3-chloro-4-fluoro-1,2,5-thiadiazole, 9.97 eV, is between the IEs of the dichloro and difluoro analogue,[7] which is in agreement with substituent effects of fluorine and chlorine atoms. The assignment of the next PE band at 11.66 eV is less straightforward. Calculations predict that ionization from n_N^- and π_2 MOs requires similar energy, and thus ionizations from two MOs are assigned to this PE band. The same situation has been observed in the spectra of difluoro and dichloro derivatives at 11.97 and 11.36 eV, respectively.[7] We note that the n_N^- and n_{Cl} MOs are strongly mixed (see SAC-CI coefficients in Table 3 and MO plots in Figure 3), but the assignment of this and the third band at 12.33 eV is supported by the relative intensity change of the corresponding bands comparing the He I and He II spectra. The assignment of the third band to one of the chlorine lone pair MOs is unambiguous considering the relatively narrow band shape and the relative intensity in the He II spectrum. The next band at 13.21 eV with a shoulder at 13.0 eV is assigned to two MOs, the first the second nitrogen lone pair, n_N^+, and the second the second chlorine lone pair MO. The next band at 13.99 eV is unambiguously assigned to n_S. The band has a vibrational fine structure, it is relatively strong in the He I spectrum, and its relative intensity is strongly reduced in the He II spectrum. All of these three characteristics have been observed in spectra of the parent and substituted 1,2,5-thiadiazoles investigated earlier.[7] It is thus a characteristic band of 1,2,5-thiadiazoles in the 13–15 eV region.

Table 3. Experimental and calculated[a] vertical ionization energies (eV) of 3-chloro-4-fluoro-1,2,5-thiadiazole

experimental	SAC-CI[b]	orbital character
9.97[c]	9.62 [0.98 (5a")]	π_3
11.66	11.13 [–0.76 (14a'), 0.58 (13a')]	n_N^-
	11.32 [–0.97 (4a")]	π_2
12.33	12.02 [–0.72 (13a'), –0.54 (14a')]	n_{Cl}
(13.0)	12.78 [0.83 (12a'), –0.33 (11a')]	n_N^+
13.21	13.17 [0.96 (3a")]	n_{Cl}
13.99[d]	13.69 [0.87 (11a'), 0.39 (12a')]	n_S
(14.3)	15.08 [0.92 (2a")]	π_1
15.86	15.76 [–0.82 (10a'), 0.49 (9a')]	n_F
16.6	16.60 [–0.82 (9a'), –0.49 (10a')]	$n_{Cl,term}$
(17.4)	17.65 [0.91 (1a")]	n_F
18.1	18.28 [0.93 (8a')]	σ_{ring}

[a]Calculated at the SAC-CI//B3LYP/aug-cc-pV(T+d)Z level. [b]Open-shell occupancy for single excitations and SAC-CI coefficients ($|c_i| > 0.3$) are provided in parenthesis. [c]Cationic vibrational wavenumbers: 1350±50 and 590±50 cm^{-1}. [d]Cationic vibrational wavenumber: 860±50 cm^{-1}; adiabatic IE: 13.89 eV.

There is a relatively low intensity band at 14.3 eV, which strongly overlaps with the n_S band. A similar band, also with low intensity, has been observed in the photoelectron spectra of other 1,2,5-thiadiazole derivatives in the 14-16 eV region,[7] thus according to this and CAS-CI calculations the band at 14.3 eV is assigned to the lowest energy π orbital. The last four PE band in the high energy region of the spectra at 15.86, 16.6, 17.4, and 18.1 eV are assigned to halogen atom lone pair orbitals and to one of the orbitals of the σ framework. The assignment is based on calculations (Table 3) and on comparing the spectra to those of the difluoro and dichloro derivatives.

5. Conclusion

The electronic, geometric, and vibrational properties of 3-chloro-4-fluoro-1,2,5-thiadiazole have been investigated in the gas phase by infrared spectroscopy, photoelectron spectroscopy, and theoretical calculations. According to calculations, the molecule has planar structure and C_S symmetry. The infrared and photoelectron spectroscopy has provided information on the fundamental vibrations and on the valence occupied levels of the neutral molecule, and on the sequence and fundamental vibrations of the low-lying cationic states.

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STUDIES ON CATALYTIC AROMATIZATION OF YANHUA FCC GASOLINE FRACTIONS

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Keywords: aromatization reaction; reaction condition; FCC gasoline; Yanhua; LPG

By using Yanhua FCC gasoline and a fraction of Yanhua FCC gasoline (boiling point < 90 °C) as a feedstock, the effects of reaction temperature, Weight Hour Space Velocity (WHSV), and feedstock performance on yields of LPG, aromatics and propylene production were studied in a confined fluidized bed reactor. The experimental results show that yields of aromatics, propylene, and aromatics + propylene for both Yanhua FCC gasoline and the selected fraction of Yanhua FCC gasoline increase with the increase of reaction temperature at the same WHSV. Yields of aromatics, propylene and aromatics+propylene decrease with the increase of WHSV at the same reaction temperature.

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Introduction

With increasing the requirements of environmental regulations to petroleum products, United States, Japan and other European countries [1] issued a new gasoline standard to decrease the olefin contents of gasoline, towards 25% (by volume) or even lower. [2] A new gasoline standard was put in practice from January 2003 in China because of the requirement of environmental protection.[3] As requested, the content of olefins, sulfur, benzene and other aromatic compounds had to be lower than 35 % (v/v), 0.08 % (m/m), 2.5 % (v/v) and 40 % (v/v), respectively, and the research octane number (RON) was required to be above 90 [4]. Owing to the enforcement of the new standards, all refineries have to face the challenge.[5] Nowadays, however, the portion of FCC (fluid catalytic cracking) gasoline in commercial gasolines is about 85 % (m/m) and their olefin concentration is roughly between 50 and 60 % (m/m) inspite of the improvement of fluid catalytic cracking technologies in China. Consequently, the average olefin content of gasoline measured in 60 refinery plants reaches 44.2%, opposite to the requirements of the new standards.[6] In order to satisfy the new Chinese Standard requirements, numerous new aromatization catalysts were studied.[7] Using these new catalysts the olefin content of gasoline could be transformed into a mixture of i-paraffins and aromatic compounds, which gradually improves the stability of gasolines and decreases their harmfully emitted amounts in the tail gas of cars, and ensures the appropriate gasoline octane number as well.[8]

In this paper, the distribution of aromatization reaction products of Yanhua FCC gasoline formed under different reaction conditions in a confined fluidized bed reactor is discussed.

EXPERIMENTAL

Feedstock

Yanhua FCC gasoline was obtained from an FCC Unit of Yanhua Petrochemical Company. The composition of gasoline fractions are shown in Table 1. The FCC gasoline was obtained from the Heavy Oil Fluid Catalytic Cracking Unit and was not treated at all, not hydrorefined and desulfurized, therefore it has high olefin content.

Table 1 Composition of Yanhua FCC gasoline and the selected fraction (b.p.<90 °C) of Yanhua FCC gasoline (%, v/v)

Feedstock	Yanhua FCC gasoline	The Yanhua FCC gasoline fraction
n-Paraffins	3.02	4.92
i-Paraffins	20.41	30.28
c-Paraffins	5.29	4.36
Olefins	51.47	57.69
Aromatics	19.81	2.75
Total	100.0	100.0

Catalyst

LBO-A catalyst (Pt/HZSM-5 (Si/Al=38) type), which was aged with 2 ml min^{-1} steam at 800 °C in a confined fluidized bed reactor, was obtained from Lanzhou Petrochemical. Its properties are shown in Table 2.

Table 2. Properties of LBO-A catalyst

Parameters	Value
Micro-activity Test Index (MATI), %	56
Apparent density, g/ml	0.8
Pore volume, ml/g	0.3
Surface area, m^2/g	85
Particle size distribution, % (by mass)	
<45.8 μm	20.6
45.8~111.0 μm	60.3
>111.0 μm	19.1

The micro-activity test index (MATI) was obtained by using a micro-reactor and light oil provided by Beijing Petroleum Chemical Institute with distillation range of 225 to 337 °C. The reaction temperature, reaction time, inflow oil amount, and catalyst weight in the micro-reactor were kept to be stable, namely 460 °C, 70 s, 1.56 g and 5.0030 ± 0.0010 g, respectively.

The liquid products of above reaction were distilled out and analyzed by using an SP 3420 Gas Chromatograph. MATI values are given as follows:

$$M = 1 - \frac{(m * W_2)}{m_1} \qquad (1)$$

where M is MATI value, %; m is liquid product weight, g; m_1 is the total inflow oil weight, g; W_2 is the mass fraction of diesel oil in the liquid product.

Apparatus

A confined fluidized bed reactor shown in Fig.1. was used in Yanhua FCC gasoline aromatization process. The instrument consists of five parts: oil and stream input system, reaction zone, temperature control, product separation, and collection system. Variable amount of distilled water was pumped into the furnace to evaporate and form steam, then the steam was mixed with the Yanhua FCC gasoline pumped by an other pump simultaneously at the outlet of a constant temperature box. The mixture was heated to approximately 450 °C in a preheated room before it entered the reactor.

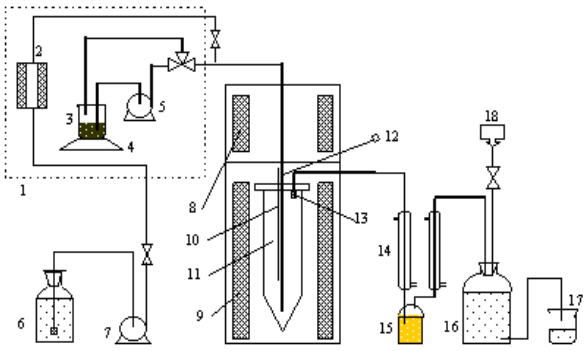

Fig.1 Schematic drawing of experimental apparatus

1-constant temperature room; 2-steam furnace; 3-feedstock; 4-electronic scale; 5-gasoline pump; 6-water tank; 7-water pump; 8-preheated room; 9-furnace; 10-thermocouple; 11-reactor; 12-catalyst inlet; 13-filter; 14-condenser; 15-liquid product collection bottle; 16-gas collection bottle; 17-beaker; 18-gas sample bag

Analytical methods

An HP6890 Gas Chromatograph with ChemStation software was used to measure the volume percentage of aromatizated gas components. The measured data were converted to mass percentage using the equation of state for ideal gases. The aromatized liquid was analyzed with TSY-1132 (Measure Coke Equipment) to obtain the mass percentage of paraffins, olefins, and aromatics. The mass percentage of coke on catalyst was measured with KJ-02 Fast and Exact Measuring Coke Equipment.

RESULTS AND DISCUSSION

Effects of reaction temperature and WHSV on the yield of products formed from Yanhua FCC gasoline

Table 3 shows the relations between reaction temperature, WHSV and the yields of reaction products formed from Yanhua FCC gasoline. When WHSV increased, gasoline had less contact time with the catalyst. It means that gasoline had not much time to react with the catalyst, so yields of off-gas, LPG and coke decreased with the increase of WHSV at the same reaction temperature, but yield of light oil increased with the increase of WHSV at the same reaction temperature. When reaction temperature increased, the catalytically active energy content of the system increased. It means that the probability of the crack reactions increased. The experimental results show that yields of off-gas, LPG, and coke increased with the increase of reaction temperature at the same WHSV, but yield of light oil decreased with the increase of reaction temperature at the same WHSV.

Table 3 Effect of reaction temperature and WHSV on the yields (%) of reaction products formed from Yanhua FCC gasoline [9]

Tempera-ture, °C	WHSV, h^{-1}	Off-gas	LPG	Light oil	Coke	Total
	10	0.4	8.7	90.3	0.6	100.0
430	20	0.3	7.6	91.6	0.5	100.0
	30	0.2	7.0	92.4	0.4	100.0
	10	0.5	10.1	88.6	0.8	100.0
450	20	0.4	8.9	90.0	0.7	100.0
	30	0.3	8.3	90.8	0.6	100.0
	10	0.6	12.1	86.4	0.9	100.0
470	20	0.5	9.5	89.2	0.8	100.0
	30	0.4	8.6	90.3	0.7	100.0

Note: Catalyst to oil and water to oil are 6 and 0.05, respectively.

Table 4 indicates the relationships between reaction temperature, WHSV and the yields of light oil. When reaction temperature increased at the same WHSV values, catalytically active energy content of the system increased. This means that the condensation and the isomerization reactions became more intensive, thus the yield of olefins decreased with the increase of reaction temperature at the same WHSV. The yields of aromatic and isoparaffin hydrocarbons, however, increased with the increase of reaction temperature at the same WHSV.

On the other hand, the yields of olefin and aromatic compounds decreased with the increase of WHSV, however, the yield of i-paraffin hydrocarbons increased with the increase of WHSV at the same reaction temperature. These phenomena can be explained as follows: contact time of gasoline and catalyst decreased with the increase of WHSV and gasoline had no more time to react with the catalyst.

Table 4 Effect of reaction temperature and WHSV on the yields (%) of light oil components from Yanhua gasoline[9]

Temperature, °C	WHSV, h^{-1}	n-Paraffins	i-Paraffins	c-Paraffins	Olefins	Aromatics
	10	3.40	25.15	6.03	29.18	36.24
430	20	3.45	26.21	5.83	28.82	35.69
	30	3.39	27.78	7.92	27.45	33.46
	10	3.48	25.46	6.14	28.17	36.75
450	20	3.54	26.45	6.04	27.69	36.28
	30	3.49	27.98	6.42	26.68	35.43
	10	4.05	31.91	6.23	17.62	40.19
470	20	4.12	32.04	7.87	16.47	39.50
	30	4.09	33.15	8.65	15.45	38.66

Table 5 shows the relations between reaction temperature, WHSV and the yields of LPG production from Yanhua FCC gasoline. When WHSV increased at the same reaction temperature, the isomerization and the crack reaction probabilities increased. The experimental results proved the above assumption, because the yields of propylene and i-butane increased, but the yields of n-butane, 2-butylene and 1-butylene decreased with the increase of WHSV at the same reaction temperature. On the other hand, when reaction temperature increased at the same WHSV, the intensity of crack reactions could be increased, while the probability of isomerization reactions was decreased. Consequently, as it was observed, the yield of propylene increased while the yield of i-butane decreased with the increase of reaction temperature at the same WHSV values.

Table 5 Effect of reaction temperature and WHSV on the yields of LPG production from Yanhua FCC gasoline (%, m/m)[9]

Temperature, °C	WHSV, h^{-1}	propane	propylene	i-butane	n-butane	2-butene	1-butene	i-butylene
	10	1.5	43.6	10.1	2.4	14.5	6.7	21.2
430	20	1.5	45.7	11.7	2.1	13.4	5.8	19.8
	30	1.4	46.1	12.2	1.7	12.7	4.9	21.0
	10	2.0	48.4	8.5	1.7	13.7	5.8	19.9
450	20	1.8	49.7	9.1	1.5	12.4	5.1	20.4
	30	1.6	50.4	10.6	1.0	11.5	4.8	20.1
	10	1.4	52.4	4.4	1.4	13.4	6.2	20.8
470	20	1.5	53.1	6.7	0.8	12.5	5.4	20.0
	30	1.5	54.0	8.6	0.5	11.1	4.9	19.4

Note: Catalyst to oil and water to oil are 6 and 0.05, respectively.

Table 6 indicates the relationship between reaction temperature, WHSV, and the yields of aromatics and propylene from Yanhua FCC gasoline. When WHSV increased at the same reaction temperature, the probability of isomerization and crack reactions simultaneously decreased. The experimental results proved the assumption that the catalyst had not much time to contact with gasoline, thus the yields of aromatics, propylene, and aromatics + propylene decreased with the increase of WHSV at the same reaction temperature. On the other hand, when temperature increased at the same WHSV, isomerization and crack reactions could be occurred. The experimental results proved that the catalytically active energy content of the system increased, thus isomerization and crack reactions occurred, therefore the yields of aromatics, propylene, and aromatics + propylene increased with the increase of reaction temperature at the same WHSV.

Table 6 Effect of reaction temperature and WHSV on the yield (%) of aromatics and propylene from Yanhua FCC gasoline (%, m/m)[9]

Temperature, °C	WHSV, h^{-1}	Aromatics	Propylene	Aromatics+ propylene
	10	36.1	3.79	39.89
430	20	35.7	3.47	39.17
	30	33.4	3.23	36.63
	10	36.7	4.89	41.59
450	20	36.3	4.42	40.72
	30	35.4	4.18	39.58
	10	40.1	6.34	46.44
470	20	39.5	5.04	44.54
	30	38.6	4.64	43.24

Note: Catalyst to oil and water to oil are 6 and 0.05, respectively.

Effects of reaction temperature and WHSV on fraction of Yanhua FCC gasoline (boiling point < 90 °C)

Table 7 shows the relationships between reaction temperature, WHSV and the yields of fraction formed from Yanhua FCC gasoline. The trends obtained using the selected fraction of Yanhua gasoline (b.p.<90 °C) were the same as the trends observed at Yanhua FCC gasoline. When WHSV increased, gasoline had less time to contact with the catalyst, so yields of LPG and coke decreased with the increase of WHSV at the same reaction temperature. The yield of light oil increased with the increase of WHSV at the same reaction temperature. When reaction temperature increased the catalytically active energy content also increased. It means that more crack reactions took place. The experimental results showed that yields of LPG and coke increased with the increase of reaction temperature at the same WHSV, while the yield of light oil decreased with the increase of reaction temperature at the same WHSV.

Table 7 Effect of reaction temperature and WHSV on the yields (%) of products from a Yanhua FCC gasoline fraction (b.p.<90 °C)

Tempera-ture, °C	WHSV, h^{-1}	Off-gas	LPG	Light oil	Coke	total
	10	0.1	5.5	93.7	0.7	100.0
430	20	0.1	5.1	93.9	0.9	100.0
	30	0.1	4.6	94.1	1.2	100.0
	10	0.1	6.7	92.4	0.8	100.0
450	20	0.2	6.0	92.8	1.0	100.0
	30	0.2	5.4	93.7	1.3	100.0
	10	0.5	9.4	89.2	0.9	100.0
470	20	0.5	8.0	90.4	1.1	100.0
	30	0.6	6.5	91.5	1.4	100.0

Note: catalyst to oil and water to oil are 6 and 0.05, respectively.

Table 8 indicates the relationships between reaction temperature, WHSV and the yields of products from a selected fraction (<90°C) of Yanhua FCC gasoline. When reaction temperature increased at the same WHSV, the catalytically active energy content increased. This means that the probability of the condensation and the isomerization reactions increased, therefore the yields of olefins and i-paraffins decreased with the increase of reaction temperature at the same WHSV, however, the yields of aromatics increased with the increase of reaction temperature at the same WHSV.

On the other hand, yields of aromatics decreased with the increase of WHSV at the same reaction temperature, but yields of i-paraffins and olefins increased with the increase of WHSV at the same reaction temperature. These phenomena are explained as follows: contact time of gasoline and catalyst decreased with the increase of WHSV and gasoline had not much time to react with the catalyst.

Table 9 shows the relationships between reaction temperature, WHSV, and yields of LPG production of a selected fraction (b.p. <90 °C) of Yanhua FCC gasoline. When WHSV increased at the same reaction temperature, the crack reactions became more frequent. The experimental results proved the assumption, that the yields of propane, i-butane, n-butane, 2-butylene, and 1-butylene were increased with the increase of WHSV at the same reaction temperature, but the yields of propylene and i-butylene decreased with the increase of WHSV at the same reaction temperature.

On the other hand, when reaction temperature increased at the same WHSV, the probability of crack and isomerization reactions decreased. For example, the yields of propylene and propane increased with the increase of reaction temperature at the same WHSV.

Table 8 Effect of reaction temperature and WHSV on the yield (%) of light oil components from a fraction (b.p.<90 °C) of Yanghua gasoline

Temperature, °C	WHSV, h^{-1}	n-Paraffins	i-Paraffins	c-Paraffins	Olefins	Aromatics
	10	4.76	35.31	8.49	36.12	15.32
430	20	4.81	35.74	7.98	36.43	15.04
	30	4.79	36.21	6.98	37.35	14.67
	10	4.87	35.64	9.81	31.84	17.84
450	20	4.80	35.98	8.64	33.33	17.25
	30	4.86	36.54	7.18	35.64	15.78
	10	4.98	37.78	8.70	28.90	19.64
470	20	5.12	38.17	7.66	29.64	19.41
	30	5.07	39.76	5.90	30.81	18.46

Note: Catalyst to oil and water to oil are 6 and 0.05, respectively.

Table 10 indicates the relationships between reaction temperature, WHSV, and the yields of aromatic hydrocarbons and propylene from the selected fraction (b.p.<90 °C) of Yanhua FCC gasoline. The trends obtained were the same as the trends observed at unfractionated Yanhua FCC gasoline. When WHSV increased at the same reaction temperature, the isomerization and the crack reactions probability decreased. The experimental results proved the assumption that the catalyst had no more time to contact with gasoline, thus the yields of aromatics, propylene and aromatics + propylene decreased with the increase of WHSV at the same reaction temperature. When reaction temperature increased at the same WHSV, isomerization and crack reactions were intensified. The experimental results proved that catalytically active energy content, the isomerization and the crack reactions, the yields of aromatics, propylene, and aromatics+ propylene increased with the increase of reaction temperature at the same WHSV.

Table 9 Effect of reaction temperature and WHSV on the yields of LPG products from the fraction of Yanhua FCC gasoline (b.p. < 90 °C) (%, m/m)[9]

Temperature, °C	WHSV, h^{-1}	propane	propene	i-butane	n-butane	2-butene	1- butene	i- butene
	10	2.3	44.7	8.6	2.1	13.8	5.2	23.3
430	20	2.7	40.6	10.4	2.9	14.1	5.4	23.9
	30	3.1	38.6	13.7	3.6	14.7	5.8	20.5
	10	2.6	48.2	8.1	1.8	12.7	4.8	21.8
450	20	2.6	44.2	9.6	3.4	13.4	5.1	21.7
	30	3.2	39.8	12.4	4.2	13.9	5.6	20.9
	10	2.8	52.4	7.7	1.8	11.5	4.8	19
470	20	3.1	51.1	8.4	2.4	11.9	5.0	18.1
	30	3.4	50.3	9.1	3.2	12.4	5.4	16.2

Note: catalyst to oil and water to oil are 6 and 0.05, respectively.

Table 10 Effect of reaction temperature and WHSV on the yields of aromatics and propylene from a fraction of Yanhua FCC gasoline (b.p. <90°C) (%, m/m)

Temperature, °C	WHSV, h^{-1}	Aromatics	Propylene	Aromatics+ propylene
	10	15.3	0.84	16.14
430	20	15.0	0.77	15.77
	30	14.6	0.67	15.27
	10	17.9	1.20	19.1
450	20	17.2	1.03	18.23
	30	15.7	0.85	16.55
	10	19.6	1.84	21.44
470	20	19.4	1.55	20.95
	30	18.5	1.20	19.7

Note: Catalyst to oil and water to oil are 6 and 0.05, respectively.

Conclusion

Aromatization reactions of Yanhua FCC gasoline and a fraction of Yanhua FCC gasoline (b.p.<90 °C) have been studied by using LBO-A as catalyst in a confined fluidized bed reactor. The experimental results are shown as follows:

(1) Yields of off-gas, LPG, and coke decreased with the increase of WHSV at the same reaction temperature, but yields of light oil increased with the increase of WHSV at the same reaction temperature; yields of off-gas, LPG, and coke increased with the increase of reaction temperature at the same WHSV, but yields of light oil decreased with the increase of reaction temperature at the same WHSV.

(2) Yields of olefin and i-paraffin hydrocarbons decreased with the increase of reaction temperature at the same WHSV, but yields of aromatics increased with the increase of reaction temperature at the same WHSV; yields of olefins and aromatics decreased with the increase of WHSV at the same reaction temperature, but yields of i-paraffins increased with the increase of WHSV at the same reaction temperature.

(3) Yields of propylene and i-butane increased with the increase of WHSV at the same reaction temperature, but yields of n-butane, 2-butylene and 1-butylene decreased with the increase of WHSV at the same reaction temperature; yields of propylene increased with the increase of reaction temperature at the same WHSV, while yields of i-butane decreased with the increase of reaction temperature at the same WHSV.

(4) Yields of aromatics, propylene and aromatics plus propylene decreased with the increase of WHSV at the same reaction temperature; yields of aromatics, propylene and aromatics + propylene increased with the increase of reaction temperature at the same WHSV.

(5) Reaction results obtained with a selected fraction (b.p. <90 °C) of Yanhua FCC gasoline showed the same trend and gave almost the same results as the Yanhua FCC gasoline.

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PRODUCT DISTRIBUTION AND REACTION KINETICS IN THE AROMATIZATION OF YANHUA FCC GASOLINE

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Keywords: reaction condition; reaction kinetics; FCC gasoline; Yanhua; LPG.

By using Yanhua FCC gasoline and a selected fraction of Yanhua FCC gasoline as feedstocks, the effects of reaction temperature, Weight Hour Space Velocity (WHSV), and feedstock performance on yields of LPG, aromatics, and propylene production were investigated in a confined fluidized bed reactor. The experimental result show that yields of aromatics, propylene, and aromatics + propylene for both Yanhua FCC gasoline and fraction of Yanhua FCC gasoline increase with the increase of reaction temperature at the same WHSV. Yields of aromatics, propylene, and aromatics + propylene decrease with the increase of WHSV at the same reaction temperature. Eight-lump kinetics and ten-lump kinetics are pointed out. The experimental results show that both kinetic models can predict the distribution of gasoline conversion and the composition of hydrocarbons of gasoline products under the different reaction conditions.

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Introduction

With increasing environmental regulations to petroleum products, USA, Japan, and EU countries[1] had to issue a new gasoline standard in order to decrease the olefin content of gasoline, towards 25% (by volume) or even lower.[2] A new gasoline standard was put into practice in January 2003 in China, because of the requirement of environmental protection.[3] As requested, the content of olefins, sulphur, benzene, and other aromatics had to be lower than 35v%, 0.08m%, 2.5v% and 40v%, respectively, and the research octane number (RON) was required to be above 90.[4] Owing to the enforcement of the new standard, many refineries have to face the challenge.[5] However, at present, the portion of fluid catalytic cracking (FCC) gasoline in commercial gasoline is about 85% and their olefin concentration is roughly between 50 and 60% in spite of the improvement of fluid catalytic cracking technology in China. The average olefin content of gasoline in 60 refinery plants reaches 44.2%. All of these are in contrast with the new standard.[6] In order to satisfy the Chinese New Standard, new aromatization catalysts were studied.[7] Using these catalysts, the olefin content of gasoline is transformed into i-paraffins and aromatics, which gradually improves the stability of gasoline and decreases their harmfully emitted amounts in the tail gas of cars, as well as ensures the gasoline octane number (Li, et al., 2003).[8] In this paper, the distribution of aromatization reaction products of Yanhua FCC gasoline are studied under different reaction condition in a confined fluidized bed reactor. Eight-lump kinetics and ten-lump kinetics are pointed out in order to predict the distribution of gasoline conversion and the composition of hydrocarbons of gasoline products.

Experimental section

Feedstock

Yanhua FCC gasoline was obtained from an FCC Unit of Yanhua Petrochemical Company. The compositions of gasoline and the selected gasoline fraction are shown in Table 1.

Table 1. Compositions of Yanhua FCC gasoline and fraction of Yanhua FCC gasoline (v%)

Feedstock	**Yanhua FCC gasoline**	**fraction of Yanhua FCC gasoline** (boiling point < 90°C)
Paraffin	27.8	38.5
Olefin	52.2	58.7
Aromatics	20.0	2.8
Total	100	100

Catalyst

LBO-A catalyst, which was aged with 2ml/min vapor at 800 °C in a confined fluidized bed reactor, was obtained from Lanzhou Petrochemical Institute. Its properties are presented in Table 2.

Table 2. Properties of LBO-A catalyst

Parameters	**Value**
Micro-activity Test Index (MATI), %	56
Apparent density, g/ml	0.8
Pore volume, ml/g	0.3
Surface area, m^2/g	85
Particle size distribution, % (by mass)	
<45.8 μm	20.6
45.8~111.0 μm	60.3
>111.0 μm	19.1

Apparatus

A confined fluidized bed reactor[9] shown in Figure 1, was applied in the Yanhua FCC gasoline aromatization. It consisted of five parts: oil and stream input system, reaction zone, temperature control, product separation, and collection system. Variable amount of distilled water was pumped into the furnace to evaporate it into steam, and then steam was mixed with the Yanhua FCC gasoline pumped simultaneously by another pump at the outlet of a constant temperature box. The mixture was heated to approximately 450 °C in a preheated room before it entered the reactor.

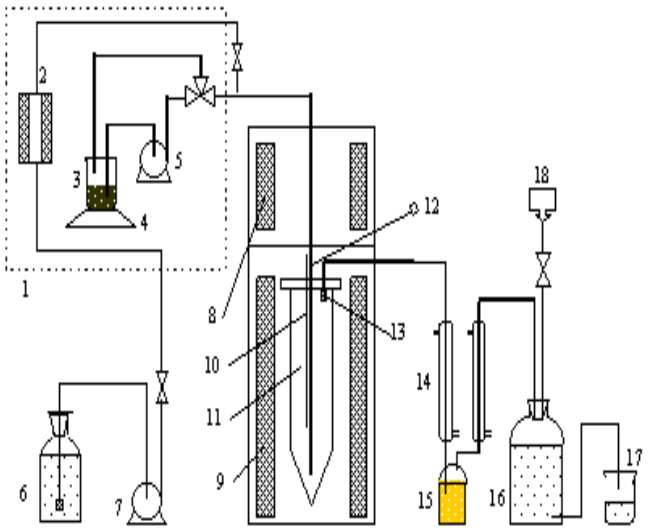


Figure 1 Schematic drawing of experimental apparatus

Analytical method

A HP6890 Gas Chromatograph with Chem Station software was used to measure the volume percentage of aromatization of gas components. These data were converted to mass percentages using the equation of state for ideal gases. The aromatized liquid was analyzed with TSY-1132 to obtain the mass percentages of paraffins, olefins, and aromatics. The mass percentage of coke on catalyst was measured with KJ-02 Fast and Exact Measuring Coke Equipment.

Results and discussion

Effects of reaction temperature and WHSV on yield of LPG, aromatics, and propylene production of Yanhua FCC gasoline

Table 3 shows the relations between reaction temperature, WHSV and the yield of LPG production of Yanhua FCC gasoline. Yields of propylene and i-butane increased with the increase of WHSV at the same reaction temperature, however, yields of n-butane, 2-butylene, and 1-butylene decreased with the increase of WHSV at the same reaction temperature. Yield of propylene increased with the increase of reaction temperature at the same WHSV, but yields of i-butane, n-butane, and 2-butylene decreased with the increase of reaction temperature at the same WHSV.

Table 4 indicates the relationship between reaction temperature, WHSV, and yield of aromatics and propylene of Yanhua FCC gasoline. Yields of aromatics, propylene, and aromatics + propylene increase with the increase of reaction temperature at the same WHSV. Yields of aromatics, propylene, and aromatics + propylene decrease with the increase of WHSV at the same reaction temperature.

Table 3. Effect of reaction temperature and WHSV on the yield of LPG production of Yanhua FCC gasoline (wt%)[9]

Temperature, °C	WHSV, h^{-1}	propane	propylene	i-butane	n-butane	2-butylene	1-butylene	i-butylene
430	10	1.5	43.6	10.1	2.4	14.5	6.7	21.2
	20	1.5	45.7	11.7	2.1	13.4	5.8	19.8
	30	1.4	46.1	12.2	1.7	12.7	4.9	21.0
450	10	2.0	48.4	8.5	1.7	13.7	5.8	19.9
	20	1.8	49.7	9.1	1.5	12.4	5.1	20.4
	30	1.6	50.4	10.6	1.0	11.5	4.8	20.1
470	10	1.4	52.4	4.4	1.4	13.4	6.2	20.8
	20	1.5	53.1	6.7	0.8	12.5	5.4	20.0
	30	1.5	54.0	8.6	0.5	11.1	4.9	19.4

Note: Catalyst to oil and water to oil are 6 and 0.05, respectively.

Effects of reaction temperature and WHSV on the yield of LPG, aromatics, and propylene production of the fraction of Yanhua FCC gasoline (boiling point < 90 °C)

Table 5 shows the relationship between reaction temperature, WHSV, and yield of LPG production for the fraction of Yanhua FCC gasoline. Yields of propane, i-butane, n-butane, 2-butylene, and 1-butylene increase with the increase of WHSV at the same reaction temperature, however, yields of propylene and i-butylene decrease with the increase of WHSV at the same reaction temperature. Yield of propylene increases with the increase of reaction temperature at the same WHSV, but yields of i-butane, n-butane, 2-butylene, 1-butylene, and i-butylene decrease with the increase of reaction temperature at the same WHSV.

Table 6 indicates the relationship between reaction temperature, WHSV, and yield of aromatics and propylene for the fraction of Yanhua FCC gasoline. Yields of aromatics, propylene, and aromatics + propylene increase with the increase of reaction temperature at the same WHSV. Yields of aromatics, propylene, and aromatics + propylene decrease with the increase of WHSV at the same reaction temperature.

Table 4. Effect of reaction temperature and WHSV on the yield of aromatics and propylene of Yanhua FCC gasoline (wt%)[9]

Temperature, °C	WHSV, h^{-1}	Aromatics	Propylene	Aromatics + Propylene
430	10	36.1	3.79	39.89
	20	35.7	3.47	39.17
	30	33.4	3.23	36.63
450	10	36.7	4.89	41.59
	20	36.3	4.42	40.72
	30	35.4	4.18	39.58
470	10	40.1	6.34	46.44
	20	39.5	5.04	44.54
	30	38.6	4.64	43.24

Note: Catalyst to oil and water to oil are 6 and 0.05, respectively.

Table 5. Effect of reaction temperature and WHSV on the yield of LPG production of the fraction of Yanhua FCC gasoline (boiling point < 90 °C) (wt%)[9]

Temperature, °C	WHSV, h^{-1}	propane	propylene	i-butane	n-butane	2-butylene	1-butylene	i-butylene
430	10	2.3	44.7	8.6	2.1	13.8	5.2	23.3
	20	2.7	40.6	10.4	2.9	14.1	5.4	23.9
	30	3.1	38.6	13.7	3.6	14.7	5.8	20.5
450	10	2.6	48.2	8.1	1.8	12.7	4.8	21.8
	20	2.6	44.2	9.6	3.4	13.4	5.1	21.7
	30	3.2	39.8	12.4	4.2	13.9	5.6	20.9
470	10	2.8	52.4	7.7	1.8	11.5	4.8	19
	20	3.1	51.1	8.4	2.4	11.9	5.0	18.1
	30	3.4	50.3	9.1	3.2	12.4	5.4	16.2

Note: Catalyst to oil and water to oil are 6 and 0.05, respectively.

Table 6. Effect of reaction temperature and WHSV on the yield of aromatics and propylene of the fraction of Yanhua FCC gasoline (boiling point < 90 °C) (wt%)[9]

Temperature, °C	WHSV, h^{-1}	Aromatics	Propylene	Aromatics + Propylene
430	10	15.3	0.84	16.14
	20	15.0	0.77	15.77
	30	14.6	0.67	15.27
450	10	17.9	1.20	19.1
	20	17.2	1.03	18.23
	30	15.7	0.85	16.55
470	10	19.6	1.84	21.44
	20	19.4	1.55	20.95
	30	18.5	1.20	19.7

Note: Catalyst to oil and water to oil are 6 and 0.05, respectively.

Table 7. Raw materials and products' lump division[10]

Gasoline (C_5-205 ºC)					LPG (C_3-C_4)		Diesel (>205 ºC)	Off-gas (C_1,C_2,H_2)	Coke
n-paraffin	i-paraffin	olefin	c-paraffin	aromatics	paraffin	olefin	diesel	gas	
Np	Ip	O	N	A	Pg	Og	Do	Dg	Ck

Table 8. Typical experimental results of FCC reaction at different conditions [10]

T(K)	$\varphi_{c/o}$	t_V (s)	y_{GP} (%)	y_{GO} (%)	y_{GN} (%)	y_{GA} (%)	y_{DG} (%)	y_{LPG} (%)	y_{LCO} (%)	y_{COKE} (%)
823	8.0	2.0	28.70	17.74	9.85	19.11	1.48	16.14	4.54	2.13
823	8.0	4.0	24.57	7.97	6.55	21.27	2.64	25.87	5.18	5.27
823	13.0	2.0	26.30	11.32	8.12	20.82	2.21	21.59	5.05	3.78
853	8.0	2.0	27.86	15.54	10.43	20.02	2.56	16.85	4.39	2.02
853	8.0	4.0	23.58	6.69	6.52	21.79	4.12	26.98	5.13	4.93
853	13.0	2.0	25.40	9.74	8.27	21.51	3.47	22.45	4.95	3.58
873	8.0	2.0	27.33	14.39	10.71	20.43	3.40	16.57	4.31	1.95
873	8.0	4.0	22.91	5.99	6.51	21.97	5.42	26.87	5.09	4.67
873	13.0	2.0	24.78	8.84	8.35	21.82	4.58	22.11	4.89	3.41

Table 9. Results of reaction kinetic parameters [10]

$k = f(T)$ (m^3 (g_{cat} $s)^{-1}$)	E_{ji}
$k_{GP,GP}$ = exp(2.4664-2830/T)	23036 ± 45
$k_{GP,GD}$ = exp(4.3282-4329/T)	35991 ± 27
$k_{GP,LPG}$ = exp(1.6540-1888/T)	15697 ± 16
$k_{GP,COKE}$ = exp(4.3775-4920/T)	40905 ± 30
$k_{GO,GP}$ = exp(2.0565-1775/T)	14757 ± 43
$k_{GO,GN}$ = exp(1.3698-1096/T)	9112 ± 13
$k_{GO,DG}$ = exp(3.2172-3169/T)	26347 ± 22
$k_{GO,LPG}$ = exp(2.3665-1574/T)	13086 ± 80
$k_{GO,LCO}$ = exp(0.7626-1221/T)	10151 ± 29
$k_{GO,COKE}$ = exp(5.1227-4975/T)	41362 ± 36
$k_{GN,GO}$ = exp(0.6411-867/T)	7208 ± 42
$k_{GN,GA}$ = exp(1.8989-1894/T)	15747 ± 29
$k_{GN,DG}$ = exp(4.7073-5235/T)	43524 ± 73
$k_{GN,LPG}$ = exp(1.4000-1795/T)	14924 ± 56
$k_{GN,LCO}$ = exp(6.4059-6720/T)	55870 ± 22
$k_{GN,COKE}$ = exp(3.8854-3801/T)	31602 ± 49
$k_{GA,DG}$ = exp(-1.7427-1865/T)	15506 ± 24
$k_{GA,LCO}$ = exp(1.8889-3786/T)	31477 ± 17
$k_{GA,COKE}$ = exp(0.3454-1607/T)	13361 ± 58
$k_{LPG,DG}$ = exp(-0.0837-1974/T)	16412 ± 71
$k_{LCO,COKE}$ = exp(1.7184-3126/T)	25990 ± 72

Eight-lump kinetics model[10]

By using Y-type zeolite as a catalyst, FCC gasoline composition is divided into eight parts, including dry gas (DG), liquefied petroleum gas (LPG), aromatics (GA), olefin (GO), naphthene (GN), paraffin (GP), coke (COKE), and light circle oil (LCO). The cracking reaction, hydrogen transfer reaction, aromatisation, isomerisation and alkylation are considered and the reaction network is reasonably simplified (see Figure 2). The kinetic parameters through the hybrid genetic algorithm are established. The results show that this model can predict the distribution of gasoline conversion and the composition of olefins and aromatics of gasoline products under the different reaction conditions.

Table 8 shows typical experimental results of FCC reaction under different conditions. In this table, it can be clearly seen that y_{GP}, y_{GO}, and y_{COKE} are decreasing, while y_{GN}, y_{DG}, y_{LCO}, and y_{GO} are increasing with the increase of reaction temperature; the y_{LPG} first increases and then decreases when reaction temperature goes up.

Table 9 indicates the estimated values of average activation energies and the expressions of kinetic constants. Table 10 represents comparison of production yields for all lumps between experimental and predicted results. The experimental results show that predicted values are close to experimental results.

Table 10. Comparison of predicted and experimental production yields [10]

Item	Experimental	Predicted	Experimental	Predicted
T (K)	773		923	
t_v (s)	2.0		1.7	
$\varphi_{c/o}$	9.5		9.0	
y_{GP} (%)	28.96	28.10	25.85	25.21
y_{GO} (%)	10.27	9.97	12.00	11.81
y_{GN} (%)	13.50	14.20	11.26	11.99
y_{GA} (%)	22.49	22.75	20.94	21.22
y_{DG} (%)	3.90	3.20	6.43	6.77
y_{LPG} (%)	13.96	14.33	17.22	16.89
y_{LCO} (%)	4.65	4.79	4.20	4.58
y_{COKE} (%)	2.27	2.57	1.68	1.94

Table 11. The calculated and experimental yields of FCC gasoline catalytic reaction as a function of apparent activation energy and frequency factor [11]

Item	y (%) (1)			y (%) (2)		
	Experimental	Predicted	Relative error (%)	Experimental	Predicted	Relative error (%)
Np	0.0625	0.0632	1.12	0.0624	0.0629	0.80
Ip	0.4081	0.4108	0.66	0.4086	0.4099	0.32
O	0.1481	0.1404	-5.20	0.1348	0.1284	-4.75
N	0.0675	0.0670	-0.74	0.0623	0.0648	4.01
A	0.1942	0.1980	1.96	0.2016	0.2007	-0.45
Pg	0.0214	0.0203	-5.14	0.0249	0.0240	-3.61
Og	0.0337	0.0342	1.48	0.0364	0.0378	3.85
Do	0.0389	0.0406	4.37	0.0398	0.0423	6.28
Ck	0.0211	0.0210	-0.47	0.0242	0.0241	-0.41
Dg	0.0046	0.0046	0.00	0.0049	0.0051	4.08

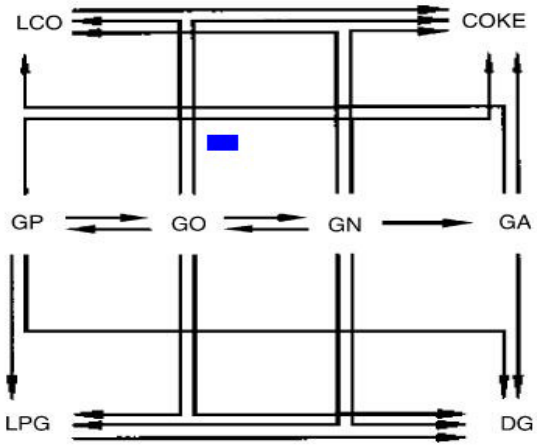


Figure 2. FCC Gasoline Eight-Lump Kinetic Model Conclusion

Ten-lump kinetics model[11]

Based on the catalytic reaction mechanism, and the chemical composition of FCC gasoline, FCC gasoline material is divided into ten-lump (see Table 7). The reaction network is reasonably simplified (see Figure 3). Ten-lump kinetic model of gasoline catalytic conversion reaction is established by estimating parameter to obtain fourteen kinetic rate constants, activation energies, and pre-exponential factors. The results show that this model can predict the distribution of gasoline conversion and the composition of hydrocarbons of gasoline products under the different reaction conditions.

Table 11 shows comparison between experimental and predicted production yields for all lumps' results. The experimental results show that predicted values are close to experimental results and their relative errors are very low.

Aromatization reaction of Yanhua FCC gasoline and a fraction of Yanhua FCC gasoline was studied using LBO-A as catalyst in a confined fluidized bed reactor.

The experimental results are summarized as follow: Yields of aromatics, propylene, and aromatics + propylene for both Yanhua FCC gasoline and fraction of Yanhua FCC gasoline (b.p.<90 °C) increased with the increase of reaction temperature at the same WHSV.

Yields of aromatics, propylene, and aromatics + propylene decrease with the increase of WHSV at the same reaction temperature. Reaction results of Yanhua FCC gasoline are almost the same as that of the fraction of Yanhua FCC gasoline. (3) Eight-lump kinetics and ten-lump kinetics are pointed out.

The experimental results show that two kinetic models can predict the distribution of gasoline conversion and the composition of hydrocarbons of gasoline products under different reaction conditions.

Experimental Principle [12]

Small ($C_2^=$~$C_5^=$) and log chain olefins can exchange each other with catalyst. Under the reactor conditions this is a gas-phase reversible reaction.

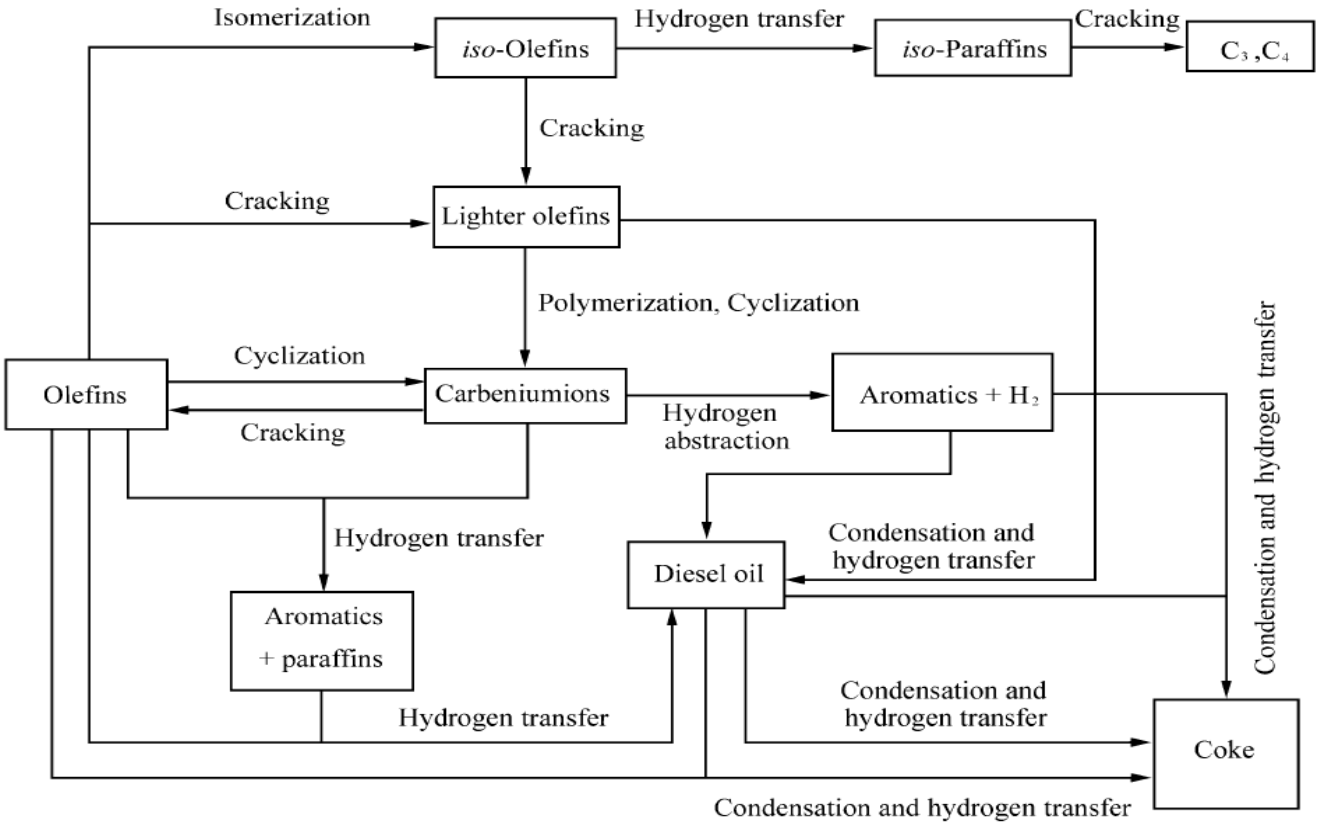


Figure 3. FCC gasoline Ten-Lump Kinetic Model

The reaction can be written as Eqn. (1):

$$\text{low olefins } (C_2^{=}\text{-}C_5^{=}) \underset{\text{cracking reaction}}{\overset{\text{oligomerization}}{\rightleftharpoons}} \text{high olefins } (C_6^{+}) \quad (1)$$

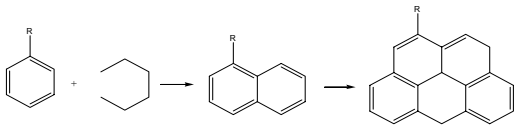
The cyclization takes place when high olefins (C_6^{+}) and catalyst are in contact. It can be expressed as:

$$\text{high olefins } (C_6^{+}) \overset{\text{cyclization reaction}}{\rightleftharpoons} \text{cycloparaffins} \quad (2)$$

Interaction of cycloparaffins with Lewis acerbity produces aromatic hydrocarbons as it can be expressed with Eqn. (3):

$$\text{cycloparaffins} \overset{\text{dehydrogenation}}{\rightleftharpoons} \text{aromatics} \quad (3)$$

Coking reactions take place when aromatics and n-paraffins can be in contacted on the catalyst surface and reacted (Eqn. (4)):



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COMPOSITION OF HYDROCARBON TYPE FUELS FORMED IN THERMAL DECOMPOSITION OF MUNICIPAL SOLID WASTE PLASTICS AND CALCIUM CARBONATE

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Keywords: waste plastics, thermal degradation, hydrocarbon, fuel, municipal, conversion, calcium carbonate, GC/MS

Random mixtures of waste plastics raw materials were thermolysed into liquid hydrocarbons at laboratory scales in a batch process by using a stainless steel reactor. Two series of experiments were carried out with random mixtures of waste plastics such as low and high density polyethylene, polypropylene, and polystyrene in the presence of 10 and 20 % calcium carbonate, respectively, at temperatures between 100 and 430 ºC. Four types of randomly mixed waste plastics were used in each series of experiments. The hydrocarbon oils formed were analyzed by using a gas chromatography and mass spectrometer (GC/MS) to determine the amounts and types of hydrocarbons. By using 10% calcium carbonate, the formed hydrocarbon mixture contained C_4 to C_{40} compounds while, in the presence of 20% calcium carbonate, the product consists of C_3 to C_{27} hydrocarbons determined by GC/MS analysis. Due to the high number of hydrocarbons in the oils formed in each series of thermal decomposition experiment, the oily products can be used as fuels for internal combustion engines or electric power plants.

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Introduction

In 1993, waste plastics accounted for roughly 10% of all municipal solid waste (MSW) in the USA [1] with percentages in land filled MSW ranging from 15 to 25% depending upon location. The energy demand continuously increases and market structures evolve[2] as well, thus utilization of renewable energy sources such as wind and solar power has gained considerable importance since the oil crisis in the 1970s.[3] Europe's total energy consumption is expected to be covered by renewable energy sources in up to 10% by 2020[2], the remaining 90% still being dependent on fossil energy sources. Total waste production increased by about 10% in Europe between 1990 and 1995, with the annual amount estimated at 1.3 billion tons in 1995. The annual amount of hazardous waste was about 36 million tons.[4] In 2010, the amount of paper, glass, and plastic waste was expected to be about 60% higher than the 1990 levels, and the number of scrapped cars was expected to have grown 35% higher.[4] Landfill and incineration are common modes of waste treatment in most European countries[4] and co-incineration is commonly used particularly in the cement industry.[5,6]

The European waste directive called for a 30% reduction of waste amount land filled by 2010. Land filling of plastic wastes is undesirable due to poor biodegradability[7] of polymer materials and, on the other hand, these plastic wastes can be regarded as a potentially cheap source of chemicals and energy. The destruction of waste plastics by incineration, however, often generates problems with unacceptable emissions.

Chemical recycling proved to be a possible alternative strategy, when waste plastics are used as feedstock in various technologies, e.g. in converting them into basic petrochemicals used as chemical feedstock or fuels in a variety of downstream processes. There are two main chemical recycling routes, namely the thermal and the catalytic degradation.[8] Thermal cracking is a well-known technique and is often used in petrochemical processes. Thermal decomposition of waste plastics in the absence of oxygen can be carried out in various types of reactors such as shaft kilns, rotary kilns, screw conveyors, autoclaves, or fluidized beds.[9-12]

Including waste-to-energy (WTE) methods, only about 20% of all MSW was recovered in various recycling technologies, and only 15% of the plastics occurred in MSW were recovered in melting ("primary") and feedstock ("secondary" and "tertiary") type recycling methods. Secondary recycling can be defined as conversion to monomers or other building blocks, whereas, tertiary recycling means conversion to other chemical feedstock or fuels. Waste-to-energy methods (sometimes referred to as "quaternary recycling") are relatively cheap. Recently, another 20% of plastics occurred in MSW have been utilized in this way, however, it requires burning a large amount of non-renewable resources as well. Public perceptions regarding safety of incineration techniques prompted us and other researchers to collaborate under the auspices of the Consortium for Fossil Fuel Liquefaction Science (CFFLS), to investigate the feasibility of coal/waste plastics processing to liquid fuels or chemical feedstock. Obviously, dominant components of MSW-type waste plastics (mainly polyethylene, polystyrene, polyethylene terephthalate and polypropylene) are rich in carbon and hydrogen – basic building elements of petroleum – thus, searching possibilities to convert the waste plastics into liquid fuels seems to be a logical alternative of plastic recycling.[13,14]

Experiments

Materials

Random mixtures of waste plastic samples were collected in a local grocery store at Stamford City which consisted of low and high density polyethylene (HDPE and LDPE), polypropylene (PP) and polystyrene (PS). The samples were contaminated with foreign materials such as food particles, paper, dust, sand. Foreign components were separated out manually and the samples were washed with periodical adding of liquid soap into the washing water. Washing of plastics is not an essential step in our plastic-to-fuel process developed, but the laboratory scale process was performed with washed samples. Random mixtures of waste plastics containing both hard and soft plastic components were prepared by cutting the soft plastics and grinding the hard ones into pieces down to size 2-3 mm. Reagent grade anhydrous calcium carbonate powder was provided by AMRESCO Co.

Process Description

Grounded random mixtures of waste plastics were transferred into the reactor chamber together with calcium carbonate additive in amount of 10% or 20 % in each experiment, respectively. The weight of every mixture was controlled to be 1000 g. The reactor chamber and its cover were tightened with a screw system to prevent from gas leaking. A condensation unit and a fuel purification device were connected to the reactor and the fuel collection tanks, respectively. The upper outlet of the condensation unit was connected to a gas cleaning system. Light gases formed were transferred into a storage system and the sediment separated by the fuel purification device was recycled to the reactor as raw material. The heating temperature was controlled between 100 and 430 °C, respectively.

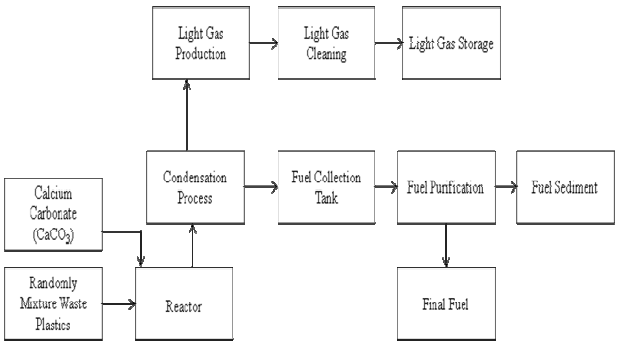

Figure 1: Random mixtures of waste plastics and calcium carbonate in the fuel production process

Calcium carbonate was used as additive in the reaction, but some acceleration effect was also observed. Waste plastics start to melt at 100 ºC and their melting was completed below 300 ºC. Long hydrocarbon chains broke down into short chain hydrocarbon due to heat treatment. The liquid slurry turned into vapour which condensed into a liquid hydrocarbon mixture. The reaction was not completed even at 300 °C, therefore, heating was continued until 430 ºC. The liquid hydrocarbon mixture formed was purified with an RCI fuel filter. Sediment was removed and reused in the next experiment as raw material. The light gas generated contained methane, ethane, propane, and butanes. The light gas formed was washed with sodium hydroxide solution. The density of the liquid formed with using 10 % calcium carbonate additive was determined as 0.78 g cm^{-3}. Yields of the products formed in the decomposition process carried out with 10 and 20 % calcium carbonate additive and 1 kg of plastics waste are shown in Table 1. When using 10% or 20 % calcium carbonate, 716.8 and 683.8 g liquid fuel, 155.1 and 98 g gas, and 128.1 and 218.2 g of solid residue were formed, respectively. It means that yields of liquid hydrocarbons, gases, and solid residues are 71,68 and 68.38 %, 15.51 and 9.8 %, 12.81 and 21.82 % in the experiments carried out with 10 and 20 % $CaCO_3$ content, respectively. The volumes of liquid phases were 922 ml and 870 ml starting form 1 kg of mixture, with 10 and 20 % of $CaCO_3$ content, respectively. Both experiments left back a black solid residue whose composition is under investigation.

Instrument

GC-MS analyses were performed on a Perkin-Elmer Clarus 500 instrument supplied with auto-sampler system. Elite-5 capillary column (30 meter length) and He as carrier gas were used. The injected volume was adjusted to be 5.0 µL, the sample split flow and the initial set point were 101.0 mL min^{-1} and 1.00 ml min^{-1}, respectively. The sample injector port temperature was adjusted to be 280 ºC, with 40 °C initial value. The temperature holding and equilibration times were 1 and 0.5 minutes, respectively. The temperature ramping was 10 ºC/ min up to 325 ºC and there was a holding for 15 minute at 325 ºC. The mass spectrometer was operated in EI+ mode, between 35.00 and 528.00 m/z units with 0.25 s scan and 0.15 s interscan times.

Results and Discussion

GC-MS analyses of liquids formed in the reaction of randomly mixed waste plastics and 10% calcium carbonate (Fig. 2 and Table 2) showed the occurrence of a variety of components. Many compounds detected contained carbon atoms within the range between C_3 and C_{27}. Based on the retention times and fragmentation patterns, different types of compounds such as hydrocarbons, halogen compounds, oxygenated compounds, and nitrogen containing compounds were identified. The GC-MS analyses showed presence of such characteristic compounds as 3-butene-1-ol (C_4H_8O) (t=1.50, m/z=41), cis-1,2-dimethylcyclopropane (C_5H_{10}) (t=2.02, m/z=55), cis-1-ethyl-2-methylcyclopropane (C_6H_{12}) (t=2.50, m/z=41), Z,Z-2,4-hexadiene (C_6H_{10}) (t= 2.96, m/z= 67), 4-methyl-1,4-hexadiene (C_7H_{12}) (t=3.77, m/z=81), 2-methyl-1,4-hexadiene (C_7H_{12}) (t=3.95, m/z=81), norbornane (C_7H_{12}) (t=4.44, m/z=81), 3-methylcyclohexene (C_7H_{12}) (t=4.86, m/z=81), 1α,3α,5α-

1,3,5-trimethylcyclohexane (C_9H_{18}) (t= 5.92, m/z= 69), styrene (C_8H_8) (t=6.95, m/z=104), 3-decyn-2-ol ($C_{10}H_{18}O$) (t=7.92, m/z=57), 4-methyldecane ($C_{11}H_{24}$) (t=8.85, m/z=43), cis-1,4-dimethylcyclooctane ($C_{10}H_{20}$)

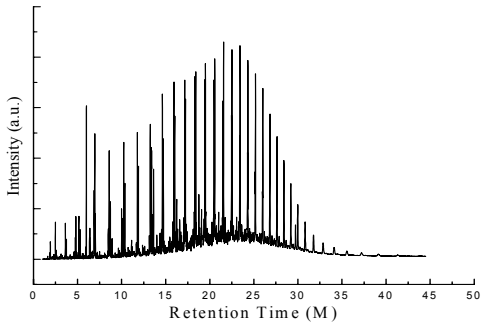

Figure 2: GC/MS chromatogram of the liquid product formed in the presence of 10 % CaCO3 containing random waste plastics in the mixture

(t=9.99, m/z=41), 1R-cis-1-(1,2,2,3-tetramethylcyclo-pentyl)-ethanone ($C_{11}H_{20}O$) (t=10.74, m/z=43), dodecane ($C_{12}H_{26}$) (t=11.91, m/z=57), N-[4-bromo-n-butyl]-2-piperidinone ($C_9H_{16}BrN$) (t=12.50, m/z=41), 4,6,8-trimethyl-1-nonene ($C_{12}H_{24}$) (t=13.63, m/z=43), 7-tetradecene ($C_{14}H_{28}$) (t=14.78, m/z=41), 1-hexadecene ($C_{16}H_{32}$) (t=15.93, m/z=41). Different kinds of hydrocarbons were formed containing aliphatic and aromatic rings, single and double bonds such as octadecane ($C_{18}H_{38}$) (t=20.56, m/z=85), octadecene ($C_{18}H_{38}$) (t=23.44, m/z=85), isomeric octadecanes ($C_{18}H_{38}$) (t=24.33, 25.19, 26.83, 28.41, m/z=57), heptacosanes ($C_{27}H_{56}$) (t=30.82, 32.87, m/z=57, and t=35.56, m/z=44), benzene (C_6H_6), toluene (C_7H_8), styrene (C_8H_8), 1-methylethylbenzene (C_9H_{12}), 1-ethyl-3-methylbenzene (C_9H_{12}), α-methylstyrene (C_9H_{10}), 1-ethenyl-2-methylbenzene (C_9H_{10}) etc..

Some alcoholic groups containing products such as 1-eicosanol ($C_{20}H_{42}O$) (t= 21.75, m/z=55) could also be detected. Dyes and additives occurring in the raw waste plastics had no influence on quality of the produced fuel-like liquid products.

The experiments were carried out without evacuation of the reactor space, thus the humidity as oxygen source might be responsible for the formation of some oxygen–containing products.

Table 1: Product yields in thermal decomposition of waste plastics in the presence of calcium carbonate

Sample weight (g.)	$CaCO_3$ % (m/m)	Fuel weight (g)	Fuel volume (ml)	Residue weight (g.)	Sample as light gas weight (g.)	Fuel Yield % (m/m)	Light gas Yield % (m/m)	Residue Yield % (m/m)
1000	10	716.8	922	128.1	155.1	71.68	15.51	12.81
1000	20	683.8	870	218.2	98	68.38	9.8	21.82

Table 2: GC/MS chromatogram compound list of liquid product formed in thermal decomposition of random waste plastics and 10% calcium carbonate mixture

No. of Peak	Retention Time (min.)	Trace Mass (m/z)	Compound Name	Compound Formula	Molecular Weight	Probability %	NIST Library Number
1	1.50	41	3-Buten-1-ol	C_4H_8O	72	17.7	114446
2	1.60	41	2-Butene	C_4H_8	56	23.4	61292
3	1.64	41	1-Propene, 2-methyl-	C_4H_8	56	19.3	61293
4	1.87	42	Cyclopropane, ethyl-	C_5H_{10}	70	23.2	19072
5	1.91	43	Pentane	C_5H_{12}	72	88.0	114462
6	1.96	55	2-Pentene	C_5H_{10}	70	15.0	19079
7	2.02	55	cis-1,2-dimethyl Cyclopropane	C_5H_{10}	70	25.0	19070
8	2.06	67	1,3-Pentadiene	C_5H_8	68	17.1	61941
9	2.13	67	1,4-Pentadiene	C_5H_8	68	13.1	209
10	2.25	67	Cyclopentene	C_5H_8	68	19.7	19032
11	2.32	43	Pentane, 2-methyl-	C_6H_{14}	86	42.7	61279
12	2.50	41	cis-1-ethyl-2-methyl Cyclopropane	C_6H_{12}	84	18.9	113658
13	2.58	57	Hexane	C_6H_{14}	86	67.2	61280
14	2.64	69	2-Pentene, 3-methyl-, (Z)-	C_6H_{12}	84	13.8	114483
15	2.68	41	3-Hexen-1-ol, (Z)-	$C_6H_{12}O$	100	6.68	114154
16	2.72	67	4-Penten-1-ol, 3-methyl-	$C_6H_{12}O$	100	15.5	113673
17	2.84	67	2,4-Hexadiene, (Z,Z)-	C_6H_{10}	82	7.79	113646

18	2.90	56	Cyclopentane, methyl-	C_6H_{12}	84	59.9	114428
19	2.96	67	2,4-Hexadiene, (Z,Z)-	C_6H_{10}	82	13.1	113646
20	3.06	56	1-Pentene, 2,4-dimethyl-	C_7H_{14}	98	49.4	114435
21	3.14	67	Cyclopentene, 3-methyl-	C_6H_{10}	82	25.1	114408
22	3.27	78	Benzene	C_6H_6	78	66.3	114388
23	3.38	79	1,3-Cyclohexadiene	C_6H_8	80	23.0	118700
24	3.52	67	Cyclohexene	C_6H_{10}	82	31.6	114431
25	3.57	56	1-Hexene, 2-methyl-	C_7H_{14}	98	35.9	114433
26	3.62	41	cis-1,2-dimethyl-Cyclopentane	C_7H_{14}	98	26.8	114027
27	3.73	43	Heptane	C_7H_{16}	100	47.6	61276
28	3.77	81	1,4-Hexadiene, 4-methyl-	C_7H_{12}	96	14.4	113135
29	3.95	81	1,4-Hexadiene, 2-methyl-	C_7H_{12}	96	7.17	840
30	4.07	81	Cyclobutane, (1-methylethylidene)-	C_7H_{12}	96	6.41	150272
31	4.16	83	Cyclohexane, methyl-	C_7H_{14}	98	54.1	118503
32	4.30	69	Cyclopentane, ethyl-	C_7H_{14}	98	28.7	940
33	4.38	79	1-Cyclohexene-1-methanol	$C_7H_{12}O$	112	16.9	52048
34	4.44	81	Norbornane	C_7H_{12}	96	7.51	114371
35	4.51	56	2,4-Dimethyl-1-hexene	C_8H_{16}	112	31.6	113443
36	4.55	81	Cyclobutane, (1-methylethylidene)-	C_7H_{12}	96	13.8	150272
37	4.60	67	3-Heptene, 4-methyl-	C_8H_{16}	112	7.60	114150
38	4.75	43	Heptane, 4-methyl-	C_8H_{18}	114	62.3	113916
39	4.80	91	Toluene	C_7H_8	92	41.5	291301
40	4.86	81	Cyclohexene, 3-methyl-	C_7H_{12}	96	9.86	236066
41	5.06	56	1-Heptene, 2-methyl-	C_8H_{16}	112	45.1	113675
42	5.15	41	1-Octene	C_8H_{16}	112	16.9	1604
43	5.23	95	Cyclopropane, (2,2-dimethylpropylidene)-	C_8H_{14}	110	8.35	60981
44	5.29	43	Octane	C_8H_{18}	114	36.7	229407
45	5.39	55	3-Octene, (Z)-	C_8H_{16}	112	11.5	113895
46	5.46	41	4-Methyl-1,4-heptadiene	C_8H_{14}	110	7.53	113473
47	5.55	69	cis-1,1,3,4-tetramethyl-Cyclopentane	C_9H_{18}	126	14.6	34789
48	5.65	43	Hexane, 3-ethyl-	C_8H_{18}	114	15.8	113940
49	5.80	67	1-Methyl-2-methylenecyclohexane	C_8H_{14}	110	26.7	113437
50	5.92	69	Cyclohexane, 1,3,5-trimethyl-, (1α,3α,5α)-	C_9H_{18}	126	24.4	114126
51	6.01	70	2,4-Dimethyl-1-heptene	C_9H_{18}	126	49.5	113516
52	6.35	69	Cyclohexane, 1,3,5-trimethyl-, (1α,3α,5β)-	C_9H_{18}	126	37.2	2480
53	6.40	91	Ethylbenzene	C_8H_{10}	106	66.0	114918
54	6.55	91	Cyclohexanol, 1-ethynyl-, carbamate	$C_9H_{13}NO_2$	167	35.5	313023
55	6.71	67	cis-1,4-Dimethyl-2-methylenecyclohexane	C_9H_{16}	124	12.2	113533
56	6.88	41	1-Nonene	C_9H_{18}	126	10.5	107756
57	6.95	104	Styrene	C_8H_8	104	33.8	291542
58	7.02	43	Nonane	C_9H_{20}	128	31.3	228006
59	7.10	55	4-Nonene	C_9H_{18}	126	8.07	113904
60	7.24	55	3-Octyne, 2-methyl-	C_9H_{16}	124	4.17	62452
61	7.44	67	Ethylidenecycloheptane	C_9H_{16}	124	5.69	113500
62	7.49	105	Benzene, (1-methylethyl)-	C_9H_{12}	120	22.7	228742
63	7.52	67	1-Cyclohexyl-1-pentyne	$C_{11}H_{18}$	150	5.42	114866
64	7.66	55	Cyclopentane, butyl-	C_9H_{18}	126	9.72	114172
65	7.86	67	Cyclopentene, 1-butyl-	C_9H_{16}	124	9.34	113491
66	7.92	57	3-Decyn-2-ol	$C_{10}H_{18}O$	154	8.40	53449

67	8.01	91	Benzene, propyl-	C_9H_{12}	120	56.2	113930
68	8.07	57	Octane, 2,3-dimethyl-	$C_{10}H_{22}$	142	17.3	114135
69	8.13	105	Benzene, 1-ethyl-3-methyl-	C_9H_{12}	120	10.7	228743
70	8.43	41	E-1,6-Undecadiene	$C_{11}H_{20}$	152	11.7	245712
71	8.49	118	α-Methylstyrene	C_9H_{10}	118	31.4	30236
72	8.59	41	1-Decene	$C_{10}H_{20}$	140	16.6	118883
73	8.73	57	Decane	$C_{10}H_{22}$	142	49.6	114147
74	8.85	43	Decane, 4-methyl-	$C_{11}H_{24}$	156	15.8	113875
75	8.92	43	Octane, 3,3-dimethyl-	$C_{10}H_{22}$	142	11.1	61706
76	9.27	117	Benzene, 1-ethenyl-2-methyl-	C_9H_{10}	118	10.6	118193
77	9.64	41	2-Undecanethiol, 2-methyl-	$C_{12}H_{26}S$	202	4.45	9094
78	9.74	91	2-Cyclohexen-1-ol, 2-methyl-5-(1-methylethenyl)-	$C_{10}H_{16}O$	152	16.3	114684
79	9.99	41	cis-1,4-dimethyl-Cyclooctane	$C_{10}H_{20}$	140	3.73	61409
80	10.06	41	Diisoamylene	$C_{10}H_{20}$	140	4.19	3659
81	10.24	41	2-Undecene, (Z)-	$C_{11}H_{22}$	154	6.19	142596
82	10.37	43	Undecane	$C_{11}H_{24}$	156	42.5	114185
83	10.43	55	5-Undecene, (E)-	$C_{11}H_{22}$	154	10.0	114227
84	10.74	43	1R-cis- 1-(1,2,2,3-tetramethylcyclopentyl)-Ethanone	$C_{11}H_{20}O$	168	5.54	186082
85	11.06	91	9-Hexadecenoic acid, phenylmethyl ester, (Z)-	$C_{23}H_{36}O_2$	344	6.61	67839
86	11.12	69	1,12-Tridecadiene	$C_{13}H_{24}$	180	6.65	7380
87	11.16	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	5.48	245485
88	11.67	41	6-Dodecene, (Z)-	$C_{12}H_{24}$	168	5.06	142611
89	11.78	41	3-Dodecene, (E)-	$C_{12}H_{24}$	168	9.21	113960
90	11.91	57	Dodecane	$C_{12}H_{26}$	170	25.2	291499
91	12.38	43	Dodecane, 2,6,10-trimethyl-	$C_{15}H_{32}$	212	6.60	68892
92	12.50	41	2-Piperidinone, N-[4-bromo-n-butyl]-	$C_9H_{16}BrNO$	233	5.17	251632
93	13.14	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	15.4	245485
94	13.25	41	2-Tridecene, (E)-	$C_{13}H_{26}$	182	8.35	142614
95	13.37	43	Hexadecane	$C_{16}H_{34}$	226	9.77	114191
96	13.40	41	3-Tridecene, (Z)-	$C_{13}H_{26}$	182	2.47	142615
97	13.51	43	Trifluoroacetic acid, n-heptadecyl ester	$C_{17}H_{31}F_3O_2$	324	2.78	216792
98	13.63	43	1-Nonene, 4,6,8-trimethyl-	$C_{12}H_{24}$	168	2.61	6413
99	13.99	43	1-Tetracosanol	$C_{24}H_{50}O$	354	2.76	16001
100	14.36	55	1,12-Tridecadiene	$C_{13}H_{24}$	180	7.61	7380
101	14.52	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	22.9	245485
102	14.63	41	1-Tetradecene	$C_{14}H_{28}$	196	5.12	34720
103	14.74	43	Tetradecane	$C_{14}H_{30}$	198	19.5	113925
104	14.78	41	7-Tetradecene	$C_{14}H_{28}$	196	4.34	70643
105	15.47	43	2-Piperidinone, N-[4-bromo-n-butyl]-	$C_9H_{16}BrNO$	233	4.48	251632
106	15.70	43	7-Hexadecenal, (Z)-	$C_{16}H_{30}O$	238	6.85	293051
107	15.83	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	22.7	245485
108	15.93	41	1-Hexadecene	$C_{16}H_{32}$	224	5.58	118882
109	16.02	43	Hexadecane	$C_{16}H_{34}$	226	22.0	114191
110	16.07	41	10-Heneicosene (c,t)	$C_{21}H_{42}$	294	3.04	113073
111	16.25	43	Trichloroacetic acid, hexadecyl ester	$C_{18}H_{33}Cl_3O_2$	386	3.59	280518
112	16.71	43	2-Piperidinone, N-[4-bromo-n-butyl]-	$C_9H_{16}BrNO$	233	3.16	251632
113	17.07	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	14.0	245485

114	17.16	55	1-Hexadecene	$C_{16}H_{32}$	224	6.90	118882
115	17.25	43	Hexadecane	$C_{16}H_{34}$	226	18.3	114191
116	17.29	41	10-Heneicosene (c,t)	$C_{21}H_{42}$	294	3.40	113073
117	17.44	41	E-2-Octadecadecen-1-ol	$C_{18}H_{36}O$	268	4.70	131102
118	18.24	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	14.8	245485
119	18.33	55	1-Nonadecene	$C_{19}H_{38}$	266	5.66	113626
120	18.41	71	Nonadecane	$C_{19}H_{40}$	268	12.6	114098
121	19.44	41	1-Nonadecene	$C_{19}H_{38}$	266	6.60	113626
122	19.51	43	Heneicosane	$C_{21}H_{44}$	296	9.78	107569
123	20.43	55	1-Docosanol	$C_{22}H_{46}O$	326	5.85	23377
124	20.56	85	Octadecane	$C_{18}H_{38}$	254	9.09	57273
125	21.50	55	1-Docosene	$C_{22}H_{44}$	308	9.78	113878
126	21.56	43	Octadecane	$C_{18}H_{38}$	254	7.19	57273
127	21.70	43	Hexadecane, 1,1-bis(dodecyloxy)-	$C_{40}H_{82}O_2$	594	6.93	36104
128	21.75	55	1-Eicosanol	$C_{20}H_{42}O$	298	3.91	113075
129	22.46	43	1-Docosene	$C_{22}H_{44}$	308	17.5	113878
130	23.39	55	1-Docosene	$C_{22}H_{44}$	308	18.6	113878
131	23.44	85	Octadecane	$C_{18}H_{38}$	254	8.86	57273
132	24.28	55	1-Docosene	$C_{22}H_{44}$	308	12.0	113878
133	24.33	57	Octadecane	$C_{18}H_{38}$	254	7.39	57273
134	25.14	55	1-Docosene	$C_{22}H_{44}$	308	9.40	113878
135	25.19	57	Octadecane	$C_{18}H_{38}$	254	4.95	57273
136	26.01	57	Hexacosane	$C_{26}H_{54}$	366	4.48	107147
137	26.83	57	Octadecane	$C_{18}H_{38}$	254	5.08	57273
138	27.62	57	Heptacosane	$C_{27}H_{56}$	380	5.54	150574
139	28.41	57	Octadecane	$C_{18}H_{38}$	254	4.59	57273
140	29.19	57	Heptacosane	$C_{27}H_{56}$	380	4.94	150574
141	29.72	306	1,1':3',1''-Terphenyl, 5'-phenyl-	$C_{24}H_{18}$	306	50.4	57402
142	29.98	57	Heneicosane, 11-(1-ethylpropyl)-	$C_{26}H_{54}$	366	4.62	16318
143	30.82	57	Heptacosane	$C_{27}H_{56}$	380	7.17	79427
144	31.77	57	Heptacosane	$C_{27}H_{56}$	380	7.88	79427
145	32.87	57	Heptacosane	$C_{27}H_{56}$	380	9.78	79427
146	34.12	57	Heptacosane	$C_{27}H_{56}$	380	10.9	79427
147	35.56	44	Heptacosane	$C_{27}H_{56}$	380	8.06	79427

Table 3: GC/MS chromatogram compound list of liquid product formed in thermal decomposition of random waste plastics and 20% calcium carbonate mixture

No. of Peak	Retention Time (M)	Trace Mass (m/z)	Compounds Name	Compounds Formula	Molecular Weight	Probability %	NIST Library Number
1	1.49	41	Cyclopropane	C_3H_6	42	50.1	18854
2	1.60	41	1-Propene, 2-methyl-	C_4H_8	56	23.3	61293
3	1.61	43	Butane	C_4H_{10}	58	18.2	61290
4	1.63	41	2-Butene	C_4H_8	56	20.5	61292
5	1.83	67	1,4-Pentadiene	C_5H_8	68	21.5	114494
6	1.87	42	2-Pentene, (E)-	C_5H_{10}	70	21.1	291780
7	1.91	43	Pentane	C_5H_{12}	72	85.8	114462
8	1.95	55	cis-1,2-dimethyl-Cyclopropane	C_5H_{10}	70	23.8	19070
9	2.07	67	1,4-Pentadiene	C_5H_8	68	19.4	114494
10	2.26	67	Cyclopentene	C_5H_8	68	15.8	19032
11	2.32	43	Butane, 2,3-dimethyl-	C_6H_{14}	86	13.9	291518
12	2.50	41	1-Hexene	C_6H_{12}	84	15.3	500
13	2.58	57	Hexane	C_6H_{14}	86	68.7	61280
14	2.64	41	2-Pentene, 3-methyl-, (Z)-	C_6H_{12}	84	12.5	114483
15	2.72	67	1,3-Butadiene, 2-ethyl-	C_6H_{10}	82	18.8	118159
16	2.84	67	2,4-Hexadiene, (Z,Z)-	C_6H_{10}	82	9.94	113646

17	2.90	56	Cyclopentane, methyl-	C_6H_{12}	84	69.2	114428
18	2.96	67	1,3-Pentadiene, 2-methyl-, (E)-	C_6H_{10}	82	12.1	113652
19	3.01	79	3-Vinyl-1-cyclobutene	C_6H_8	80	13.3	214892
20	3.06	79	1,3-Cyclopentadiene, 5-methyl-	C_6H_8	80	13.9	419
21	3.15	67	Cyclopentene, 3-methyl-	C_6H_{10}	82	18.8	114408
22	3.20	41	1-Hexene, 5-methyl-	C_7H_{14}	98	9.13	918
23	3.27	78	Benzene	C_6H_6	78	69.0	114388
24	3.32	67	Cyclobutene, 3,3-dimethyl-	C_6H_{10}	82	7.04	62288
25	3.38	79	1,4-Cyclohexadiene	C_6H_8	80	16.5	114497
26	3.42	43	Hexane, 3-methyl-	C_7H_{16}	100	62.7	113081
27	3.45	81	Dihydromyrcene	$C_{10}H_{18}$	138	5.24	292831
28	3.52	67	Cyclohexene	C_6H_{10}	82	27.0	114431
29	3.58	56	1-Hexene, 2-methyl-	C_7H_{14}	98	34.5	114433
30	3.62	41	1-Heptene	C_7H_{14}	98	28.1	107734
31	3.74	43	Heptane	C_7H_{16}	100	46.5	61276
32	3.78	81	Cyclopropane, trimethylmethylene-	C_7H_{12}	96	9.46	63085
33	3.84	55	2-Heptene	C_7H_{14}	98	33.7	113119
34	3.89	41	2-Hexene, 3-methyl-, (Z)-	C_7H_{14}	98	7.85	114046
35	3.96	81	2,3-Dimethyl-1,4-pentadiene	C_7H_{12}	96	8.68	113670
36	4.07	81	Cyclopentane, 1-methyl-2-methylene-	C_7H_{12}	96	12.6	62523
37	4.17	83	Cyclohexane, methyl-	C_7H_{14}	98	60.0	118503
38	4.31	69	Cyclopentane, ethyl-	C_7H_{14}	98	49.6	940
39	4.39	79	1-Cyclohexene-1-methanol	$C_7H_{12}O$	112	18.5	52048
40	4.44	81	Norbornane	C_7H_{12}	96	6.07	114371
41	4.50	79	1,3,5-Heptatriene, (E,E)-	C_7H_{10}	94	15.3	118126
42	4.55	81	Cyclopentene, 4,4-dimethyl-	C_7H_{12}	96	14.4	38642
43	4.61	67	Cyclopentane, ethylidene-	C_7H_{12}	96	22.5	151340
44	4.76	43	Heptane, 4-methyl-	C_8H_{18}	114	59.6	113916
45	4.81	91	Toluene	C_7H_8	92	37.6	291301
46	4.87	81	Cyclohexene, 3-methyl-	C_7H_{12}	96	10.6	236066
47	4.96	67	Cyclopropane, (2-methylenebutyl)-	C_8H_{14}	110	6.19	62733
48	5.01	41	1,4-Octadiene	C_8H_{14}	110	26.5	113431
49	5.07	56	1-Heptene, 2-methyl-	C_8H_{16}	112	27.3	113675
50	5.15	41	1-Octene	C_8H_{16}	112	27.6	1604
51	5.23	55	2-Octyn-1-ol	$C_8H_{14}O$	126	12.2	113247
52	5.30	43	Octane	C_8H_{18}	114	35.6	229407
53	5.39	55	3-Octene, (Z)-	C_8H_{16}	112	12.3	113895
54	5.55	83	cis-1,1,3,4-tetramethyl-Cyclopentane	C_9H_{18}	126	12.4	34789
55	5.92	69	Cyclohexane, 1,3,5-trimethyl-, (1α,3α,5β)-	C_9H_{18}	126	20.1	2480
56	6.00	43	2,4-Dimethyl-1-heptene	C_9H_{18}	126	55.7	113516
57	6.35	69	Cyclohexane, 1,3,5-trimethyl-, (1α,3α,5β)-	C_9H_{18}	126	31.6	2480
58	6.40	91	Ethylbenzene	C_8H_{10}	106	70.8	114918
59	6.55	91	Cyclohexanol, 1-ethynyl-, carbamate	$C_9H_{13}NO_2$	167	29.4	313023
60	6.70	41	Cyclohexane, 1-propenyl-	C_9H_{16}	124	11.0	26935
61	6.78	70	Heptane, 3-methylene-	C_8H_{16}	112	6.46	60836
62	6.88	41	cis-2-Nonene	C_9H_{18}	126	11.0	113508
63	6.94	104	Styrene	C_8H_8	104	37.5	291542

64	7.02	43	Nonane	C_9H_{20}	128	29.7	228006
65	7.10	55	4-Nonene	C_9H_{18}	126	11.6	113904
66	7.24	55	2-Octyn-1-ol	$C_8H_{14}O$	126	10.5	113247
67	7.66	55	Cyclopentane, butyl-	C_9H_{18}	126	16.1	114172
68	7.87	67	Cyclopentene, 1-butyl-	C_9H_{16}	124	41.1	113491
69	8.43	41	1,9-Decadiene	$C_{10}H_{18}$	138	14.3	118291
70	8.49	118	Azetidine, 3-methyl-3-phenyl-	$C_{10}H_{13}N$	147	32.0	4393
71	8.59	41	1-Decene	$C_{10}H_{20}$	140	13.7	118883
72	8.73	57	Decane	$C_{10}H_{22}$	142	52.8	114147
73	8.81	55	2-Decene, (Z)-	$C_{10}H_{20}$	140	11.6	114151
74	8.85	43	Decane, 4-methyl-	$C_{11}H_{24}$	156	10.8	5261
75	8.92	43	Octane, 3,5-dimethyl-	$C_{10}H_{22}$	142	9.96	114062
76	9.39	41	2,4-Pentadien-1-ol, 3-pentyl-, (2Z)-	$C_{10}H_{18}O$	154	6.46	142197
77	9.75	91	Bicyclo[3.1.1]heptan-3-ol, 6,6-dimethyl-2-methylene-, [1S-(1α,3α,5α)]-	$C_{10}H_{16}O$	152	15.3	151861
78	9.99	41	1-Octene, 3,7-dimethyl-	$C_{10}H_{20}$	140	3.22	3653
79	10.06	41	5-Tridecene, (Z)-	$C_{13}H_{26}$	182	5.28	142618
80	10.24	41	1-Undecene	$C_{11}H_{22}$	154	7.34	5022
81	10.30	41	E-10-Pentadecenol	$C_{15}H_{30}O$	226	4.48	245484
82	10.37	43	Undecane	$C_{11}H_{24}$	156	48.2	114185
83	10.43	41	3-Undecene, (Z)-	$C_{11}H_{22}$	154	9.86	142598
84	10.58	41	2-Decyn-1-ol	$C_{10}H_{18}O$	154	9.00	53366
85	11.06	41	4-Chloro-3-n-hexyltetrahydropyran	$C_{11}H_{21}ClO$	204	13.2	216835
86	11.12	69	2-Isopropenyl-5-methylhex-4-enal	$C_{10}H_{16}O$	152	6.71	191046
87	11.16	41	1b,5,5,6a-Tetramethyl-octahydro-1-oxa-cyclopropa[a]inden-6-one	$C_{13}H_{20}O_2$	208	6.62	194131
88	11.66	41	Z-1,8-Dodecadiene	$C_{12}H_{22}$	166	7.63	245715
89	11.79	41	3-Dodecene, (E)-	$C_{12}H_{24}$	168	9.43	113960
90	11.91	43	Dodecane	$C_{12}H_{26}$	170	22.1	291499
91	12.38	41	2-Piperidinone, N-[4-bromo-n-butyl]-	$C_9H_{16}BrNO$	233	3.98	251632
92	12.49	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	6.62	245485
93	12.62	41	1-Nonadecanol	$C_{19}H_{40}O$	284	4.45	13666
94	13.14	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	8.47	245485
95	13.26	41	2-Tridecene, (E)-	$C_{13}H_{26}$	182	7.28	142614
96	13.37	43	Tetradecane	$C_{14}H_{30}$	198	13.6	113925
97	13.51	43	4-Trifluoroacetoxytridecane	$C_{15}H_{27}F_3O_2$	296	2.38	245473
98	13.63	43	1-Octanol, 2-butyl-	$C_{12}H_{26}O$	186	3.49	114639
99	14.36	41	1,12-Tridecadiene	$C_{13}H_{24}$	180	6.25	7380
100	14.53	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	11.8	245485
101	14.64	41	7-Tetradecene, (E)-	$C_{14}H_{28}$	196	4.90	142631
102	14.74	43	Tetradecane	$C_{14}H_{30}$	198	18.4	113925
103	14.79	41	7-Tetradecene	$C_{14}H_{28}$	196	5.46	70643
104	15.48	41	1-Nonadecanol	$C_{19}H_{40}O$	284	8.74	13666
105	15.94	55	1-Hexadecene	$C_{16}H_{32}$	224	6.29	118882
106	16.03	43	Hexadecane	$C_{16}H_{34}$	226	21.5	114191
107	16.08	41	E-2-Hexadecacen-1-ol	$C_{16}H_{32}O$	240	4.99	131101
108	17.17	41	1-Hexadecene	$C_{16}H_{32}$	224	5.93	118882
109	17.26	41	Hexadecane	$C_{16}H_{34}$	226	17.8	114191
110	17.29	41	1-Hexadecene	$C_{16}H_{32}$	224	4.10	118882
111	17.45	41	10-Heneicosene (c,t)	$C_{21}H_{42}$	294	3.10	113073
112	18.25	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	13.1	245485
113	18.34	83	1-Nonadecene	$C_{19}H_{38}$	266	5.65	113626

114	18.42	43	Octadecane	$C_{18}H_{38}$	254	11.2	57273
115	18.45	55	10-Heneicosene (c,t)	$C_{21}H_{42}$	294	5.31	113073
116	18.76	43	Trichloroacetic acid, hexadecyl ester	$C_{18}H_{33}Cl_3O_2$	386	5.30	280518
117	19.07	43	1-Docosanol	$C_{22}H_{46}O$	326	5.25	23377
118	19.44	55	1-Nonadecene	$C_{19}H_{38}$	266	6.65	113626
119	19.52	43	Nonadecane	$C_{19}H_{40}$	268	12.2	114098
120	19.70	43	1-Decanol, 2-hexyl-	$C_{16}H_{34}O$	242	9.73	114709
121	20.43	55	E-2-Octadecadecen-1-ol	$C_{18}H_{36}O$	268	13.1	131102
122	20.50	55	1-Nonadecene	$C_{19}H_{38}$	266	10.1	113626
123	20.57	85	Heptadecane	$C_{17}H_{36}$	240	9.96	107308
124	21.50	55	1-Docosene	$C_{22}H_{44}$	308	9.51	113878
125	21.57	57	Nonadecane	$C_{19}H_{40}$	268	10.3	114098
126	22.47	83	1-Docosene	$C_{22}H_{44}$	308	11.8	113878
127	22.52	57	Nonadecane	$C_{19}H_{40}$	268	7.43	114098
128	23.39	55	1-Docosene	$C_{22}H_{44}$	308	18.1	113878
129	23.44	43	Nonadecane	$C_{19}H_{40}$	268	5.88	114098
130	24.29	55	1-Docosene	$C_{22}H_{44}$	308	14.8	113878
131	24.33	43	Eicosane	$C_{20}H_{42}$	282	6.10	290513
132	25.14	43	1-Docosene	$C_{22}H_{44}$	308	12.0	113878
133	25.19	57	Octadecane	$C_{18}H_{38}$	254	5.34	57273
134	26.02	57	Hexacosane	$C_{26}H_{54}$	366	5.27	107147
135	26.83	57	Nonadecane	$C_{19}H_{40}$	268	4.38	114098
136	27.62	57	Eicosane, 2-methyl-	$C_{21}H_{44}$	296	5.46	113884
137	28.40	57	Octadecane	$C_{18}H_{38}$	254	5.41	57273
138	29.17	57	Heneicosane, 11-(1-ethylpropyl)-	$C_{26}H_{54}$	366	4.02	16318
139	29.95	57	Heptacosane	$C_{27}H_{56}$	380	4.35	79427
140	30.78	57	1-Decanol, 2-hexyl-	$C_{16}H_{34}O$	242	3.96	113815
141	31.72	57	1-Heptacosanol	$C_{27}H_{56}O$	396	4.82	16909
142	32.79	57	Heptacosane	$C_{27}H_{56}$	380	6.95	79427
143	34.02	57	1-Heptacosanol	$C_{27}H_{56}O$	396	8.96	16909
144	35.45	57	10-Octadecenal	$C_{18}H_{34}O$	266	4.84	36160
145	37.09	57	1-Heptacosanol	$C_{27}H_{56}O$	396	9.81	16909

GC-MS results of the liquid product formed in thermal decomposition of the mixture containing 20 % $CaCO_3$ and waste plastics can be seen in Fig. 3 and Table 3.

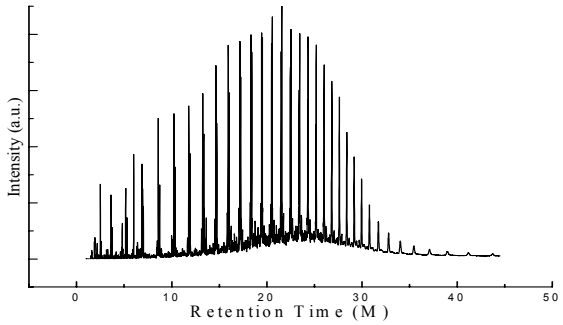

Figure 3: GC/MS chromatogram of liquid product formed in thermal decomposition of the mixture containing 10 % $CaCO_3$ and random waste plastics

The analysis showed the presence of a variety of compounds formed with carbon atoms between C_3 and C_{27}. Based on the retention times and fragmentation patterns, hydrocarbons, as well as halogen, oxygen, or nitrogen containing organic compounds were detected. The most important hydrocarbon constituents found were cyclopropane (C_3H_6) (t=1.49, m/z=41), 2-butene (C_4H_8) (t= 1.63, m/z=41), cis-1,2-dimethylcyclopropane (C_5H_{10}) (t=1.95, m/z=55), hexane (C_6H_{14}) (t=2.58, m/z= 57), methylcyclopentane (C_6H_{12}) (t=2.90, m/z=56), 2-methyl-1-hexene (C_7H_{14}) (t=3.58, m/z=56), methylcyclohexane (C_7H_{14}) (t=4.17, m/z=83), 1-octene (C_8H_{16}) (t=5.15, m/z=41), 1α,3α,5β-1,3,5-trimethyl-cyclohexane(C_9H_{18}) (t=5.92, m/z=69), decane ($C_{10}H_{22}$) (t=8.73, m/z=57), undecane ($C_{11}H_{24}$) (t=0.37, m/z=43), dodecane ($C_{12}H_{26}$) (t= 11.91, m/z=43), tetradecane ($C_{14}H_{30}$) (t=14.74, m/z=43), nonadecanes ($C_{19}H_{40}$) (t=19.52 and t=21.57, m/z=43), eicosane ($C_{20}H_{42}$) (t=24.33, m/z=43), 11-(1-ethylpropyl)-heneicosane ($C_{26}H_{54}$) (t=29.17, m/z=57). Different kinds of aromatic compounds such as benzene (C_6H_6) (t= 3.27, m/z=78), toluene (C_7H_8) (t=4.81, m/z=91), and styrene (C_8H_8) (t=6.94, m/z=104) were mainly found in the liquid products formed from wastes containing polystyrene. Oxygen-containing compounds such as cyclohexenenylmethanol ($C_7H_{12}O$) (t=4.39, m/z=79), Z-10-pentadecen-1-ol ($C_{15}H_{30}O$) (t=18.25, m/z=41), or 1-heptacosanol ($C_{27}H_{56}O$) (t=34.02, m/z=57) could also

be detected. Some halogen containing products such as N-[4-bromo-n-butyl]-2-piperidinone ($C_9H_{16}BrNO$) (t=12.38, m/z=41) were probably formed due to presence of additives or dyes in the waste plastics.

Conclusion

Thermal degradation of random mixtures of waste plastics containing low and high density polyethylene, polypropylene, and polystyrene, and 10% or 20% calcium carbonate in a steel reactor at temperatures 100-430 °C resulted in a fuel-like liquid decomposition product. GC/MS studies showed that, in the presence of 10% or 20 % calcium carbonate, the fuel-like hydrocarbon ranges were found to be C_4-C_{40} or C_3-C_{27}, respectively. Both liquid fractions contain mainly aromatic and aliphatic hydrocarbons such as benzene (C_6H_6), toluene(C_7H_8), ethylbenzene (C_8H_{10}), propylbenzene (C_9H_{12}), α-methylstyrene (C_9H_{10}), and 1-ethenyl-2-methylbenzene (C_9H_{10}). When using a higher amount (20 %) of $CaCO_3$, the amount of residue increased and the amount of light gas and liquid products decreased, with the liquid seeming to be thicker.

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