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A CONTRIBUTION TO THE RECOGNITION OF BIODIESEL FUELS ACCORDING TO THEIR FATTY ACID METHYL ESTERS PROFILES BY THE ARTIFICIAL NEURAL NETWORKS

Zilya Mustafa*, Stanimir Surchev, Rumyana Milina, Sotir Sotirov

University "Prof. Dr. Assen Zlatarov", Bourgas 8010, Bulgaria
zmustafa@abv.bg ; ssurchev@gmail.com; rumjana_milina@abv.bg; ssotirov@btu.bg

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Abstract

A chemometric approach using artificial neural network for classification of biodiesels was developed. It is based on artificial neural network in its classic form Multilayer Perceptron. Gas chromatography (GC) and Gas Chromatography – mass spectrometry (GC-MS) were used for quantitative and qualitative analysis of biodiesels, produced from different feedstocks, and FAME (fatty acid methyl esters) profiles were determined. Totally 93 analytical results for 7 different classes of biofuel plants: sunflower, rapeseed, corn, soybean, palm, peanut, "unknown" were used as objects. The analysis of biodiesels showed content of five major FAME (C16:0, C18:0, C18:1, C18:2, C18:3) and those components were used like inputs in the model. After training with 85 samples, for which the origin was known, ANN was tested with eight "unknown" samples. The "unknown" samples were properly recognized with an error between 1 and 4 %. The present research demonstrated the successful application of neural network for recognition of biodiesels according to their feedstock which give information upon their properties and handling.

Key words: Biodiesel fuels; fatty acid methyl esters; Gas chromatography; Gas Chromatography – mass spectrometry; artificial neural networks.

1. Introduction

Biodiesel fuel is defined as methyl esters of long chain fatty acids (FAME) produced from plant oils, animal fats and other lipids [1-3]. As a "green" fuel biodiesel has advantages over petrodiesel such as derivation from renewable feedstocks, biodegradability, nontoxic and essentially free of metals, sulfur, carcinogenic aromatics and low greenhouse effect and a positive energy balance.

Feedstock availability for biodiesel production depends on the geography, climate and economics of different countries. At present, the dominant feedstock (about 80 %) is vegetable oils, namely soybean oil in USA, rapeseed and sunflower oil in Europe and palm oil in Southeast Asia. Other feedstock having real or potential commercial interest are animal fats, non-edible and waste oils. Traditional for Bulgaria feedstocks are sunflower and rapeseed oils.

Since biodiesel is a mixture of fatty acid methyl esters (FAME), its properties depend on the chemical structure of the individual FAME and their contents (FAME profile). FAME profiles of biodiesel are influenced by the stocks and origin of the oils used [1, 4] and can be obtained by chromatographic methods [5-9] providing valuable multi-component information. So, FAME profiles appears to be an instrument for selection of feedstock [4, 10], investigations [11-12], fuel spillage and remedial actions in the environment [13]. This information can only be extract by using effective chemometrics methods and intelligent data analysis for classification, modeling and interpretation of large data sets [14-16].

The target of this work was to classify biodiesels from different feedstocks by a method based on neural network using their gas chromatographic FAME profiles. To the aim some

available literature data on FAME profiles of biodiesels from several types of oils were used [1, 4, 10, 16-17]. In the investigations also our data of FAME of Bulgarian biodiesels and samples produced in our laboratory by trans esterification of plant oils were utilized. Only those samples meeting the requirement of EN 14214 [18] were included in our study. The analysis of the samples was performed using gas chromatography (GC) and mass spectrometry (MS).

2. Experimental

2.1 Materials

Two commercial biodiesel fuels, labeled as samples 28 and 47 (Table 1), produced from sunflower and rapeseed oils respectively; 3 biodiesels – laboratory synthesized by methanol trans esterification of commercial oils, namely sample 9 (sunflower), sample 48 (rapeseed oil) and sample 88 (palm), samples 86, 87 and 89 to 91 were bought from the market, as for samples 86, 87 and 91 we had the information from the producers that the feedstocks were corn, sunflower and rapeseed oils respectively, for samples 89, 90, 92 and 93 the raw materials were completely unknown.

Certified reference materials: Fatty Acid Methyl Ester (B100), Methyl heptadecanoate (C17:0) were purchased from Spex CertiPrep; F.A.M.E. Mix Standard Rapeseed oil (cat № 18917) – from Supelco; Fatty acid methyl esters – myristate (C14:0), palmitate (C16:0), palmitoleate (C16:1), stearate (C18:0), oleate (C18:1), linoleate (C18:2), linolenate (C18:3), arachidate (C20:0), cis-11-eicosenoate (C20:1), behenate (C22:0), cis-13-docosanoate (C22:1), tetracosanoate (C24:0), cis-15-tetracosanoate (C24:1) – from Sigma-Aldrich. Reagents of recognized analytical grade were used.

2.2 Gas chromatography

All GC analyses were performed on a GC system Agilent Technologies 7890A equipped with FID, split/splitless injector and Agilent 7693A automated liquid sampler. The fussed silica capillary column HP-INNOWAX, 30m x 0.32mm ID and 0.25μm film thickness was used. Helium was used as a carrier gas, column flow was 1.5 ml/min. Hydrogen and air flows were set to 40 ml/min and 400 ml/min, respectively, makeup gas (nitrogen) 40 ml/min. The injection volume was 1 μl and split ratio was 1:80. The temperatures of the injector and the detector were 250ºC and 300ºC, respectively. The temperature program of the oven was initial temperature 210ºC for 9 minutes and then to 230ºC at 20ºC/min and hold there for 10 minutes.

ChemStation for GC (Agilent Technologies) was used for instrumental control, data acquisition and data analysis. GC-MS analyses were carried out using GC system Agilent Technologies 7890A combined with MSD 5975 C Inert XL EI/CI, electron impact ionization (70eV), mass range 30 – 500 m/z and the same chromatographic conditions. The components of biodiesels were identified by injection of standards and by comparison of mass spectra with those of a NIST MS computer library.

Sample 0.3 μl were injected with split ratio 1:100. GC chromatograms of FAME from sunflower and rapeseed oil are shown in Fig. 1 and Fig. 2. Peaks identified by GC-MS, are as follows: C14:0, C16:0, cis9 C16:1, C17:0 (IS), C18:0, cis9C18:1, cis9cis12C18:2, cis9cis12cis15 C18:3, C20:0, cis11C20:1, C22:0, cis13C22:1, C24:0, cis15C24:1. The composition (percentage of the esters) was calculated by the method of the internal standard (IS - methyl heptadecanoate).

2.3 Artificial Neural Networks (ANN)

The artificial neural networks [19-20] are the one of the tools that can be used for recognition and identifying the things. In the first step it have to be learned and after that we can use for the recognitions and for predictions of the properties of the materials. Fig. 3 shows in abbreviated notation of a classic tree-layered neural network.

In the many-layered networks, the one layer's exits become entries for the next one. The equation**s** describing this operation are:

$$a^3=f^3(w^3f^2(w^2f^1(w^1p+b^1)+b^2)+b^3)$$, where:

- a^m is the exit of the m-layer of the neural network for m =1, 2, 3;
- w is a matrix of the weight coefficients of the everyone of the entries;
- b is neuron's entry bias;
- f^m is the transfer function of the m-layer.

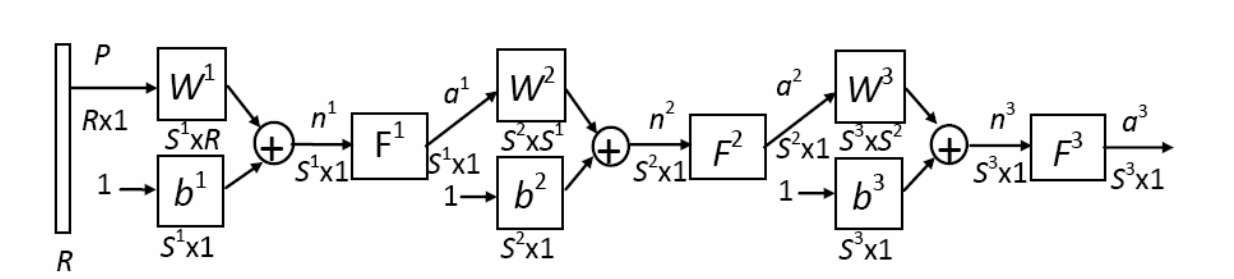

Fig. 3. Tree-layered neural network

The neuron in the first layer receives outside entries p. The neurons' exits from the last layer determine the neural network's exits a.

Because it belongs to the learning with teacher methods, to the algorithm are submitted couple numbers (an entry value and an achieving aim – on the network's exit)

$$\{p_1, t_1\}, \{p_2, t_2\}, \ldots, \{p_Q, t_Q\}$$

$Q \in (1...n)$, n – numbers of learning couple, where p_Q is the entry value (on the network entry), and t_Q is the exit's value replying to the aim. Every network's entry is preliminary established and constant, and the exit have to reply to the aim. The difference between the entry values and the aim is the error – $e = t\text{-}a$.

The "back propagation" algorithm [21] use least-quarter error (MSE):

$$\hat{F} = (t-a)^2 = e^2.$$

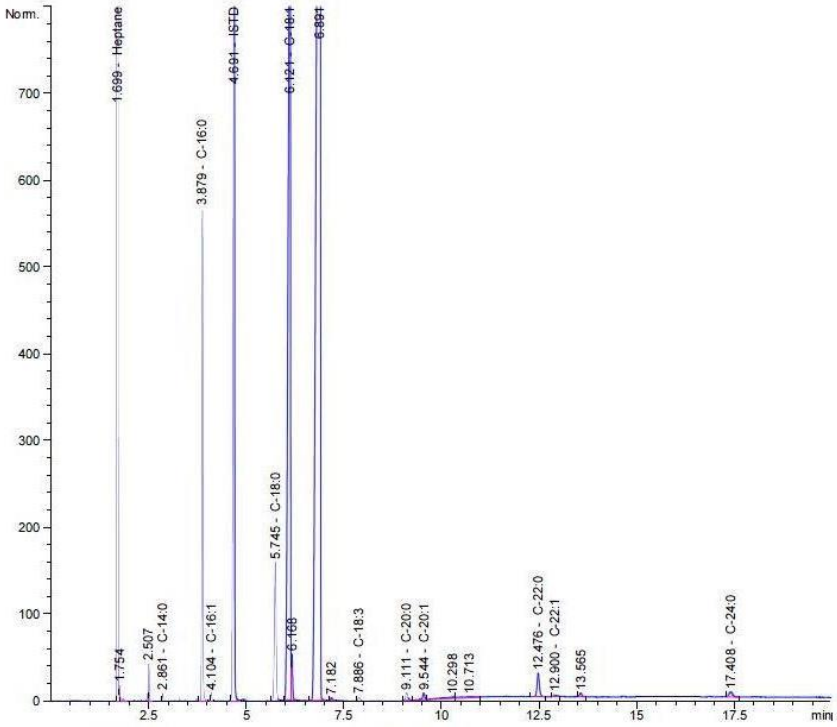

Fig. 1 GC chromatogram of sunflower oil biodiesel

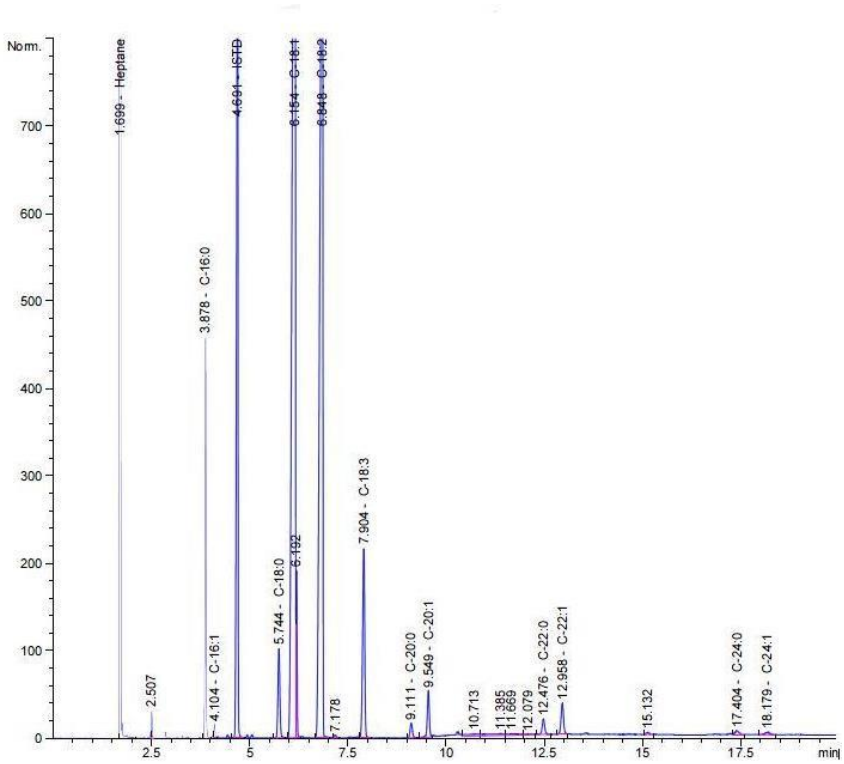

Fig. 2 GC chromatogram of rapeseed oil biodiesel

3. Results and discussion

Of the 13 esters, shown in Fig. 1 and Fig. 2, five typically dominate the FAME profiles of biodiesels derived from plant oils: methyl esters of palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2) and linolenic (C18:3) acids. The content of those major components in biodiesels used in this work is summarized in Table 1. Some of samples (indicated above) are analyzed in our laboratory and other data of FAME profiles of biodiesels are taken from the literature.

Totally 93 analytical results for 7 different classes of biofuel plants: class 1- sunflower, class 2 – rapeseed, class 3 – corn, class 4 –soybean, class 5 – palm, class 6 – peanut, class 7 – "unknown" were used as objects of the classification and multivariate statistical interpretation (Table 1). The percentage of five fatty acid methyl esters (C16:0, C18:0, C18:1, C18:2, C18:3) represent five inputs in this ANN model.

The ANN model was built using the biodiesels for which the origin was known. After training with 85 samples, the neural network was tested with eight "unknown" samples. Below the target and conditions of training and results obtained are given (Table 2).

Table 2 Target of the Neural Network

Class of the sample	Values of the outputs of the NN					
Class 1	1	0	0	0	0	0
Class 2	0	1	0	0	0	0
Class 3	0	0	1	0	0	0
Class 4	0	0	0	1	0	0
Class 5	0	0	0	0	1	0
Class 6	0	0	0	0	0	1

The number of the hidden layer neurons are 25, number of the epochs 1000. For the learning function we use– trainlm and type of transfer function tansig.

In Fig. 4 the parameters used for the training of Neural Network are shown.

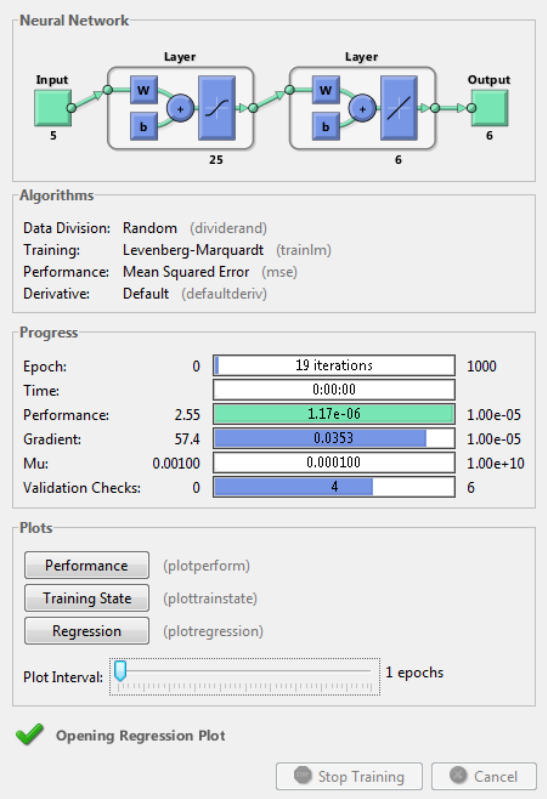

Fig. 4. Parameters for the training of Neural Network

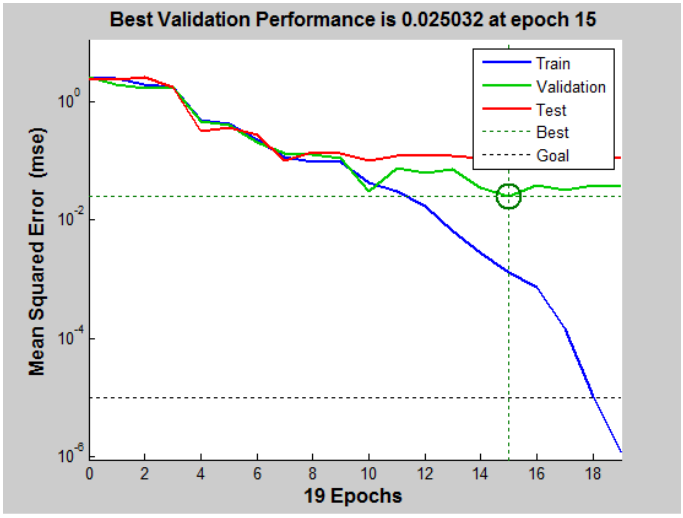

Fig. 5. Propagation of the MSE

In Fig. 5 one can see the graphics of propagation of the MSE during the training process.

For testing of ANN samples 86 to 93 (class 7) were used with the same five inputs and the real outputs and errors obtained are given in Table 3 and Fig. 6.

Table 3 Outputs and errors for the "unknown" samples

Sample	Output1	Output2	Output3	Output4	Output5	Output6	Recognition class	Error (%)
86	-0.0236	0.0056	0.9711	0.0360	-0.0076	-0.0044	3	1
87	1.0062	-0.0037	0.0072	-0.0218	0.0020	-0.0001	1	1
88	0.0223	-0.0023	-0.0090	-0.0057	0.9997	-0.0007	5	4
91	0.0023	1.0013	-0.0042	0.0099	0.0005	0.0009	2	4

It can be seen that the samples 86 to 88 and 91 are properly recognized with an error between 1 and 4 %. Three of biodiesels were declared by the manufacturer as produced from corn, sunflower and rapeseed oils, the fourth "unknown" sample (sample 88) was synthesized in our laboratory using palm oil as feedstock and it was confirmed by the ANN method proposed.

Completely unknown samples 89 and 90 are defined as biodiesels produced from peanut and soybean respectively, and samples 92 (class 1- sunflower) and 93 (class 1- sunflower and class 3 – corn).

The quality of the prediction of mixed samples composition cannot be confirmed since there is no exact information from the producers about feedstocks used.

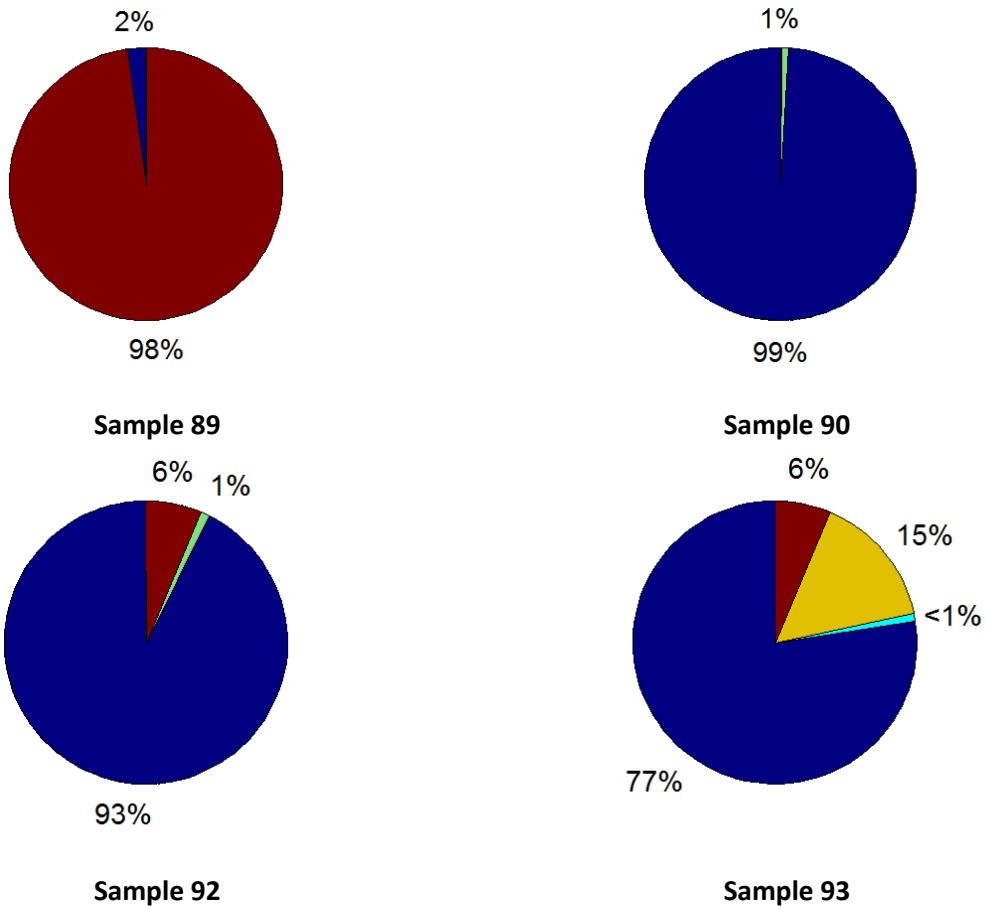

Fig. 6. Circle diagrams of the values of the outputs for testing samples

4. Conclusion

The present research demonstrates the successful application of artificial neural network for recognition of biodiesels according to their feedstock. The proposed model was created on the base of content of five major components: esters of C16:0, C18:0, C18:1, C18:2, C18:3 acids in the FAME profiles of biodiesel from vegetable oils origin. Those components were used like inputs in the model. Totally 93 analytical results for 7 different classes of biofuel plants: sunflower, rapeseed, corn, soybean, palm, peanut, "unknown" were used as objects. The model was trained with 85 samples, for which the origin was known, and then was tested with eight "unknown" samples. The obtained predictions correlate well with the available information of the samples. The quality of the prediction of mixed samples composition cannot be confirmed since there is no exact information from the producers about oils used. We anticipate further application of the model to recognize of biodiesels, produced from mixed oils.

The overview of predicted results indicates that the proposed model is of significant value for the determination of unknown biodiesels and could be implemented as an efficient method that enables the prediction of the raw material. The latter provides information upon the properties and handling of biodiesel fuels.

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Table 1 FAME (percentage levels) of biodiesel samples

Sample №	Class	C16:0	C18:0	C18:1	C18:2	C18:3	Sample №	Class	C16:0	C18:0	C18:1	C18:2	C18:3
1	1	6.3	3.9	20.8	67.8	0.2	48	2	4.6	1.8	55.9	17.7	5.3
2	1	6.1	4.1	24	64.3	0.1	49	2	4.8	2	60.4	23.3	9.5
3	1	6.2	3.9	27.1	59.9	1.3	50	2	4	2.5	61.2	20.6	11.7
4	1	7.2	4.5	25.6	61.1	0.2	51	3	11.8	2.1	27.4	57.7	0.6
5	1	6.2	4.1	26.8	61.4	0.1	52	3	10.7	1.8	30.2	55.5	0.9
6	1	6.1	4	25.2	63.2	0.1	53	3	10	2.3	36.9	47.1	2.2
7	1	6.1	4.1	26.7	61	0.6	54	3	10.1	1.6	26.9	59.9	0.7
8	1	6.2	4	25.8	62.2	0.4	55	3	11.8	2.1	35.5	46.6	1.4
9	1	6	3.8	29.6	57.7	1.2	56	3	12.3	1.7	25.3	60	0.7
10	1	6.5	2.8	23.2	66.1	0.1	57	3	12.9	1.7	25.3	59.5	0.6
11	1	7	3.4	23.2	64.9	0.1	58	4	11.4	4.1	23.5	53.5	6.6
12	1	6	4	28.3	60.1	0.1	59	4	10.9	3.6	26	52.6	5.5
13	1	6.1	4.1	25.1	63.5	0.5	60	4	9.6	3.5	30.3	49.2	5.9
14	1	6.3	4.1	27.4	61.4	0.7	61	4	10	4.2	24.9	53.2	6.9
15	1	6.2	4.1	27.1	61.8	0.7	62	4	10.4	4.2	25.9	50.8	7.5
16	1	6.2	4.2	27	60.9	0.5	63	4	10.5	4.2	24.4	52.1	7.5
17	1	6.2	4	28.3	59.7	0.9	64	4	10.5	4.3	24.6	53.1	7.6
18	1	6.4	3.7	25.8	63.5	0.5	65	4	10.2	4	23.1	55.1	7.1
19	1	6.8	4.3	26.4	60.5	1.3	66	4	10.9	3.8	27.2	49.5	6.4
20	1	6	4.4	27.1	60.9	0.9	67	4	11.9	3.8	25.7	52.7	5.8
21	1	6.4	4.8	25.3	61.8	1	68	4	9.7	3.9	25.1	54.2	5.9
22	1	5.9	4.5	24.1	61.7	0.9	69	4	13.9	2.1	23.2	56.2	4.3
23	1	6.6	4.1	29.9	57.8	1.3	70	4	10	4	23	51	7
24	1	6.6	4.7	24.5	62.8	0.3	71	4	11.9	4.1	23.2	54.2	6.3
25	1	6.4	4.4	24.4	63.7	0.4	72	4	11.7	3.8	22	52.6	7.7
26	1	6	3	17	74	0	73	4	11.3	3.6	24.9	53	6.1
27	1	6.4	2.9	17.7	72.9	0	74	4	11.6	3.9	23.7	53.8	5.9
28	1	6.2	3.7	25.2	63.2	0.2	75	4	11.2	4	21.9	53.8	7.3
29	1	6.1	3.1	30	57.9	0.5	76	5	42.4	4.2	40.9	10	0.3
30	1	6.4	3.6	21.7	66.3	1.5	77	5	42.5	4.2	41.3	9.5	0.3
31	1	6.2	3.7	25.2	63.1	0.2	78	5	42.5	4.4	40.5	10.1	0.2
32	1	6.4	3.1	27.4	62.1	0.1	79	5	36.7	6.6	46.1	8.6	0.3
33	2	4.1	1.6	62.2	20.6	8.7	80	5	46.1	4.3	38.4	10	0.2
34	2	5.1	2.3	55.9	27.4	6.8	81	6	10.3	2.8	47.6	31.5	0.5
35	2	4.8	1.8	62.6	20	9.5	82	6	11.4	2.4	48.3	32	0.9
36	2	5.5	1.7	59	21.3	9.3	83	6	8	1.8	53.3	28.4	0.3
37	2	4.8	1.9	61.6	20.9	8	84	6	10	3.3	60	21.3	0.2
38	2	5.4	2	53.2	28.9	7.3	85	6	9.6	3.3	57.7	20.7	0.2
39	2	4.5	1.7	64.9	18.6	8.3	86	7	11.5	1.9	26.6	58.7	0.8
40	2	5.7	2.1	54.6	26.8	8	87	7	5.6	4.2	25.7	58.9	1.7
41	2	6.2	2.2	52.2	29	8	88	7	45	5	40	10	0
42	2	4.2	1.6	59.5	21.5	8.4	89	7	9.7	3.4	59.3	20.5	0.1
43	2	3.5	0.9	64	22	8.1	90	7	10.5	4.2	25.5	52	7.8
44	2	3.5	0.9	54.1	22.3	8	91	7	5.1	1.9	59.2	22.3	9.3
45	2	4.1	1.8	58.6	22.2	13.3	92	7	0.1	3.5	22.2	54.6	0.1
46	2	4.1	1.6	55.7	17.8	7.6	93	7	0.2	2.9	38.4	45.9	2.5
47	2	4.5	1.6	60.8	17.7	7.9							