KEY PARAMETERS TO MONITOR THE USED METALWORKING FLUIDS

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This paper presents simple statistical instruments to identify some characteristic parameters for water-based metalworking fluids monitoring and to develop a regression model for spent emulsions evaluation. By Factor Analysis and Loading Plot, the surface tension and pH values are proposed as significant physical-chemical parameters that can be adequately used to monitor and to characterize metalworking fluids. Two modified exponential equations have been developed to correlate these surface tension - pH measurements data in order to monitor and label the spent metalworking fluids. The results obtained are valuable as they are based on easy, fast and low-cost measurement of the two parameters, thus contributing to maintain the quality of machinery functioning and to reduce pollution by minimizing the waste.

Keywords: metalworking fluids, statistical analysis, surface tension, pH

1. Introduction

Metalworking fluids (MWFs) are special designed fluids used in different operations such as cutting [1], drilling, turning, grinding [2], and milling. Metalworking fluids utilized in metal processing are recognized in particular for their lubricating and cooling capacity, assuring protection against thermal damage of the workpiece material and diminish wear of the tool [3]. Another important role of MWFs is to remove chips from the machining area of the metal part, thus improving the quality of the machinery functioning [4].

Based on DIN 51385 standard of German Institute for Standardization MWFs can be oil-based or water-based (which include oil-water emulsion). Water-based MWFs are most used in less severe operations [5], being regularly formulated as oil-in-water emulsions containing a continuous aqueous phase and a dispersed oil phase, with a concentration of 1 to 10% v/v and a narrow droplet size distribution with a mean droplet size of 0.1 to 2.0 μm [6]. MWFs formulation

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includes different additives (emulsifiers, coupling agents, corrosion inhibitors, biocides, anti-wear agents, etc.), which can provide the use of parameters specific to a given type of processing [7].

During operation, metal chips and fines, tramp oil, and dissolved salts are usual contaminants responsible for MWFs compositional changes. Besides that, essential components are removed from the fluid through evaporation or thermal and biological decomposition [8]. In order to maintain the predefined performance of the MWF, its properties have to be kept inside specified limits. This is accomplished through the addition of water and chemicals to restore their composition during operation. Consequently, close control and monitoring of the selected MWF parameters to determine its degradation degree is required. MWFs are designed to work in the alkaline range at a pH between 8.0 and 9.5 knowing that alkalinity helps to control corrosion and decreases the growth of microorganisms. A low pH in MWFs is usually the result of bacterial activity and can serve as an indicator for the overall state of the fluid [9, 10].

The purpose of this work was to identificate some parameters for monitoring water-based MWFs used in an electronic equipment factory for the manufacture of metal components. In this respect, a relevant strategy on parameters selection is proposed for characterization of MWFs in some workshop – specific machinery processing actions.

2. Materials and methods

The industrial MWFs samples investigated in this paper are provided by, an electric engine factory, ICPE Bucharest, Romania, while the tests and data processing have been jointly performed together with a research center from University POLITEHNICA of Bucharest. The samples description and their allocated codes are presented in Table 1.

The samples belong to two main categories: commercial fluids samples, as different products and production batches (denoted as A, B, C1, C2, C3, C4), and industrial MWFs samples collected from the storage tanks of different processing machineries. From the perspective of their composition, the commercial fluid samples A (Eco Cool 67- semi-synthetic metalworking fluid), B (Oltec Cool 2600- mineral metalworking fluid), C (Oltec Cool 1651- mineral metalworking fluid) contain organic esters in different percentages, the highest content being in the case of sample B. Stock working MWFs (A0, B0, C2-0, C3-0, C4-0) were prepared from each commercial oil sample received, in the same conditions as in factory workshops, according to the processing operation.

The industrial MWFs samples were collected from the storage tanks of four different processing machineries. These samples come from the processing of metal parts by turning, milling, drilling. Samples can be classified into two major categories:

- time-dependent sample sets: were taken at different times from the same machinery (ex. A1 – A4).
- samples from different metal processing machineries (ex. C3-2, C3-4, C4-2).

Table 1

MWFs samples

Nr. crt	Code	Sample description
1	A0	Stock working MWF
2	A1	MWF until the first completion
3	A2	MWF used 80 h
4	A3	MWF used 130 h
5	A4	Spent MWF (collected as waste)
6	B0	Stock working MWF
7	B1	MWF
8	B2	MWF used 60 h
9	B3	MWF used 129 h
10	B4	Spent MWF(collected as waste)
11	C2-0	Stock working MWF
12	C2-1	MWF used 86 h
13	C2-2	MWF used 150 h
14	C2-3	MWF used 210 h
15	C2-4	Spent MWF (collected as waste)
16	C3-0	Stock working MWF
17	C3-1	Stock MWF
18	C3-2	Milling machinery
19	C3-3	Spent MWF - 400 h round grinding (collected as waste)
20	C3-4	Spent MWFs-500 h planar grinding (collected as waste)
21	C4-0	Stock working MWF
22	C4-1	3 months milling - CMX 600 machinery
23	C4-2	6 months turning - EMCO machinery
24	C4-3	45 days grinding - DM60 machinery
25	C4-4	73 days grinding - old machinery

2.1. Methods

2.1.1. Physical-chemical characterization

The main physical-chemical parameters of MWFs emulsion samples were determined according to following methods [16]:

- **density** by pycnometer method according to EN ISO 3675 [17]
- **electrical conductivity** by using an electrical conductivity meter according to SR ISO 6297:2002 [18]
- **pH** with a pH meter according to SR EN ISO 10523 [19]
- **kinematic viscosity** by using Ostwald viscometer according to EN ISO 3104/AC:1999

- **surface tension** by using Du Nouy ring method, on a Sigma 702 force tensiometer, according to SR EN 14370:2005.

For all analyzed samples, three measurements were performed for each parameter in the list, and the average value has been considered.

2.1.2. Statistical methods

Selection of representative parameters from a data set is an essential condition for monitoring processes in different fields. For this purpose, the use of a statistic software is useful for getting valuable information on the parameters in order to choose the relevant ones [11, 12].

For the oil samples received (denoted as A, B, C1, C2, C3, C4), an identifying run of the important characterization parameters was performed by factor analysis (FA), in order to reduce the multitude of variables and to decrease the number of factors. This technique extracts the maximum common variance from all variables and places them in a common score. Factor statistical analyses were performed using the Statgraphics Centurion XVII program, version 17.2.07, which is a specific product for statistical analysis, data visualization and predictive analytics [13]. Based on the factor analysis results, the laboratory measurements have been performed for both stock and related used MWFs samples collected from the storage tanks. The final data set of measurements was evaluated in order to identify a relationship between the input characteristics of stock MWFs and related spent MWFs. Data interpretation was performed by using confidence intervals, table of means, quantile and box-and-whisker plots.

The scree plot displays the number of the factor *versus* its corresponding eigenvalue or characteristic value, which are ordered from largest to smallest.

Another statistical instrument was loading plot in order to discover which variable / parameter (pH, electrical conductivity, density, viscosity, superficial tension) have the most important effect. Loadings, meaning factor 1 and factor 2, can range from -1 to 1. Loadings close to -1 or 1 indicate that the variable strongly influences the factor. The evaluation of the loadings for analyzed variable package assured a valuable characterization for each parameter.

Analysis of variance (ANOVA) represents a selection of statistical models and their correlated evaluation methods are used to evaluate the differences between means. The Least Significant Difference (LSD) evaluation method specifies that if 0 value is not obtained after the calculation of lower and upper limits, the data sets significantly differ statistically.

The dispersion measurement (instead of standard deviation) is made by the interquantile range (IQR). This method is based on the median principle which divides the sample measurements into two equal halves; if each of these halves is further divided into two, the points of division are called the upper and the lower quantiles. The simplest way of graphical representation is the box-and-whisker plot in which it stands out the greater value on a wide pattern of samples.

Cluster analysis (CA) is a method for separating similar objects of a group in classes. The method for searching clusters consists in seeing each object from a class part of a cluster and comparing the distance between them. The couple of points whose distances are nearby are merged to form a new cluster. The successive stages of grouping can be shown on a dendrogram.

3. Results and discussion

3.1. Statistically significant physical-chemical parameters identification

It is known that the control and monitoring properties of emulsifiable oils are important for technical applications. The purpose of this study was to identify characteristic parameters which are suitable for quality control of emulsifiable oils as such or in the form of MWFs. Therefore, for commercial MWFs was performed a ranking/classification of the measured parameters (see Table 2) by cluster analysis, which is a part of Analysis of Statistical Factors. The parameters correspond to the F1-F5 factors and the assignment of the interest factors (F1-F2) was realized by statistical analysis. Firstly, the scree plot, a useful tool to select the number of factors was used for MWFs evaluation based on the size of the eigenvalues and two factors, F1 (surface tension) and F2 (pH) were identified. (see Fig.1a)

Table 2

Physical-chemical properties of water dispersed oil, used for MWF preparation

Oil sample	Surface Tension (mN/m)	pH	Electrical Conductivity (µS/cm)	Density (g/cm^3)	Viscosity (mPa×s)
	F1	F2	F3	F4	F5
A	24.74	10.45	2.65	1.04	68.00
B	25.47	9.83	20.20	1.00	178.99
C1	25.55	10.28	110.00	0.96	73.23
C2	24.27	9.38	338.33	0.96	83.45
C3	24.49	8.71	400.33	0.96	77.84
C4	23.05	10.26	446.00	0.96	70.32

In order to confirm this conclusion, another powerful tool, loading plot, was used. The graphical representation of the loadings is based on the factorial analysis of the main component of the correlation matrix. This matrix is constructed based on the physical-chemical parameters of the samples assimilated as variables, for which the orthogonalization calculations were performed. The results obtained are summarized in Table 3, in which for each parameter was calculated the loadings / two factors.

Table 3

Factor loadings

Variable	**Loading**	
	Factor1	**Factor2**
pH	**0.873**	0.182
Electrical conductivity	-0.738	0.663
Density	0.785	-0.29
Viscosity	-0.074	-0.831
Superficial tension	0.225	**-0.854**
Variance	1.9792	1.9783

According to this method the surface tension is considered factor 1 (F1; 0.873), since it has the highest value from the set of variables package, showing that this parameter can be used for monitoring and characterizing the set of emulsifiable oils while the factor 2 (F2; -0.854), is selected as being the pH. These two characteristic parameters identified based on the factor analysis, ***surface tension (ST)*** and ***pH***, and confirmed by Loading Plot, can be used to monitor and to characterize the set of emulsifiable oils.

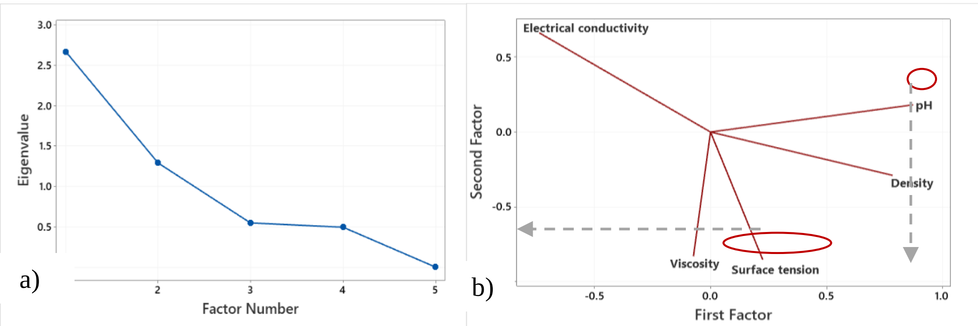

Fig.1. Graphical representation of analysis results: a) scree plot; b) loading plot

3.2. Statistical evaluation of industrial MWFs tested

Based on these preliminary studies, the next tests performed were focused on:

- stock working MWFs (A0, B0, C2-0, C3-0, C4-0, Table 1) obtained according to mechanical operation (turning, milling, drilling);
- industrial MWFs samples received from the industrial workplace (A1 …, B1 …, C2-1 …, C3-1…, C4-1…, Table 1)

3.2.1. Characteristic parameters measurements

Surface tension (ST) and pH measurements, both for stock working and industrial MWFs, have been performed and the results are presented in the figures 2-6. From analysis of data in figs. 2-6 one can see that in all cases, the measured parameters show higher values for the stock working MWFs samples than those of the spent industrial MWFs samples. This behavior is common for both pH and surface tension.

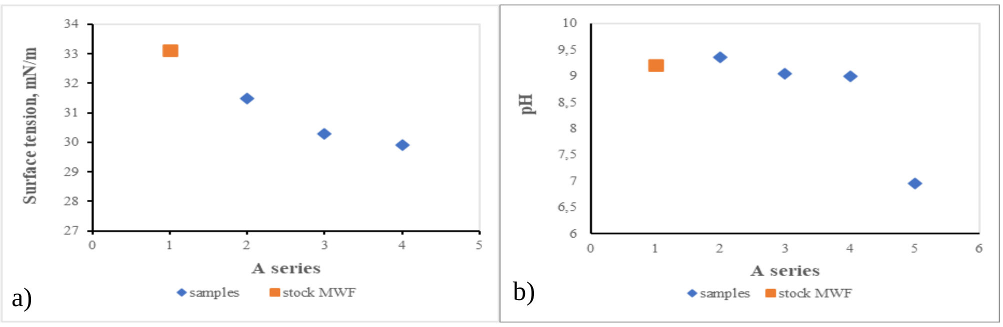

Fig.2. Parameters variation for A samples time series vs. stock MWF: a) surface tension, b) pH

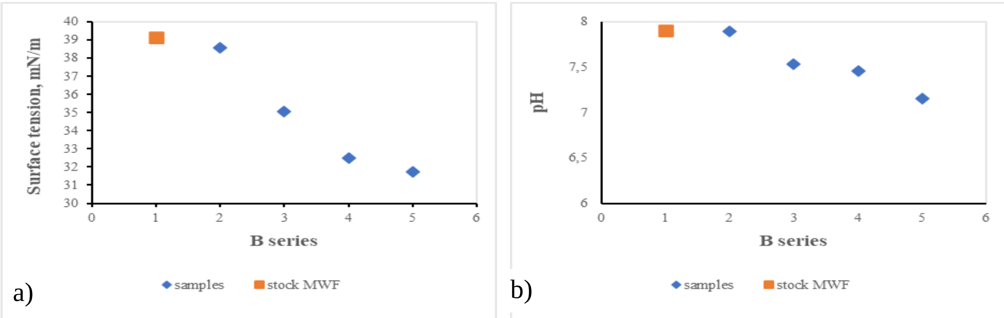

Fig.3. Parameters variation for B samples time series vs. stock MWF: a) surface tension, b) pH

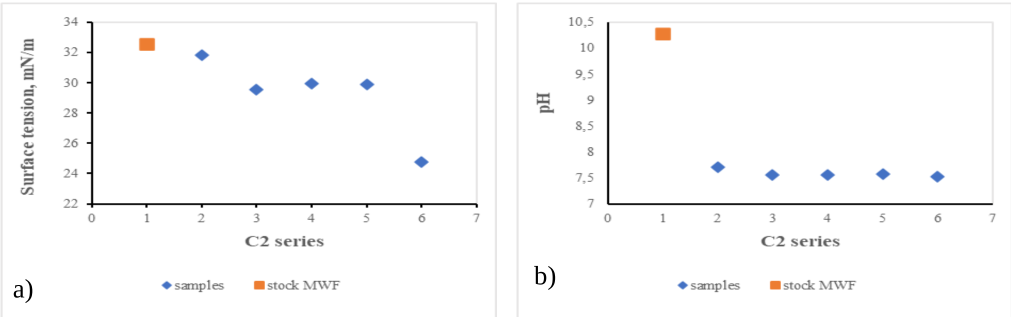

Fig.4. Parameters variation for C2 samples time series vs. stock MWF: a) surface tension, b) pH

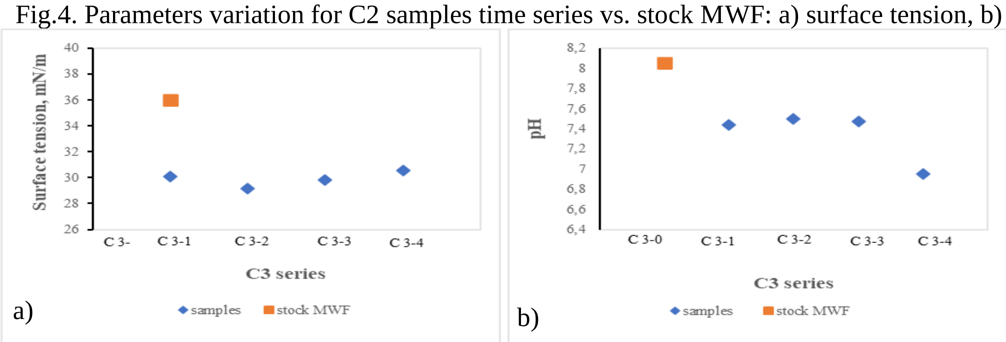

Fig.5. Parameters variation for C3 samples series vs. stock MWF: a) surface tension, b) pH

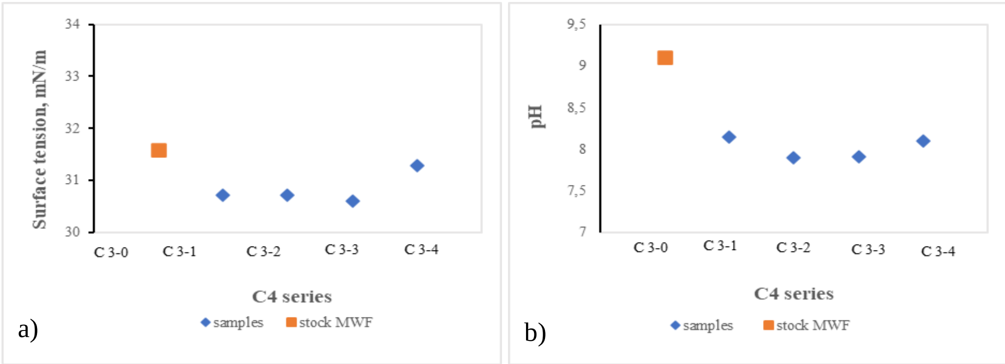

Fig.6. Parameters variation for C4 samples series vs. stock MWF: a) surface tension, b) pH

3.2.2. ANOVA statistical analysis

For a detailed analysis of the experimental results, the data package was organized into three subcategories: stock, used and spent MWFs measurements. This assumes that each subgroup will contain data in the form of pH-surface tension pairs (Table 3).

In order to obtain qualitative and quantitative significance of measured data, a statistical analysis was performed.

3.2.2.1. Confidence intervals

A confidence level of 95% represents the domain in which the probability that one parameter will fall between a pair of values around the mean is 95%. In addition, the confidence interval gives information about the degree of certainty in a sampling method. Table 4 shows 95.0% confidence intervals for the means and standard deviations of each of the variables.

Table 4

Statistical variability of MWFs parameter values

	Mean	Stnd. error	Lower limit	Upper limit	Sigma	Lower limit	Upper limit
pH stock	8.24	0.19	7.82	8.67	0.59	0.41	1.08
ST stock	32.98	0.55	31.75	34.22	1.73	1.19	3.16
pH used	7.78	0.19	7.35	8.21	0.64	0.45	1.12
ST used	31.32	0.89	29.33	33.31	2.96	2.07	5.19
pH spent	7.47	0.12	7.20	7.73	0.37	0.26	0.68
ST spent	30.10	0.66	28.61	31.58	2.07	1.43	3.79

These confidence intervals link the sampling errors to the estimations of the parameters of the populations from which the records come from. They may be used to assess the precision of the population means and standard deviations estimation. The confidence levels are calculated assuming that the populations from which the samples come can be represented by a normal distribution. While the confidence intervals for the mean values are rather solid and not very sensitive to violations of this assumption, the confidence intervals for the standard deviations are to some extend sensitive and show deviations from the normal distribution.[15]

3.2.2.2. Means Analysis

Table 5 shows the mean for each set of data (stock MWF, used MWF and respectively spent MWF). It also shows the standard error of each mean, which is a measure of its sampling variability and the corresponding lower and upper limits.

Table 5

Table of Means with 95.0 percent LSD intervals

	Mean	*Stnd. error (pooled s)*	*Lower limit*	*Upper limit*
pH stock	8.25	0.54	7.49	9.01
ST stock	32.98	0.54	32.22	33.74
pH used	7.78	0.51	7.06	8.51
ST used	31.32	0.51	30.59	32.04
pH spent	7.47	0.54	6.71	8.23
ST spent	30.10	0.54	29.33	30.86
Total	19.65			

The intervals currently displayed by lower and upper limits (Table 5) are based on Fisher's least significant difference (LSD) procedure. They are constructed in such a way that if two means are the same, their intervals will overlap 95.0% of the time.

From the table 5, it can be also seen that the lower and the upper limit do not contain 0. Therefore, it can be noticed that values of data pair (stock respective spent solution) are statistically different.

3.2.2.3 Graphical statistical analysis

Graphical representations were generated based on statistical studies on the data package. In Fig. 7 graphical quantiles of the data for each component of the corresponding subgroup are shown. In Fig. 8 the selected data are represented using Box-and-Whisker plot in order to observe the variance of data and also the overlapping domains, if they exist [14].

From the statistical analysis, one can notice the overlapping absence between the stock working and spent subgroups data. Consequently, the statistical interpretation of pH - surface tension couple measurements recommend that tracking these parameters represents a useful instrument to assess the degree of wear of MWFs.

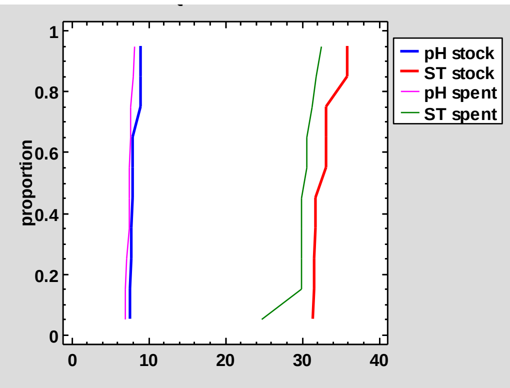

Fig.7. Quantile Plot of stock and spent MWFs

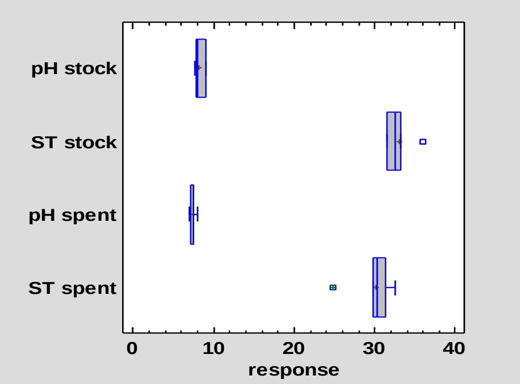

Fig.8. Box-and-whisker plot of stock and spent MWFs

3.3. Development of a regression model between surface tension (ST) and pH

The analysis of the pair set combined with their graphical representation led to the identification of two dependences of pH - surface tension pairs (see Fig.9). These two curves are based on the identified values, in the range of pH 6.95-7.46 for ST spent_1 and in the range 7.47-8.1 for ST spent_2.

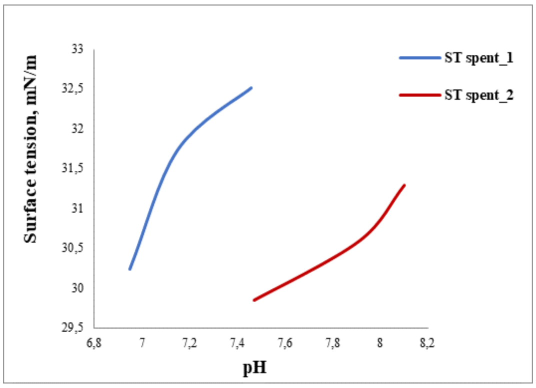

Fig.9. Surface tension vs pH variation for spent MWFs industrial samples

By analyzing the contributions of industrial samples to these two dependences, it was identified that in the first curve (ST spent_1 blue line in Fig.9) are grouped the samples belonging to samples A and B, while the second curve (ST spent_2 red line in Fig. 9) is populated by samples belonging only to samples from batches C. This behavior is sustained by cluster analyses of the physical properties data package for the six emulsifiable industrial oil samples. (Table 2).

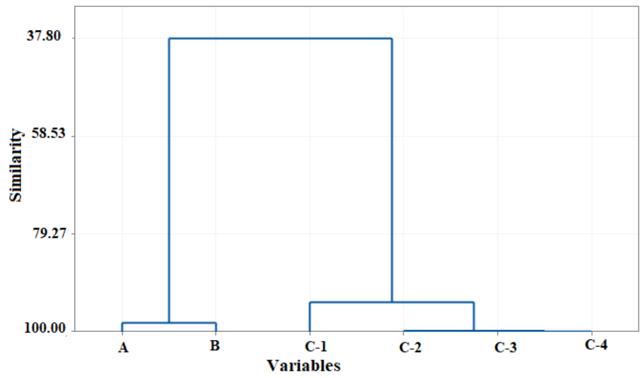

Fig.10. Dendrogram of industrial emulsifiable oils based on physical parameters package

Figure 10 shows that there are two distinct blocks in dendrogram. The first block consists of industrial samples A and B, while the second block corresponds to type C, these samples being part of different batches. This behavior could be attributed to their composition differences, namely esters percentage.

The program Statgraphics Centurion XVII version 17.2.07 was used to identify the outliers [15], and the characteristic equations for the two curves were identified. The correlation between pH and surface tension is described by the general equation from the modified exponential equation group, which has the expression:

$$ST_{spent} = a * exp^{b/pH_{spent}} \quad (1)$$

were,
ST_{spent} represents the surface tension of spent MWFs, mN/m
pH_{spent} represents the pH value of spent MWFs,
a and *b* represent constants specific to each curve.

All the developed equations parameters for each curve are briefly presented in the Table 6.

Tabel 6

Overview of descriptors related to correlation equations

	ST Spent_1	ST Spent_2
Name	Modified exponential	
Kind	Regression	
Equation	y=a*exp(b/x)	
Confidence interval	95%	95%
Standard error	0.47	0.22
Correlation Coeff. (r)	0.96	0.98
Coeff. of Determination (r^2)	0.92	0.95
Parameters		
a	84.02	53.03
b	-7.05	-4.31

Calculations have been performed to verify the developed equations using the pH - surface tension couple measurements for different spent MWFs resulted from mechanical operations.

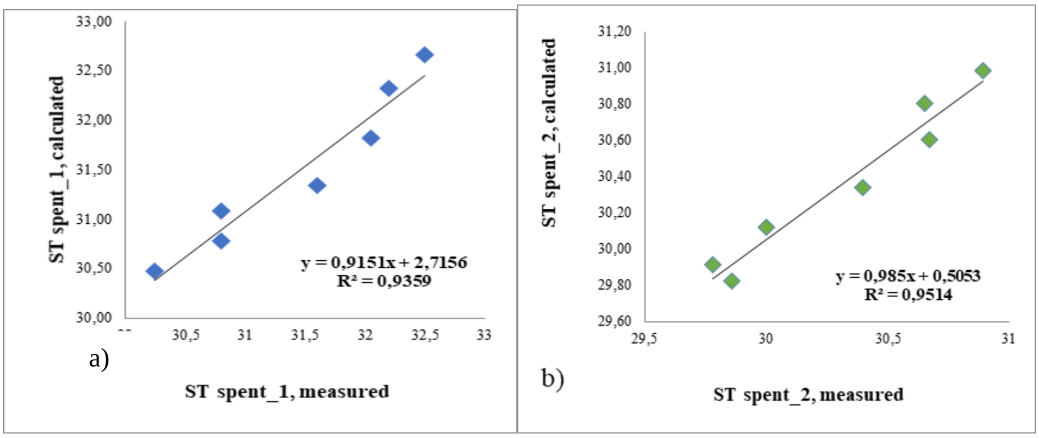

Fig.11. Evaluating the reproducibility of correlations developed for spent MWFs:
a) ST spent_1 correlation, b) ST spent_2 correlation

As it can be seen from Fig 11, the measured values are consistent with the statistical predictions for both identified curves, the calculated values falling within the confidence interval. The use of these two correlations specific to the curves identified for the industrial emulsions used in the factory can be used as valuable tools to monitor and label the spent MWFs.

pH and surface tension measurements were realized, in triplicate, on one spent MWF sample. In order to evaluate the consistency of the measured parameters compared to those calculated, the t-Student Statistical Test was applied (Table 7).

Table 7

Spent MWFs evaluation

ST _spent 1 measured	ST_spent 1 calculated	t calculated	t tabulated	p	Significance
38.61	34.49	1.48	1.53	0.084	p <0.10
38.53	34.42				
38.57	34.46				

The t tabulated for four degrees of freedom at the 90% confidence level is 1.53, which is higher than the calculated value (1.48), meaning that there is no statistical difference in the two values, calculated and measured and, the MWF sample could be appreciated as spent.

4. Conclusions

The results provided by this work are useful to identify some characteristic parameters for water-based metalworking fluids (MWFs) monitoring and to develop a regression model for spent MWFs evaluation.

The surface tension (ST) and pH have been chosen, by Factor Analysis (FA) and Loading Plot, as significant physical-chemical parameters that can be properly used to monitor and characterize MWFs.

ANOVA and Graphical Statistical Analysis of surface tension (ST) and pH data measured for various metalworking fluids (MWFs) coming from an electric engine factory from Bucharest, Romania revealed a significant difference between the working stock and spent MWFs. This behavior underlines that the surface tension (ST) and pH measurements allow the discrimination between stock working, either reused at different time intervals or finally spent MWFs.

A regression model is proposed to correlate the surface tension (ST) and pH measurements data for a specific MWF. The developed two equations, specific to the pH ranges identified, can be used together with the t-Student Statistical Test to monitor and label the spent MWFs.

Statistical analysis provides consistent and predictable data by placing them in the confidence interval. The results obtained are valuable as they are based on easy, fast and low-cost measurements of one parameter, pH, in order to decide based on calculated surface tension when the recycled metalworking fluid must be finally replaced and removed as waste.

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