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AN EXPERIMENTAL DESIGN FOR THE DETERMINATION OF Cu AND Pb IN MARINE SEDIMENTS USING TAGUCHI'S METHOD

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Taguchi's method appears to be an ideal statistical tool for the post-analysis correct determination of chemical composition in marine sediment samples. Using Taguchi's method in the chemistry laboratory, controllable factors such as mass per volume ratio, digestion temperature, digestion time and acids can be isolated to provide centring and variance control in Cu and Pb measurements or a "correct determination of Cu and Pb concentrations" minimizing the effect of noise factors. Statistical analysis is performed to identify the effect of parameters and their interactions. Also the expected cost savings under optimum condition is calculated. The results are confirmed by further measurements.

Keywords: Total quality control; Experimental analysis; Heavy metals concentrations

INTRODUCTION

Taguchi has developed a method for application of designed experiments, including a practitioner's handbook [1–3]. This method has taken the design of experiments from the exclusive world of the statistician and brought it more fully into the world of biologists and others. His contribution has also made the work of the practitioner simpler by advocating the use of fewer experimental designs and providing a clearer understanding of the natural variation and the economic consequences of quality engineering in the world of biology scientists [2,4]. Taguchi introduces his approach to use experimental design [4] for:

- Designing products/processes so that they are robust to environmental conditions;
- Designing/developing products/processes so that they are robust to component variation;
- Minimizing variation around a target value.

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Taguchi has outlined a three-step approach for assigning nominal values and tolerances to product and process design characteristics [1–9]: System design, Parameter design and Tolerance design.

System design is the process of applying scientific and engineering knowledge to produce a basic functional prototype design. The prototype model defines the initial settings of product or process design characteristics.

Parameter design is an investigation conducted to identify settings that minimize (or at least reduce) the performance variation. A product or process can perform its intended function at many settings of its design characteristics. However, variation in the performance characteristic may change with different settings. This variation increases the product manufacturing cost, the lifetime cost and the cost that is incurred by society when the customer ''uses'' a product/process whose quality characteristics differ from the nominal, namely as social cost [1,2,10,11]. The term *parameter design* comes from an engineering tradition of referring to product or process characteristics as product/process parameters. An exercise to identify optimal parameter settings is therefore called parameter design.

Tolerance design is a method for determining tolerances that minimize the sum of product manufacturing and lifetime costs. The final step in specifying product and process design is to determine tolerances around the nominal settings identified by parameter design. It is still a common practice in industry to assign tolerances by convention rather than scientifically. Tolerances that are too narrow increase manufacturing cost and tolerances that are too wide increase performance variation and hence a product's lifetime and social cost [1–3,10,11].

Considerable quality advantages can be obtained by Taguchi-technique implementation in the chemical analysis of marine sediment samples.

It is important to determine the quantity of heavy metals that enter the marine environment through anthropogenic processes as well as the total amount of metals in marine sediments. Surface marine sediments are considered to be the ''reservoir'' of heavy metals for the marine environment, binding and releasing metals by various biochemical and physical processes [12,13].

The chemical analysis of surface marine sediment, in general, includes a number of parameters that may affect the correct determination of chemical composition. Consequently, the produced laboratory data deviate from the real values that are to be determined. A quite significant amount of research and development work has already been done to optimize marine sediment chemical analysis and improve the quality of data produced. In recent years large inter-calibration projects have been undertaken with the participation of many biology and chemistry laboratories in an effort to determine all those factors that can produce biased results [14,15].

Taguchi's technique in parameter design appears to be a systematic and efficient method for determining near optimum settings of those parameters. So, biochemical and analytical chemical analysis is an ideal field to apply Taguchi's test methods for continuous and rapid quality improvement of laboratory measurements.

The focus of this paper is the robustness in measurements of Cu and Pb concentrations in marine sediment samples. The basic steps for achieving this target are summarized below:

- Determine the concentrations of Cu and Pb as the quality characteristics. Cu is an element, which is found both naturally and as a result of anthropogenic processes

in the marine environment, but under certain conditions and in elevated concentrations can be toxic. Pb on the other hand is an anthropogenic metal, which even in lower concentrations has toxic effects on marine biota [16]. The aim of determining Cu and Pb concentrations during the laboratory process is ''the correct determination of Cu and Pb concentrations'', minimizing the effect of uncontrollable parameters.

- Make the marine sediment chemical analysis under the experimental conditions dictated by the chosen orthogonal array (OA) and parameter levels. Collect data.
- Analyse the data. An analysis of variance (ANOVA) table can be generated to determine the statistical significance of the parameters. Plot response graphs to determine preferred levels of each parameter.
- Make decisions regarding optimum settings of the parameters and predict the results of the new optimum levels of each of the parameters.
- Calculate the expected social cost savings under optimum conditions.
- Verify that the optimum settings result in the predicted improvement in the quality measure of Cu and Pb.

EXPERIMENTAL

Surface sediment was sampled in the Gulf of Iraklion, Crete (Greece), from a depth of 100 m by means of a sediment grab (Smith–McIntyre sampler). The sediment samples that were taken on board using a plastic corer were separated into two fractions using a 63-µm sieve, namely the silt and clay fractions. Then the sub-samples (both fractions) were divided in the laboratory. The divided sub-samples were deep frozen (-20°C) and freeze-dried. Freeze-drying is a suitable method of drying the sediment samples in order to avoid any possible contamination. Freeze-dried samples of specific weight from the silt and clay fraction were treated with supra-pure acids in a microwave oven (Millestones) for a certain period of time (hours). After digestion, the samples were diluted with nanopure water to a certain volume, centrifuged, re-diluted with nanopure water and analyzed with an AAS Spectrophotometer (Perkin Elmer 4100 Graphite Furnace with Zeeman correction) for Cu and Pb.

Sub-samples were sent to certified analytical chemical laboratories inland and abroad for an inter-calibration procedure. After analysis of these samples a final concentration was determined, which is 20.500 µg/g dry weight (DW) (standard deviation (SD) 1.800) for Cu and 0.175 µg/g DW (SD 0.043) for Pb. Along with the sediment samples from the study area reference, sediment samples from National Research Council Canada (BCSS-1) were analysed to control the method used and verify the values of Cu and Pb. According to refs. [17,18] it is necessary to maintain a certain level of quality in chemical analysis. Including analysis of reference samples is among the most reliable techniques for metal analysis.

In this work three variations of metal analysis were performed and examined, one of which is significantly closer to the above Cu and Pb values. The purpose is to determine the best method of heavy metal analysis in marine sediments, when three methodology variations are applied.

These variations of methodology were examined according to Table I. A mass of sediment sample was treated with a volume of acid at three different mass/vol ratios (0.01, 0.05 and 0.1). Nitric acid, a mixture of nitric with perchloric acid (3:1 v/v)

TABLE I   Process parameters with their values at three levels

Parameter destination	Process parameters	Level 1	Level 2	Level 3
A	Mass per volume ratio (mass/vol)	0.01	0.05	0.1
B	Digestion temperature ($^\circ$C)	70	120	180
C	Digestion time (h)	48	72	96
D	Acid	HNO_3	$HNO_3 : HClO_4$ (3 : 1 v/v)	HF

and hydrofluoric acid were used separately for digestion. Each sample was digested at three different temperatures and left in the oven for 48, 72 and 96 h each time. With the acid treatment a quantity of metals is extracted from the sediment. HF is a strong acid and extracts the total amount of metal, whereas HNO_3 and $HNO_3 : HClO_4$ extract the metal which participates mainly in the organic phase of the sediment. Digestion temperature and time play a key role in the degree of the metals' extraction. The combinations of these parameters are expected to reveal the best variation of methodology for determining the Cu and Pb concentrations in marine sediments.

Experimental Design

Experience reveals that non-linear behaviour of parameters of marine sediment chemical analysis can be determined only if more than two levels are used [12]. Therefore, each parameter is analysed at three levels. The parameters, along with their values in the selected levels, are given in Table I.

According to literature [12,13] the imposed mass per volume ratio (factor A), in conjunction with the digestion temperature (factor B) and time (factor C) affects the chemical analysis of sediment samples. Moreover, each type of acid (factor D) has certain chemical characteristics and extracts the metals from the sediment in a certain chemical form independent of the time of digestion (factor C) or the temperature (factor B) used. So, the effects of factor D in conjunction with other factors are left out of consideration. The interactions that are considered for examination, are the mass per volume ratio (mass/vol) imposed and the digestion temperature (A × B), the mass/vol imposed and digestion time (A × C), the digestion temperature and time (B × C). Since each interaction has four degrees of freedom (DOF), a total of six columns (two columns for each interaction) are needed for assigning the interactions. The total DOF for four factors and three interactions in each of three levels is $4 \times (3-1) + 3 \times (3-1) \times (3-1) = 20$ [3]. Then, a three-level OA with at least 20 DOF has been selected. This array specifies 27 experimental runs and has 10 columns (Table II).

RESULTS AND DISCUSSION

Experimental Analysis

Data from an experiment are traditionally used to analyse the mean response. Taguchi's method, however, stresses the importance of studying also the response variation, using the signal-to-noise (S/N) ratio, resulting in the minimization of the quality characteristic variation due to uncontrollable parameters. Cu and Pb values determined

TABLE II L_{27} OA process parameters and interactions assigned

Run	A	B	$A \times B$	$A \times B^2$	C	$A \times C$	$A \times C^2$	$B \times C$	D	$B \times C^2$
1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	2	2	2	2	2	2
3	1	1	1	1	3	3	3	3	3	3
4	1	2	2	2	1	1	1	2	2	3
5	1	2	2	2	2	2	2	3	3	1
6	1	2	2	2	3	3	3	1	1	2
7	1	3	3	3	1	1	1	3	3	2
8	1	3	3	3	2	2	2	1	1	3
9	1	3	3	3	3	3	3	2	2	1
10	2	1	2	3	1	2	3	1	2	1
11	2	1	2	3	2	3	1	2	3	2
12	2	1	2	3	3	1	2	3	1	3
13	2	2	3	1	1	2	3	2	3	3
14	2	2	3	1	2	3	1	3	1	1
15	2	2	3	1	3	1	2	1	2	2
16	2	3	1	2	1	2	3	3	1	2
17	2	3	1	2	2	3	1	1	2	3
18	2	3	1	2	3	1	2	2	3	1
19	3	1	3	2	1	3	2	1	3	1
20	3	1	3	2	2	1	3	2	1	2
21	3	1	3	2	3	2	1	3	2	3
22	3	2	1	3	1	3	2	2	1	3
23	3	2	1	3	2	1	3	3	2	1
24	3	2	1	3	3	2	1	1	3	2
25	3	3	2	1	1	3	2	3	2	2
26	3	3	2	1	2	1	3	1	3	3
27	3	3	2	1	3	2	1	2	1	1

by means of chemical analysis are the quality characteristic type with object "nominal is best". Therefore, the S/N ratio is used for that type of response, and is given by [1–3,9]:

$$\text{S/N ratio (dB)} = 10 \log\left(\hat{Y}_i^2 / S_i^2\right), \tag{1}$$

where the average and the standard deviation of sample i are denoted by $\hat{Y}_i$ and S_i respectively.

S/N ratios are computed in each of the 27 trial conditions and the average of each trial for Cu and Pb are shown in Tables III and IV, respectively.

In order to study the parameter significance for means of Cu and Pb concentrations, analysis of variance (pooled ANOVA) is performed in Tables V and VII, respectively. Also, Tables VI and VIII present the pooled ANOVA of signal-to-noise ratio (S/N) of Cu and Pb concentrations variability, respectively. Table V indicates that the most significant parameters (un-pooled factors) affecting the mean of Cu concentration are D (acids) and C (digestion time) with 69.265 and 8.628%, respectively. Furthermore, the un-pooled factor B (digestion temperature) and its interaction with factor A (mass/vol ratio) ($A \times B$) affects the Cu concentration mean with 2.924 and 3.828%, respectively. Moreover, the interactions $A \times B$ and $A \times C^2$ have the main effect on Cu concentration variability with 18.371 and 7.792%, respectively (Table VI). Table VI indicates that the un-pooled factor A affects Cu measurement variability with 12.571%. Table VII demonstrates that the un-pooled factors D, C and the interaction $A \times B$ have the main effect on the Pb concentration mean with 57.456, 16.211 and 5.534%, respectively. Similarly, the un-pooled factors D, B and A affect the Pb

TABLE III   Cu values and S/N ratio against trial numbers

Trial	Repetition			Average	S/N ratio
	1	2	3		
1	12.50	11.49	12.05	12.013	27.5103
2	15.20	16.27	16.14	15.870	28.6852
3	19.05	18.50	18.23	18.593	32.9658
4	14.82	15.04	15.28	15.047	36.3115
5	20.11	19.81	20.41	20.110	36.5258
6	14.25	13.97	14.71	14.310	31.6639
7	18.12	19.01	18.50	18.543	32.3657
8	13.44	13.01	12.10	12.850	25.4746
9	16.12	16.58	17.01	16.570	31.4176
10	14.11	14.83	13.78	14.238	28.5152
11	18.79	19.01	19.55	19.117	33.7832
12	16.85	15.90	16.52	16.423	30.6425
13	17.59	18.41	19.20	18.400	27.1799
14	15.20	14.88	14.01	14.697	27.5553
15	13.88	14.21	14.92	14.337	28.6198
16	13.72	13.63	13.08	13.477	31.7986
17	16.31	15.44	16.05	15.933	31.0481
18	21.05	20.81	22.54	21.467	27.1982
19	17.20	18.49	17.11	17.600	27.1570
20	11.48	12.23	10.87	11.527	24.5685
21	13.92	14.78	14.21	14.303	30.2885
22	12.54	13.23	12.94	12.903	31.4210
23	16.59	17.01	15.12	16.240	24.2777
24	21.53	20.74	22.05	21.440	30.2386
25	14.75	13.44	13.81	14.000	26.3319
26	20.87	20.05	21.40	20.773	29.6977
27	17.64	18.50	17.92	18.020	32.2730

M = average of all observations = 16.259 µg/g DW Cu.

concentration variability with 32.461, 6.063 and 5.409%, respectively (Table VIII). Interactions $A \times C^2$, and $B \times C^2$ also have significant effects on Pb concentration variability with 16.671 and 4.279%, respectively.

In order to determine the best levels of the above significant control factors, the average values of mean and S/N ratio responses are plotted. Specifically, the Cu and Pb concentration average values of the above factors in levels 1, 2 and 3 are plotted in Fig. 1 and Fig. 3, respectively. The average values of Cu and Pb S/N ratios calculated by these factors in different levels are shown in Fig. 2 and Fig. 4, respectively.

In Fig. 1, the Cu concentration is shown as "at nominal value" in the 3rd level of the un-pooled factors, D, C and B (Table V), as they have the closest values to the Cu mean concentration. Moreover, the S/N ratio analysis (Fig. 2) suggests the 1st level of the un-pooled factor A (Table VI). It is regarded as the best level in reducing the Cu concentration variability because it has the maximum S/N value among the S/N values of all levels. Therefore, a combination of the best levels of the control factors must be chosen (A_1, B_3, C_3, D_3), for the determination of Cu concentration. It must be noted that the combination of factorial levels (A_1, B_3, C_3, D_3) is not one of the 27 combinations tested in the experiment, as shown in Table II. This is expected because of the high fractionality of the employed experimental design (27 from $3^5 = 243$ possible combinations).

In Fig. 3, the Pb concentration is shown as "at nominal value" in the 3rd level of the un-pooled factors D and C, (Table VII), as they have the closest values to the Pb mean

TABLE IV   Pb value and S/N ratio against trial numbers

Trial	Repetition			Average	S/N ratio
	1	2	3		
1	0.078	0.092	0.081	0.084	21.1003
2	0.102	0.109	0.099	0.103	26.0797
3	0.182	0.164	0.170	0.172	25.4677
4	0.081	0.090	0.085	0.085	25.5402
5	0.163	0.154	0.157	0.158	30.7509
6	0.100	0.089	0.094	0.094	24.6741
7	0.110	0.114	0.102	0.109	25.0009
8	0.095	0.099	0.089	0.094	25.4563
9	0.121	0.118	0.130	0.123	25.8874
10	0.105	0.100	0.112	0.106	24.8757
11	0.154	0.161	0.148	0.154	27.5023
12	0.115	0.101	0.106	0.107	23.5961
13	0.129	0.125	0.118	0.124	26.9548
14	0.091	0.087	0.080	0.086	23.7763
15	0.128	0.135	0.130	0.131	31.2059
16	0.077	0.086	0.080	0.081	24.9475
17	0.110	0.118	0.121	0.116	26.2175
18	0.185	0.197	0.180	0.187	26.6251
19	0.141	0.137	0.130	0.136	27.7571
20	0.091	0.082	0.087	0.087	25.6749
21	0.100	0.095	0.104	0.100	26.8889
22	0.095	0.091	0.087	0.091	27.1396
23	0.115	0.125	0.128	0.123	25.1155
24	0.168	0.182	0.171	0.174	27.4436
25	0.138	0.131	0.140	0.136	29.2025
26	0.151	0.159	0.160	0.157	30.0375
27	0.148	0.131	0.145	0.141	23.8491

M = average of all observations = $0.1207\,\mu g/g$ DW Pb.

concentration. Moreover, the S/N ratio analysis (Fig. 4) suggests the 2nd level of the un-pooled factor B (Table VIII), and the 3rd level of un-pooled A and D factors (Table VIII). They are regarded as the best levels in reducing the Pb concentration variability because they have the maximum S/N value among the S/N values of all levels.

Therefore, a combination of the best levels of the control factors must be chosen (A_3, B_2, C_3, D_3), for the determination of Pb concentration. The best combination of factorial levels for determination of Pb (A_3, B_2, C_3, D_3) is included in experimental trials (24th trial) (Table II). This combination gives the best value of $0.174\,\mu g/g$ DW Pb, which is close to the nominal value $0.175\,\mu g/g$ DW of Pb (Table IV).

Estimation of Predicted Cu and Pb Mean

Using Taguchi's estimation model based on the average values of factorial factors and equivalent "β-factors" a predicted mean estimation of Cu and Pb is achieved by Eqs. (2) and (3) [1–3,9]:

$$\hat{\mu}(Cu) = M\beta(M) + (A_1 - M)\beta(A) + (B_3 - M)\beta(B)$$
$$+ (C_3 - M)\beta(C) + (D_3 - M)\beta(D) \tag{2}$$
$$\hat{\mu}(Pb) = M\beta(M) + (A_3 - M)\beta(A) + (B_2 - M)\beta(B)$$
$$+ (C_3 - M)\beta(C) + (D_3 - M)\beta(D), \tag{3}$$

TABLE V   Cu mean pooled ANOVA (at least 90% confidence)

Factor	Sum square	DOF	$V = SS/DOF$	F-ratio	P%
A	3.059889506	(2)		Pooled	
B	24.53324136	2	12.26662068	4.632	2.924
C	62.06773395	2	31.03386698	11.719	8.628
D	461.0530636	2	230.5265318	87.048	69.265
$A \times B$	30.48487840	2	15.24243920	5.756	3.828
$A \times B^2$	3.548041358	(2)		Pooled	
$A \times C$	4.146985802	(2)		Pooled	
$A \times C^2$	4.391785802	(2)		Pooled	
$B \times C$	4.912237654	(2)		Pooled	
$B \times C^2$	12.12008210	(2)		Pooled	
Error	47.66858889	20	2.648254938		15.355
Total	657.9865284	26	25.30717417		100.000

$T = M^2/N = 21394.1$.

TABLE VI   S/N ratio of Cu pooled ANOVA (at least 90% confidence)

Factor	Sum square	DOF	$V = SS/DOF$	F-ratio	P%
A	40.2860600	2	20.14303002	5.8	12.571
B	5.33742360	(2)		Pooled	
C	10.4156219	(2)		Pooled	
D	12.7183744	(2)		Pooled	
$A \times B$	55.6784253	2	27.83921266	8.0	18.371
$A \times B^2$	13.7885621	(2)		Pooled	
$A \times C$	9.22427089	(2)		Pooled	
$A \times C^2$	27.6023292	2	13.80116464	4.0	7.792
$B \times C$	12.2693231	(2)		Pooled	
$B \times C^2$	8.85310249	(2)		Pooled	
Error	69.2268738	20	3.461343689		61.267
Total	265.400367	26	10.20770642		100.000

$T = M^2/N = 24031.718$.

TABLE VII   Pb mean pooled ANOVA (at least 90% confidence)

Factor	Sum square	DOF	$V = SS/DOF$	F-ratio	P%
A	0.002474395	(2)		Pooled	
B	0.001757951	(2)		Pooled	
C	0.012914469	2	0.006457235	25.871	16.211
D	0.044502691	2	0.022251346	89.151	57.456
$A \times B$	0.004737654	2	0.002368827	9.491	5.534
$A \times B^2$	0.001357358	(2)		Pooled	
$A \times C$	0.000282099	(2)		Pooled	
$A \times C^2$	0.001736617	(2)		Pooled	
$B \times C$	0.000114469	(2)		Pooled	
$B \times C^2$	0.001716469	(2)		Pooled	
Error	0.004991852	20	0.000249593		20.799
Total	0.076586025	26	0.002945616		100.000

$T = M^2/N = 1.181$.

TABLE VIII   S/N ratio of Pb pooled ANOVA (at least 90% confidence)

| Factor	Sum square	DOF	$V = SS/DOF$	F-ratio	P%
A	9.65957810	2	4.82978902	3.8	5.409
B	10.5198975	2	5.25994872	4.1	6.063
C	3.70187830	(2)		Pooled	
D	45.2556333	2	22.6278166	17.8	32.461
$A \times B$	6.35369646	(2)		Pooled	
$A \times B^2$	3.10319417	(2)		Pooled	
$A \times C$	0.93562678	(2)		Pooled	
$A \times C^2$	24.4783643	2	12.2391821	9.6	16.671
$B \times C$	1.06616662	2		Pooled	
$B \times C^2$	8.17311223	2	4.08655612	3.2	4.279
Error	20.3373148	64	1.27108217		35.116
Total	131.582669	80	8.22391681		100.000

$T = M^2/N = 18605.671$.
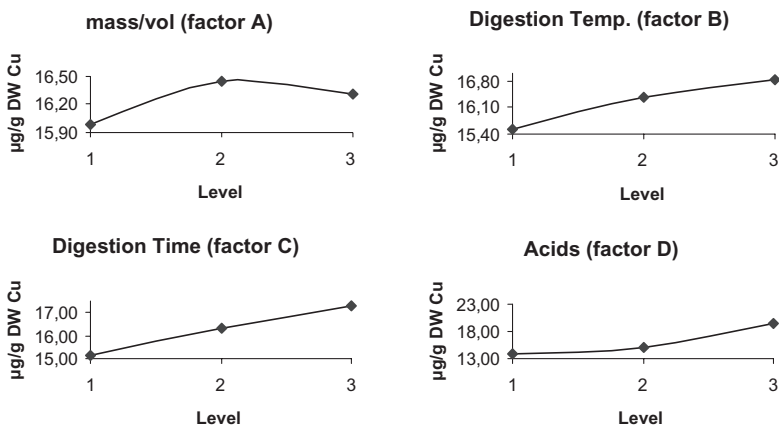
FIGURE 1   Effects of control factors on average values of Cu concentration.
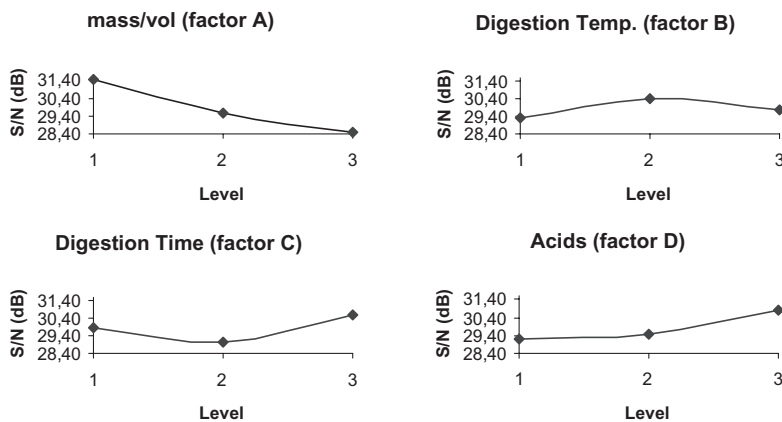
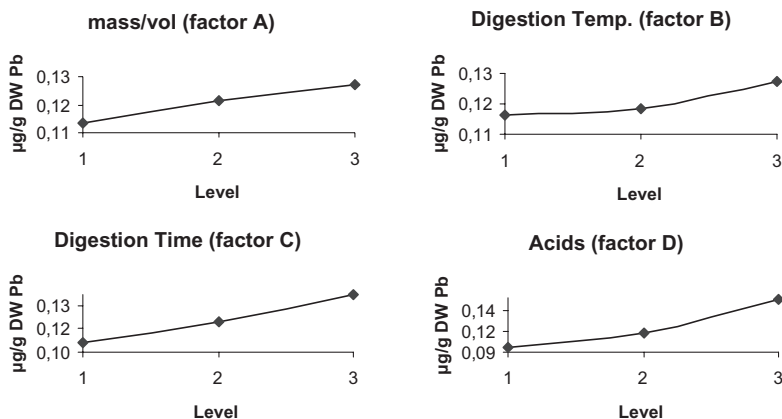

FIGURE 2   Effects of control factors on S/N ratio of Cu.

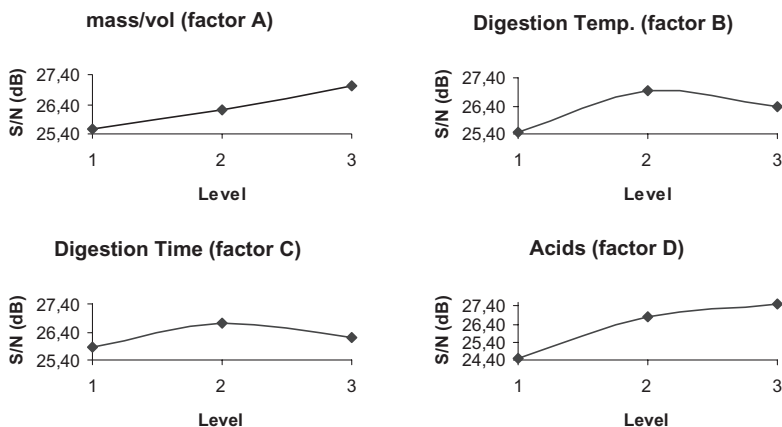FIGURE 3   Effects of control factors on average values of Pb concentration.

FIGURE 4   Effects of control factors on S/N ratio of Pb.

where: M is the total average of trials; $\beta(A)$, $\beta(B)$, $\beta(C)$, $\beta(D)$ are the β-factors of factors A, B, C, D respectively and are defined as:

$$\beta(P) = 1 - 1/F_P, \tag{4}$$

where: F_P is the F-ratio of factor P; (A_1, B_3, C_3, D_3) and (A_3, B_2, C_3, D_3) are the best conditions for Cu and Pb experiments, respectively; $\beta(M)$ is the overall β-factor which is defined as [1–3,9]:

$$\beta(M) = 1 - V_e/T, \tag{5}$$

where: T is the sum square of trials and V_e is the variance due to error.

From Tables III and V it can be computed that: $M(Cu) = 16.259\,\mu g/g$ DW, $T = 21394.1$, $V_e = 2.648254938$.

Therefore, the predicted mean Cu estimate is calculated as $20.905\,\mu g/g$ DW.

Also, from Tables IV and VII it can be computed that: $M(Pb) = 0.1207\,\mu g/g$ DW, $T = 1.181$, $V_e = 0.000249593$.

Therefore, the predicted mean Pb estimate is calculated at $0.167\,\mu g/g$ DW.

Estimation of Predicted Confidence Interval

The confidence limits of the above prediction can be calculated using Eq. (6) [1–3,9]:

$$CI = \sqrt{\frac{F(1, \alpha, u_e) \times V_e}{n_{eff}}}, \tag{6}$$

where: $F(1, \alpha, u_e)$ is the F-ratio required for risk $= \alpha$; confidence $= 1 - \alpha$; u_e is the degree of error freedom (DOF); V_e is the pooled error variance and n_{eff} is the effective sample size:

$$n_{eff} = \frac{N}{1 + \sum_P (u_P \beta(P))}, \tag{7}$$

where: N total number of trials, u_P is the DOF of factor P and $\beta(P)$ is the β-factor of factor P.

Considering a confidence level of 90% for both Cu and Pb, $F(10\%, 1, 26) = 2.91$, $V_e(Cu) = 2.648254938$, $V_e(Pb) = 0.000249593$ and the effective size of samples is $n_{eff}(Cu) = 4.23557764$, $n_{eff}(Pb) = 5.50991203$. The confidence interval for Cu and Pb is computed as $CI = 1.348869$ and $CI = 0.011481272$, respectively. Therefore, the 90% confidence interval of the predicted optimum is:

$$[\hat{\mu}(Cu) - CI] < \hat{\mu}(Cu) < [\hat{\mu}(Cu) + CI] \Rightarrow 19.556\,\mu g/g\ DW < \hat{\mu}(Cu)$$
$$< 22.541\,\mu g/g\ DW \tag{8}$$

$$[\hat{\mu}(Pb) - CI] < \hat{\mu}(Pb) < [\hat{\mu}(Pb) + CI] \Rightarrow 0.155\,\mu g/g\ DW < \hat{\mu}(Pb)$$
$$< 0.178\,\mu g/g\ DW. \tag{9}$$

Expected Cost Savings at Optimum S/N Condition

The variability of Cu and Pb concentrations at optimum condition is estimated considering only the significant factors and interactions. The un-pooled factors A and the interactions $A \times B$ and $A \times C^2$ significantly affect the variability of Cu concentration (Table VI). The S/N ratio values of Cu and Pb of best levels of factors, and their contributions under optimum conditions, are given in Tables IX and X, respectively.

A review of interactions $A \times B$ and $A \times C^2$ indicates that they both have significant contributions at level 2 (Table IX). Furthermore the significant factors of Pb concentration variability are A, B, D and the interactions $A \times C^2$ and $B \times C^2$ (Table VIII). The review of interactions indicates that the best contribution of $A \times C^2$ and $B \times C^2$ is at level 2 (Table X). The best levels A_1 and interactions $(A \times B)_2$,

TABLE IX   Cu S/N ratio and factor main contributions at optimum condition

Factor	Level 1	Level 2	Level 3	Best level	S/N contribution
A	31.4356	29.5934	28.4727	1	1.6017
$A \times B$	29.4604	31.7494	25.5620	2	1.9155
$A \times C^2$	31.2638	29.1174	29.1206	2	1.4299
				S/N (Total contribution) =	4.9471
				S/N (average) =	29.8339
				Expected results at optimum condition =	34.7810

TABLE X   Pb S/N ratio and factor main contributions at optimum condition

Factor	Level 1	Level 2	Level 3	Best level	S/N contribution
A	25.5509	26.1891	27.0121	3	0.7614
B	25.4381	26.9557	26.3582	2	0.7050
D	24.4683	26.7793	27.5045	3	1.2538
$A \times C^2$	25.2577	27.5349	25.9595	2	1.2842
$B \times C^2$	25.5264	26.8591	26.3666	2	0.6084
				S/N (Total contribution) =	4.6128
				S/N (average) =	26.2506
				Expected results at optimum condition =	30.8634

$(A \times C^2)_2$ have a total contribution on Cu concentration in the region of 4.9471 db. As the current grand average of performance is 29.8339 db, the expected result at the optimum condition is estimated at 34.7810 db. Therefore, the expected improvement is 14.2236%. Moreover, the best levels A_3, B_2, D_3 and interactions $(A \times C^2)_2$ and $(B \times C^2)_2$ have a total contribution on Pb concentration in the region of 4.6128 db. As the current grand average of performance is 26.2506 db, the expected result at the optimum condition is estimated at 30.8634 db. Therefore, the expected improvement is 14.94577%.

In order to calculate the expected cost savings, Taguchi's loss function has been used [2,3]. Savings in dollars ($) can be calculated when the S/N ratio is known. The lack of current performance status (in terms of S/N) and the cost savings in relation to loss in the average performance (average S/N of all trials) can be calculated using Eq. (10)

$$L = \left\{ 1 - 10^{[(S/N)_1 - (S/N)_2]/10} \right\} \times 100\% \quad \text{of} \ \ L_1, \tag{10}$$

where L_1 is the percentage loss before the experiment, $(S/N)_1$ is the average S/N performance of all trials and $(S/N)_2$ is the optimum performance.

Using Eq. (10), the expected savings for a chemical laboratory from the decrease of Cu and Pb measurement variability are calculated at 67.9898 and 65.4282 cents per $1 loss, respectively.

Confirmation Experiments

In order to confirm the predicted confidence interval of concentrations obtained from Eqs. (8) and (9), three experiments were conducted at the optimum settings of the Cu (A_1, B_3, C_3, D_3) and Pb (A_3, B_2, C_3, D_3) factors in a chemistry laboratory in Crete, Greece. The Cu and Pb average concentrations were calculated at 20.100

and 0.172 µg/g DW, respectively, included in the predicted confidence intervals from Eqs. (8) and (9), respectively.

SUMMARY AND CONCLUSIONS

In the present article, high performance and accuracy analytical equipment has been used in a laboratory environment to investigate the role of various parameters in the quality of measurement of Cu and Pb concentrations. A primary target of this study was to give guidelines for the use of Taguchi's approach in chemical analysis of heavy metals. The level of complexity of the technique applied was kept low, so that it can be understood and easily adopted by biologists, chemists and laboratory technicians. Specifically, the experiment conducted shows that variations of the following parameters affecting Cu and Pb chemical analyses in marine sediment have significant effects on Cu and Pb determination: Mass/Volume ratio, Digestion temperature, Digestion time and Acids.

The percentage contribution of each parameter to the variation of the Cu and Pb chemical analysis in the marine sediment samples is summarized in Table XI. The optimal levels of factors for the optimum determination of Cu and Pb in marine sediment samples porosity were calculated and listed in Table XII.

The results demonstrate that for determining the total concentrations of Cu and Pb in marine sediment samples, the most efficient technique is using HF acid for a digestion time of 96 h. The mean concentration of Cu at the optimal condition of laboratory parameters was estimated at 20.905 µg/g DW with a 90% confidence interval between 19.556 and 22.541 µg/g DW. The corresponding mean value of Pb was estimated at 0.167 µg/g DW with a 90% confidence interval between 0.155 and 0.178 µg/g DW.

Furthermore, as the current S/N average of all trials was 29.8339 db for Cu and 26.2506 db for Pb, the expected result at the optimum condition was estimated

TABLE XI Percentage effects of control factors on the Cu and Pb mean concentrations and their variability

Factor	Cu mean	Cu variability	Pb mean	Pb variability
A	No effect	12.571%	No effect	5.409%
B	2.924%	No effect	No effect	6.063%
C	8.628%	No effect	16.211%	No effect
D	69.265%	No effect	57.456%	32.461%

TABLE XII Optimal values of control factors in order to determine Cu and Pb concentrations

Factor	Cu concentration		Pb concentration	
	Value	Level	Value	Level
A	0.01	1	0.1	3
B	180°C	3	120°C	2
C	96 h	3	96 h	3
D	HF	3	HF	3

at 4.9471 db for Cu and 4.6128 db for Pb. Therefore the expected improvement in reduction of Cu and Pb variability concentrations was 14.2236 and 14.9457%, respectively. Finally, the expected cost savings of Cu and Pb laboratory analyses under optimum condition was calculated at 67.9898 and 65.42824 cents per $1 loss before using Taguchi's experimental approach.

Finally, three confirmation experiments were conducted at the optimum settings of the Cu (A_1, B_3, C_3, D_3) and Pb (A_3, B_2, C_3, D_3) factors. The Cu and Pb average concentrations were calculated at $20.100\,\mu g/g$ DW and $0.172\,\mu g/g$ DW respectively. These experiments confirmed the predicted Cu and Pb concentrations intervals, under optimum condition, estimated by Taguchi's method.

Acknowledgements

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