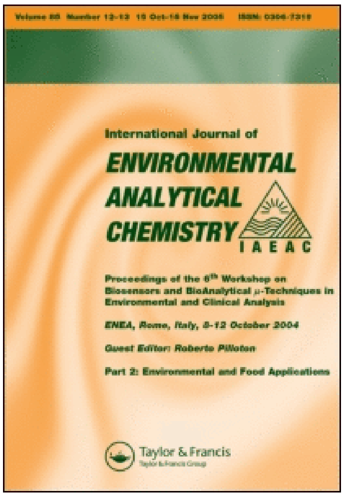

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Taguchi's method in a marine sediment's heavy-metal determination

John G. Vlachogiannis[a]; George V. Vlachonis[b]
[a] Total Quality Management Laboratory (TQM-Lab), 35100 Lamia, Greece [b] Department for Environment Physical Planning of the Hellenic Republic/Region of Sterea Ellada, 35100 Lamia, Greece

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Taguchi's method in a marine sediment's heavy-metal determination

JOHN G. VLACHOGIANNIS*† and GEORGE V. VLACHONIS‡

†Total Quality Management Laboratory (TQM-Lab),
R.S. Lianokladiou, 35100 Lamia, Greece
‡Department for Environment Physical Planning of the Hellenic
Republic/Region of Sterea Ellada, 35100 Lamia, Greece

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In this article, the Taguchi method is used as a statistical tool for the correct determination of chemical composition in marine sediment samples. Using Taguchi's experimental design technique in the analytical chemistry laboratory, factors such as mass per volume ratio, digestion temperature, digestion time and acids can be isolated to provide centring and variance control in heavy-metal measurements such as Cd and Cr measurement in marine sediments, thus minimizing the effect of noise factors during chemical analysis. A statistical analysis is performed to identify the effect of parameters and their interactions. The expected performance and the cost savings under optimum conditions are calculated. The results are confirmed by further measurements.

Keywords: Atomic absorption spectrometry; Heavy metals; Sediments; Taguchi method

1. Introduction

Taguchi has developed a method for application of designed experiments, including practitioner's handbooks [1–6]. This method is derived from the design of experiments and hugely extended, especially in engineering. His contribution has also made the work of the practitioner simpler by advocating the use of less experimental designs and by providing a clearer understanding of the natural variation of various parameters. Of great importance are the economic consequences of quality engineering in the world of chemistry and biology scientists. Taguchi introduces his approach to use experimental design for [1–6]:

- designing products/processes so that they are robust to environmental conditions;
- designing products/processes so that they are robust to component variation;
- minimizing variations around a target value.

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*Corresponding author. Fax: +30-22310-62095. Email: vlachogiannis@yahoo.com

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The philosophy employed by Taguchi considers a three-step approach for assigning nominal values and tolerances to product/process design characteristics [1–6]: system, parameter 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/process design characteristics.

Parameter design is an investigation conducted to identify settings that minimize (or at least reduce) the performance variation. A product/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 variability increases the procedure cost and the cost that is incurred socially when the customer 'uses' a process whose quality characteristics differ from the nominal, namely as social cost [1–6]. The parameter design term comes from an engineering tradition of referring to product/process characteristics as factors or parameters. An exercise to identify optimum parameter settings is therefore called the parameter design.

Tolerance design is a method for determining tolerances that minimize the product/process lifetime and social cost. The final step in specifying product/process design is to determine tolerances around the nominal settings identified by parameter design. Tolerances which are too narrow increase product/process lifetime and social costs, and tolerances that are too wide increase performance variation and hence a product/process lifetime and social cost [1–6].

Considerable quality advantages can be obtained by Taguchi's technique implementation in the chemical analysis of marine sediments. Several interesting applications of Taguchi method in chemical experiments can be found in Wu and Wu [7].

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 with various biochemical and physical processes [8, 9].

The chemical analysis of surface marine sediment, in general, includes a number of parameters that may affect the correct determination of chemical composition and consequently deviate the laboratory-produced data from the real values that are to be determined. To this date, a significant amount of research and development work has been done to optimize the 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 [10–12]. It is widely known that in general, the complexity of the marine ecosystems does not always allow the application of linear correlations. However, there are natural correlations, which are more clear and distinctive (for example, the relation between metal concentrations in sediments and sediment fractions). In laboratory sediment analysis, as part of the approach for a better comprehension of the natural processes in the marine environment and in some cases the anthropogenic effects, non-parametric statistical methods are used. One of them is the Spearman non-parametric correlation, for the estimation of the degree of relation between two parameters, when they do not follow a normal distribution. This statistical test could be applied also for non-linear correlations [13].

Taguchi's technique in parameter design appears to be a systematic and efficient method for determining near-optimum settings of those factors. Thus, biochemical and analytical chemical analysis has been an ideal field in which to apply Taguchi's test method for continuous and rapid quality improvement of laboratory measurements.

The focus of this article is the robustness in measurements of Cd and Cr concentrations in the marine sediment samples. The basic steps of achieving this target are summarized below:

- Determine the concentrations of Cd and Cr as the quality characteristics. Cd is an element, which is found both naturally and as a result of anthropogenic processes in the marine environment. However, under certain conditions, elevated concentrations can be toxic. On the contrary, Cr is an anthropogenic metal, which, even in lower concentrations, has toxic effects on marine biota [14]. The aim of Cd and Cr concentration determination during the lab process is 'the correct determination of Cd and Cr concentrations' minimizing the effect of uncontrollable factors (noise) [1–6, 15–19].
- Perform the marine sediment chemical analysis under the experimental conditions dictated by the chosen orthogonal array (OA) and parameter levels [15–19]. Collect data.
- Analyse the data. An analysis of variance (ANOVA) table can be generated to determine the statistical significance of the parameters. Response graphs are plotted to determine the preferred levels of each parameter [1–6, 15–19].
- Make decisions regarding optimum settings of the parameters, and predict the results of the new optimum levels in each of the parameters [15–19].
- Calculate the expected social cost savings under optimum conditions [20].
- Verify that the optimum settings result in the predicted improvement in the quality measure of Cd and Cr.

2. Experimental

2.1 *Metal sampling and analysis*

Surface sediment was sampled in the Gulf of Iraklion, Crete/Greece, from a depth of 100 m by means of 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 fraction. 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 to avoid any possible contamination. Freeze-dried samples of specific weights from the silt and clay fraction were treated with suprapure acids in a microwave oven (Millestones) for a certain period of time (h). After digestion, the samples were diluted with nanopure water to a certain volume, centrifuged, re-diluted with nanopure water and analysed with an atomic absorption spectrophotometer (Perkin Elmer 4100 graphite furnace with Zeeman correction) of Cd and Cr.

In environmental analysis and especially in chemical analysis of environmental parameters laboratory, the total error reflects the natural variances as well as the set of the partial errors during sampling, sub-sampling, sample treatment and final measurement. Hence, the final data deviate from the real result or the expected value. Utilizing the reference material (certified sediment samples) during the analysis in the laboratory and the chemical treatment repeat, the analyst minimizes the total error, and the results are less biased. The total metal concentrations in this work have been tested against reference material during the laboratory analysis.

Sub-samples were sent to certified analytical chemical laboratories inland and abroad for an inter-calibration procedure. After the analysis of these samples, a final concentration was determined, which is $0.240\,\mu g\,g^{-1}$ dry weight (DW) with a standard deviation (SD) of 0.038 for Cd and $9.500\,\mu g\,g^{-1}$ DW with SD 0.945 for Cr. 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 Cd and Cr. According to [21, 22], it is necessary to maintain a certain level of quality in chemical analysis. This is one of the most reliable techniques for metal analysis (including analysis of reference samples).

In this article, three variations of metal analysis were performed and examined, one of which is significantly closer to the above Cd and Cr values. The purpose is to obtain 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 1. 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). Hydrochloric acid (HCl), nitric acid (HNO_3) and hydrofluoric acid (HF) 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 extracts the metal, which participates mainly in the organic phase of the sediment. HCl extracts the metal fraction, which is more mobile and exchangeable in the sediment. The digestion temperature in conjunction with digestion time plays a key role in the degree of metal extraction [8, 9]. The combinations of these parameters are expected to reveal the best variation of methodology for determining the Cd and Cr concentrations in marine sediments.

2.2 *Experimental design*

Experience shows that non-linear behaviour of the parameters analysed in the marine sediment chemical analysis can be determined only if more than two levels are used [8, 9]. Therefore, each parameter is analysed at three levels. The parameters, along with their values in the selected levels, are given in table 1.

According to literature, the imposed mass per volume ratio, in conjunction with the digestion time and temperature, affects the chemical analysis of sediment samples [8, 9]. So, the interaction effect of these parameters is considered for examination. These interactions 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

Table 1. 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 (°C)	70	120	180
C	Digestion time (h)	48	72	96
D	Acid	HCl	HNO_3	HF

Table 2. OA_{27} process parameters and interactions assigned.

Run	A	B	A × B	A × B^2	C	A × C	A × C^2	B × C	D	B × 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

of freedom (DOF), a total of six columns (two columns for each interaction) are needed for assigning the interactions [15–19]. The total DOF for four factors and three interactions in each of the three levels is $4 \times (3-1) + 3 \times (3-1) \times (3-1) = 20$ [15–19]. Then, a three-level OA with at least 20 DOF has been selected. This array specifies 27 experimental runs and has 10 columns (table 2) [15–19].

3. Results

3.1 *Experimental analysis*

The purpose now is to determine the optimum levels of control factors so that the determination of Cd and Cr in marine sediments is robust to noise factors of lab analysis. Data from an experiment are traditionally used to analyse the mean response. Taguchi's method, however, stresses the importance also of studying the response variation. A statistical measure of performance, called the signal-to-noise (S/N) ratio, is used, resulting in the minimization of the quality characteristic variation, due to uncontrollable parameters (noise) [1–6, 15–19].

Cd and Cr values determined by means of chemical analysis are the quality characteristic type with the object 'nominal is best'. Therefore, the S/N ratio is used for that type of response and is given as [1–6]:

$$\mathrm{S/N\ ratio\ (dB)} = -10\log(\widehat{Y}_i - t)^2. \tag{1}$$

The average of the *i*-sample is denoted as $\widehat{Y}_i$, and the target value as *t*.

The Cd and Cr target value are $t = 0.240\,\mu\mathrm{g\,g^{-1}}$ DW (dry weight) and $t = 9.500\,\mu\mathrm{g\,g^{-1}}$ DW, respectively.

S/N ratios are computed by means of the selected three-level OA_{27} in each of the 27 trial conditions, and the averages of each trial for Cd and Cr are shown in tables 3 and 4, respectively.

A common approach method for studying the parameter significance of Cd and Cr concentration variability, called the pooled ANOVA [1–6, 20] of the S/N ratio, is shown in tables 5 and 6, respectively, by means of the selected three-level OA_{27}.

From table 5, it can be seen that the most significant factors (unpooled), with at least 90% confidence, D and A, have a major effect on Cd concentration variability: 63.185 and 7.274%, respectively. Furthermore, interaction of factor A with factor B ($A \times B$) affects the Cd concentration variability with a percentage of 6.501%. Moreover, the interactions $A \times C^2$ and $B \times C$ have the main effect on Cd concentration variability: 3.215 and 4.982%, respectively. From table 6, it can be deduced that the most significant factors (unpooled) with at least 90% confidence, D, C and A, have a major effect on Cr concentration variability: 76.965, 4.883 and 2.729%, respectively.

To determine the best levels of above significant control factors, the average values of S/N ratio response are plotted. Specifically, the Cd and Cr average values of the above significant factors in levels 1, 2 and 3 are plotted in figures 1 and 2, respectively [20]. The average values of Cd and Cr S/N ratios calculated

Table 3. Cd values and S/N ratio against trial numbers.

Trial no.	Repetition 1	Repetition 2	Repetition 3	S/N ratio
1	0.105	0.113	0.115	17.783
2	0.125	0.141	0.130	19.314
3	0.092	0.185	0.200	26.364
4	0.135	0.140	0.129	19.540
5	0.205	0.210	0.199	28.966
6	0.140	0.135	0.131	19.598
7	0.198	0.205	0.200	28.154
8	0.122	0.118	0.130	18.653
9	0.145	0.151	0.138	20.401
10	0.130	0.125	0.122	18.832
11	0.201	0.195	0.192	27.099
12	0.137	0.142	0.150	20.251
13	0.210	0.198	0.195	28.060
14	0.120	0.115	0.118	18.247
15	0.198	0.215	0.204	29.106
16	0.141	0.160	0.151	20.947
17	0.195	0.211	0.203	28.502
18	0.248	0.261	0.240	37.738
19	0.235	0.239	0.250	43.767
20	0.118	0.112	0.120	18.175
21	0.181	0.174	0.190	24.627
22	0.110	0.122	0.130	18.444
23	0.198	0.187	0.200	26.866
24	0.225	0.218	0.234	36.049
25	0.185	0.174	0.160	23.378
26	0.214	0.197	0.226	30.423
27	0.112	0.128	0.120	18.403

Table 4. Cr value and S/N ratio against trial numbers.

Trial no.	Repetition 1	Repetition 2	Repetition 3	S/N ratio
1	2.410	3.120	3.240	−16.374
2	6.700	5.280	7.050	−10.233
3	10.120	8.050	9.100	0.543
4	5.020	6.010	4.550	−12.769
5	8.119	9.230	9.500	1.804
6	3.270	5.020	4.300	−14.570
7	7.100	6.280	7.920	−7.930
8	4.320	3.560	4.100	−14.833
9	6.110	5.240	5.840	−11.568
10	5.120	6.880	7.010	−10.314
11	8.050	8.360	7.900	−2.983
12	4.019	4.810	3.610	−14.611
13	6.910	7.580	8.010	−6.238
14	2.200	3.910	4.050	−15.807
15	6.780	5.690	7.020	−9.711
16	4.550	3.670	5.020	−14.181
17	4.010	6.330	7.240	−11.790
18	8.510	9.250	9.560	4.575
19	7.880	9.230	10.010	0.062
20	3.660	4.019	4.230	−14.863
21	7.050	8.109	8.650	−4.604
22	5.110	3.260	4.120	−14.632
23	6.520	7.910	7.500	−7.107
24	10.120	9.580	10.020	6.567
25	7.360	7.810	6.230	−7.813
26	9.230	8.910	9.560	8.491
27	3.140	4.780	4.230	−14.796

Table 5. S/N ratio of Cd pooled ANOVA (at least 90% confidence).

Factor	Sum square	DOF	Variance	*F*-ratio	Pure sum	*P* (%)
A	101.478	2	50.739	7.196	87.377	7.274
B	(6.886)	(2)		Pooled		
C	(16.977)	(2)		Pooled		
D	773.088	2	386.544	54.822	758.986	63.185
A × B	43.490	2	21.745	3.084	29.388	2.446
A × B^2	62.810	2	31.405	4.454	48.708	4.055
A × C	(12.927)	(2)		Pooled		
A × C^2	52.720	2	26.360	3.738	38.618	3.215
B × C	73.955	2	36.977	5.244	59.853	4.985
B × C^2	(14.566)	(2)		Pooled		
Error	93.660	14	6.690			14.843
Total	1201.206	26				100.000

by these significant control factors in different levels are shown in tables 7 and 8, respectively.

In figure 1, the Cd concentration appears to be at a nominal value reducing the variability in the third level of factors D, A. Moreover, the first level of interactions A × B and B × C ($(A \times B)_1$, $(B \times C)_1$) and second level of interactions A × B^2 and A × C^2 ($(A \times B^2)_2$, $(A \times C^2)_2$) are proved to be the best levels in reducing the Cd concentration variability. In figure 2, the Cr concentration appears to be at a nominal value, reducing the variability in the third level of factors D, C and A (D_3, C_3, A_3).

Table 6. S/N ratio of Cr pooled ANOVA (at least 90% confidence).

Factor	Sum square	DOF	Variance	*F*-ratio	Pure sum	*P* (%)
A	91.025	2	45.512	4.202	69.364	4.883
B	(0.747)	(2)		Pooled		
C	60.432	2	30.216	2.789	38.771	2.729
D	1114.765	2	557.382	51.464	1093.104	76.965
A × B	(32.164)	(2)		Pooled		
A × B^2	(6.811)	(2)		Pooled		
A × C	(8.068)	(2)		Pooled		
A × C^2	(13.384)	(2)		Pooled		
B × C	(25.380)	(2)		Pooled		
B × C^2	(2.482)	(2)		Pooled		
Error	154.018	20	7.701			15.423
Total	1420.245	26				100.000

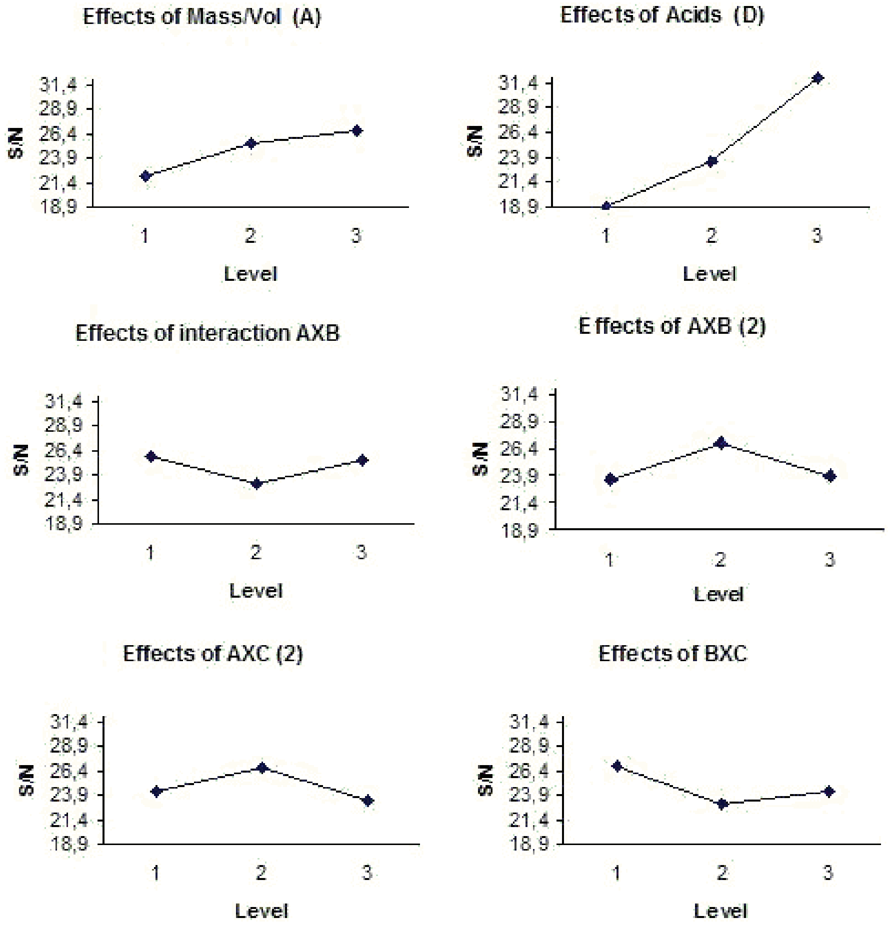

Figure 1. Effects of significant factors and interactions on S/N ratio of Cd concentration.

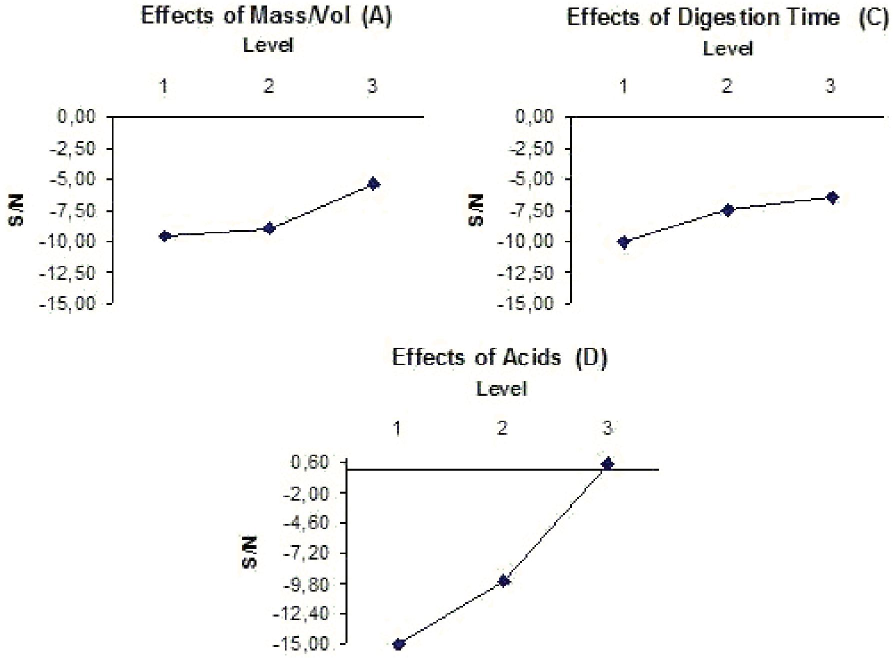

Figure 2. Effects of significant factors on S/N ratio of Cr concentration.

Table 7. Main contributions of Cd S/N ratio and factors under optimum conditions.

Factors	Level 1	Level 2	Level 3	Best level	S/N contribution
A	22.086	25.420	26.681	3	1.952
D	18.944	23.396	31.847	3	7.117
A × B	25.778	22.943	25.465	1	1.049
A × B^2	23.453	26.873	23.861	2	2.144
A × C^2	24.267	26.624	23.296	2	1.894
B × C	26.968	23.019	24.200	1	2.239

S/N (total contribution) = 16.395
S/N (average) = 24.729
Expected results under optimum conditions = 41.124

Table 8. Main contributions of Cr S/N ratio and factors under optimum conditions.

Factors	Level 1	Level 2	Level 3	Best level	S/N contribution
A	−9.548	−9.007	−5.411	3	2.577
C	−10.021	−7.480	−6.464	3	1.524
D	−14.963	−9.545	0.543	3	8.531

S/N (total contribution) = 12.632
S/N (average) = −7.988
Expected results under optimum conditions = 4.644

3.2 *Estimation of optimum confidence S/N interval*

Among the 10 factors and their interactions studied, only six for Cd and three for Cr concentration determination are found to be significant with at least 90% confidence. It is customary to include only the significant factors in estimating the performance at the optimum condition. The optimum condition and the expected performance for determination of Cd and Cr concentrations are shown in tables 7 and 8, respectively [20].

The confidence interval (CI) in the optimum performance of Cd and Cr are calculated using the following procedure. The confidence S/N ratio interval of Cd and Cr can be estimated by the following equation [1–6, 20]:

$$\mathrm{CI} = \sqrt{\frac{F(1, \alpha, u_{\mathrm{e}}) V_{\mathrm{e}}}{n_{\mathrm{eff}}}}, \tag{2}$$

where, $F(1, \alpha, u_{\mathrm{e}})$ is the F-ratio required for risk $= \alpha$; confidence $= 1 - \alpha$; u_{e} is the degree of freedom of error (DOF); V_{e} is the pooled error variance; and n_{eff} is the effective sample size [1–6, 20]:

$$n_{\mathrm{eff}} = \frac{N}{1 + \sum_P (u_P \beta(P))}, \tag{3}$$

where, N is the 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 Cd and Cr, $V_{\mathrm{e}}(\mathrm{Cd}) = 6.69$, $V_{\mathrm{e}}(\mathrm{Cr}) = 7.701$ and the effective size of samples is $n_{\mathrm{eff}}(\mathrm{Cd}) = 5.4$, $n_{\mathrm{eff}}(\mathrm{Cr}) = 3.85714$, the confidence interval of Cd and Cr is computed $\mathrm{CI} = 1.829$ and $\mathrm{CI} = 2.278$, respectively. The expected S/N results under optimum conditions are 41.124 dB (table 7) for Cd and 4.644 dB (table 8) for Cr.

Therefore, the 90% confidence interval of the predicted optimum is:

$$39.295 < \mathrm{S/N_{opt}(Cd)} < 42.953 \tag{4}$$

$$2.366 < \mathrm{S/N_{opt}(Cr)} < 6.922. \tag{5}$$

3.3 *Expected cost savings under optimum S/N conditions*

The variability of Cd and Cr concentration measurements under optimum conditions is estimated [20]. The best levels of un-pooled factors D_3, A_3 and the best levels of interactions $(A \times B)_1$ $(A \times B^2)_2$ and $(A \times C^2)_2$, $(B \times C)_1$ significantly affect the variability around the target of Cd (0.240 $\mu\mathrm{g\,g^{-1}}$ DW) as presented in table 5 and figure 1.

Also, the best levels of unpooled factors D_3, C_3 and A_3 significantly affect the variability around the target of Cr (9.500 $\mu\mathrm{g\,g^{-1}}$ DW), as shown in table 6 and figure 2.

The values of Cd and Cr S/N ratio in each level of factors, the best levels of each factor and their contributions at optimum condition are summarized in tables 7 and 8, respectively [20]. As the total contribution of all significant factors of Cd and Cr is 16.395 dB (table 7) and 12.632 dB (table 8), the expected result at the optimum condition is estimated at 41.124 and 4.644 dB, respectively. It must be emphasized that the current grand average of Cd and Cr concentration performance estimated at 24.729 and −7.988 dB was also considered. Therefore, the expected improvement for determination of Cd and Cr concentration is 39.867 and 272%, respectively.

In order to calculate the expected social cost savings in dollars ($), Taguchi's loss function is used [1–6, 20]. On account of the lack of current performance status (in terms of S/N), the cost savings in relation to the average performance loss (average S/N of all trials) can be calculated using the following formula [20]:

$$L = \left\{1 - 10^{[(S/N)_1 - (S/N)_2]/10}\right\} \times 100\% \text{ of } L_1, \tag{6}$$

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 equation (6), the expected social cost savings of chemical laboratory from the decrease in Cd and Cr measurement variability are calculated at 97.706 and 94.545 cents per $1 loss, respectively.

3.4 *Confirmation experiments*

Five experiments were conducted under the optimum settings of the Cd (A_3, C_3, D_3) and Cr (A_3, C_3, D_3) factors, confirming the predicted confidence interval of the S/N ratio obtained by equations (4) and (5). For the experimental purposes, the level 3 of factor B is selected as the optimum. The Cd and Cr average concentration were calculated at $0.237\,\mu g\,g^{-1}$ DW and $9.506\,\mu g\,g^{-1}$ DW, respectively. The variability of Cd and Cr concentration measurements was calculated at 41.138 and 4.902 dB included in the predicted confidence intervals (equations (4) and (5)), respectively. The experimental tests were conducted in a chemistry laboratory in Crete, Greece.

4. Discussion and conclusions

In the present article, high-performance, accurate analytical equipment such as a graphite furnace atomic absorption spectrophotometer with Zeeman correction, equipped with an auto-sampler, has been used in the laboratory to investigate the role of various parameters on the quality measure of Cd and Cr determination. The main aim in this study was to provide guidelines for using Taguchi's approach in chemical analysis of heavy metals. The level of complexity of the technique applied was kept low, so that it could be understood and easily adopted by chemists, biologists and laboratory technicians. Specifically, the experiments conducted show that variations of parameters affecting Cd and Cr chemical analysis in marine sediments have a significant effect on Cd and Cr determination. The percentage contribution of significant factors to the variation of the Cd and Cr chemical analysis in the marine sediment samples is as follows:

	Cd variability	Cr variability
Mass/Vol ratio	7.274%	4.883%
Digestion temperature	No effect	No effect
Digestion time	No effect	2.729%
Acids	63.185%	76.965%

From the above results, it was concluded that the type of acids and their chemical behaviour played a key role in metal extraction from the sediment. The final metal concentrations resulting from the method were strongly related to the acid used, rather than the temperature or digestion time. More specifically, the availability of metals in surface sediments depends mainly on how strong the acid is and the chemical relation between the acid and the metal fraction. The temperature and time during this extraction have a minor effect.

The optimum levels of the above factors for Cd and Cr optimum determination in the marine sediment samples were calculated as follows:

	Cd (best level)	Cr (best level)
Mass/Vol ratio	0.1 (3)	0.1 (3)
Digestion time	96 h (3)	96 h (3)
Acids	HF (3)	HF (3)

Consequently, to determine the total concentrations of Cd and Cr in marine sediment samples, the most efficient technique is by using a mass/vol ratio of 0.1 in HF acid for a digestion time of 96 h. It should be noted that during the laboratory experiment, a microwave oven (Millestones) was used for digestion. In the case of an open heating digestion or a digestion in closed steel tubes in an oven, the digestion time in relation to temperature could be different. The results are strictly related to the laboratory material that has been used. The data produced by a certain method, which is used in laboratory, can indicate the degree of contamination in a marine environment, such as the sediment in the present study. Metals occur in sediments in different forms, according to local biochemical and physical conditions. This could affect the distribution of metals in the sediment layer and the degree of their bioavailability [23, 24]. Therefore, it is of primary importance not only to describe exactly which method and chemicals are used in the laboratory but also the variability of the produced data. The variability of concentration of Cd under optimum conditions of lab parameters was estimated with a 90% confidence interval between 39.295 and 42.953 dB. The corresponding interval for Cr was estimated with 90% confidence between 2.366 and 6.922 dB.

Furthermore, as the current S/N average of all trials was 24.729 dB for Cd and −7.988 dB for Cr, the expected result at the optimum condition was estimated at 41.124 dB for Cd and 4.644 dB for Cr. Therefore, the expected improvement in reduction in Cd and Cr variability concentrations was 39.867 and 272%, respectively. So, the expected social cost savings of laboratory for Cd and Cr analysis under optimum conditions were calculated at 97.706 and 94.545 cents per $1 loss before the experimental method of Taguchi.

Conclusively, five confirmation experiments were conducted with the optimum settings of the Cd (A_3, B_3, C_3, D_3) and Cr (A_3, B_3, C_3, D_3) factors. The Cd and Cr average concentrations were calculated at $0.237\,\mu g\,g^{-1}$ DW and $9.506\,\mu g\,g^{-1}$ DW, respectively. The variability of Cd and Cr concentration measurements was calculated at 41.138 and 4.902 dB, respectively. These experiments confirmed the predicted intervals of S/N ratio of Cd and Cr concentrations, under optimum conditions, estimated by Taguchi's method. Moreover, the non-optimized average concentrations of Cd and Cr were at $0.18\,\mu g\,g^{-1}$ DW and $6.356\,\mu g\,g^{-1}$ DW, and the variability of Cd and Cr concentration measurements was calculated at 24.729 dB for Cd and −7.988 dB, respectively. As a final result of this study, we can calculate the real cost savings (equation 6) of the chemical laboratory, comparing the above non-optimized measurements with the validated measurements. The cost savings for Cd and Cr concentration measurements are at 97.714 and 94.860 cents per $1 loss, respectively, which is only slightly better than expected.

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