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Viability of Analysis of Variance Applied to the Data Obtained From the Atomic Absorption Spectrometric Determination of the Metal Content in Welding Fumes†

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The conditions in a shipyard that could affect the metal content in welding fumes were studied. Personal samples were collected on cellulose filters in compliance with standard methods. The total metallic particles content was determined by gravimetry. The filters were then dissolved by acid digestion and the metals (Fe, Mn, Zn, Cu, Cr, Ni and Cd) were determined either by flame or electrothermal AAS. A detailed statistical study was performed. An initial exploratory data analysis based on the outlier determination was made, followed by a descriptive data analysis. Finally, an analysis of the variance was applied to study nine factors that could affect the metal content. In all cases validation of the model was accomplished by checking the basic hypothesis.

Keywords: *Welding fumes sampling and analysis; flame atomic absorption spectrometry; electrothermal atomic absorption spectrometry; outliers; metal determination; statistics; analysis of variance*

Environmental studies in the area of industrial hygiene typically require the collection of a large number of samples and the determination of the concentrations of various chemical components. Naval welding processes pollute the working environment with fumes that are mainly composed of metal oxides. The metallic components must be analysed in order to control work place environmental factors that could affect the health or efficiency of the workers.

Despite the large range of sensitive analytical techniques for trace element determinations, AAS occupies the place of the major routine analytical technique, owing to the combination of many advantages, such as high sensitivity and selectivity, good accuracy, adequate precision, large element coverage, moderately price equipment and well established methodology.

In the present work, FAAS was used as the main technique to achieve the objective of the study. The total metallic particle content was determined by gravimetry.

Samples were collected at Astilleros Españoles shipyard (Puerto Real, Spain) following standard methods.[1] The selection of the metals evaluated (Fe, Mn, Cu, Cr, Ni, Cd and Zn) was made taking into account the composition of the materials leading to generation of the fumes and the possibility of producing noxious effects on the welder's health.[2,3]

With the data obtained, a detailed statistical study was performed. An exploratory data analysis based on the determination of outliers was followed by a descriptive data analysis. Then an analysis of variance (ANOVA) was applied to study the factors that could affect the amount of metals aspirated by the workers. In all cases the model validation was accomplished by checking its basic hypothesis.

Useful conclusions were drawn related to welding procedures and to the shipyard conditions which can affect welders' health.

EXPERIMENTAL

Reagents

All reagents used were of analytical-reagent grade.

Hydrochloric acid. 25%, Merck, Suprapur.

Nitric acid. 65%, Merck, Suprapur.

Multi-element stock solution. 1000 mg l^{-1} of Fe, Mn, Cu, Ni, Cr, Cd and Zn prepared following instructions in the spectrometer data book supplied with Merck G. R. reagents.

The dilutions were made with doubly distilled water.

Apparatus

The experimental set-up used consisted of the following: a Philips PU 9200 X atomic absorption spectrometer equipped with a PU 9390 X electrothermal atomizer; a Mettler AE 240 analytical balance with a precision of ±0.01 mg; and MSA Model Fix-Flow high flow-rate sampling pumps and the associated calibration equipment.

Sampling

A total of 140 personal samples were collected at the Astilleros Españoles S. A. shipyard in Puerto Real during the year 1993. The shipyard is located in Cádiz Bay and occupies a total area of 100 Ha. For each sample the different factors that could influence the concentration of the fumes aspirated by the welders were registered. They were: the area, level of confinement, welder's posture, welding position, presence or absence of extractors, type of welding, type of electrode, electrode trade mark, shop-primer painting and/or coating.

Sampling was achieved in compliance with the National Institute for Occupational Safety and Health (NIOSH) standard methods for personal samples of welding fumes.[1] After calibrating the sampling equipment a volume of air similar to that aspirated by the welder is passed through a cellulose filter by means of an aspiration pump. Cellulose filters of 0.8 μm diameter pore size were used. Each filter is in a polystyrene cassette of 37 mm diameter furnished with a cellulose support.

Sampling was carried out by attaching the sampler to the worker's belt and placing the filter holder near his respiratory tract. As soon as the worker began welding, the pump was started and evolved fumes were collected for 15 min. If the welding was interrupted, the sampling pump was stopped and started again when the worker recommenced welding. After each sample had been collected, the filter was kept in its holder

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until required for analysis. The filters used to determine total particles were all pre-weighed.

Analysis Procedure

Determination of the total particulate content in the welding fumes

The analysis of the total particulate content was carried out by gravimetry. The filter was weighed before and after sampling. The difference gave the total particles collected at the work place. The concentration (c) in mg m^{-3} was calculated from the difference in mass and the air volume aspirated by the pump (which was determined from the pump flow rate and sampling time) by means of the expression:

$$c=\frac{(m_2-m_1)\times 60\times 10^3}{Qt}$$

where m_1 = mass of filter without sample in grams; m_2 = mass of filter with sample in grams; Q = pump flow rate in m^3 h^{-1}; and t = sampling time in minutes.

Filter digestion and determination of the metals

The filter is taken out of the cassette and placed in a 100 ml Erlenmeyer flask. Ten ml of concentrated HCl and 5 ml of concentrated HNO_3 are added. The flask is placed on a hot plate and boiled gently for 15 min. The filter and sample are dissolved completely. This solution is transferred into a calibrated flask and diluted to 50 ml. The solutions are stored refrigerated in polyethylene flasks.

In order to determine the metals, a set of standards was prepared, to produce the calibration curves from the 1000 mg l^{-1} multi-element stock solution by appropriate dilution with doubly distilled water.

Five blanks were also prepared with filters but without any welding fumes passing through. They were subjected to acid attack in the same way as the samples.

The concentration of Fe, Mn and Zn was determined by FAAS under established operating conditions for this matrix.[4] The Cu, Cr, Ni and Cd were determined by ETAAS, also under established operating conditions.[5] When a concentration was higher than the highest standard it was diluted appropriately with doubly distilled water.

The metal concentrations determined in mg l^{-1} or ng l^{-1} were converted into mg m^{-3}, as in the case of the total particulate content determination.

RESULTS AND DISCUSSION

The statistical analysis was performed with the Statgraphics Version 7 Plus software.

Exploratory Data Analysis

The data from the 140 samples were examined for omissions and codification errors. Some observations were also eliminated because the sampling conditions were not constant.

The very high concentration data of the distribution were located.[6] They were superior outliers and strict superior outliers. There were neither inferior outliers nor strict inferior outliers. Firstly, a complete statistical analysis was carried out with all the outliers included. Using the outliers gave non-normal distributions, which could not be converted into a normal distribution by Box–Cox transformations.[7] Therefore, the data were homogenized eliminating only the strict superior outliers.[8] The strict outliers were located using graphic methods (scatter plots, cluster analysis and sun-ray plots) and using a descriptive method in which a strict outlier is defined as $x >$ third quartile + 3 interquartile range. The number of strict superior outliers detected was seven (0.05% of the totality of the samples collected). These samples were analysed again by AAS to asses the experimental reliability.

Accordingly, 28 samples were eliminated; therefore, the descriptive data analysis starts with 112 samples.

Descriptive Data Analysis

The more representative statistical parameters were calculated for 112 personal samples. The blank values had previously been subtracted. The results are shown in Table 1.

The values of the average, median and mode associated with the variables indicate that the ranking of metal and particle (Prt) concentrations is as follows: Prt > Fe > Mn > Zn > Cu > Cr > Ni > Cd.

All the samples have relatively high concentrations of particles, Fe, Mn and Zn (μg g^{-1}), Cu, Cr, Ni and Cd being found at lower concentrations (ng g^{-1}). This can be explained by taking into account that the composition of the fumes depends mainly on the panel being welded, on the electrode used and on the shop-primer paint composition. For this reason, Fe is the most concentrated because it is present in the welded panels (carbon steel), in the electrodes and sometimes in the shop-primer paintings (iron oxides). The Mn is present in the electrodes and, in small amounts, is present in the welded panels. The Zn is an important constituent of the shop-primer paint (zinc silicate) in most cases.

The histograms of the distribution functions and the Box–Whisker plots for metals and particles are represented in Figs. 1 and 2. Box–Whisker plots divide the data into four areas of equal frequency. The box encloses the middle 50%. The median is drawn as a vertical line inside the box. The lower whisker is drawn from the first quartile to the smallest data point. The other whisker is drawn from the third quartile to the largest data point.

Table 1 Descriptive data analysis

	Analyte							
Parameter	Fe	Mn	Cu	Cr	Ni	Cd	Zn	Prt*
Number of samples	112	112	112	112	112	112	112	112
Average/mg m^{-3}	5.98	1.95	0.04	0.01	2×10^{-3}	3×10^{-4}	1.19	38.41
Median/mg m^{-3}	4.03	1.01	0.03	3×10^{-3}	9×10^{-4}	0.5×10^{-4}	0.39	32.67
Mode/mg m^{-3}	3.82	0.47	0.00	0.00	0.00	0.00	0.12	35.11
Standard deviation/mg m^{-3}	5.98	2.45	0.03	0.01	4×10^{-3}	7×10^{-4}	1.81	29.92
First quartile/mg m^{-3}	1.44	0.32	0.01	0.00	0.00	0.00	0.12	18.06
Third quartile/mg m^{-3}	7.89	2.50	0.06	0.01	2×10^{-3}	3×10^{-4}	1.49	46.44
Skewness	1.54	2.28	0.90	1.77	4.20	4.07	2.17	2.18
Coefficient of variation	99.90	125.60	94.55	143.24	199.52	230.31	151.21	77.90

* Prt = particles.

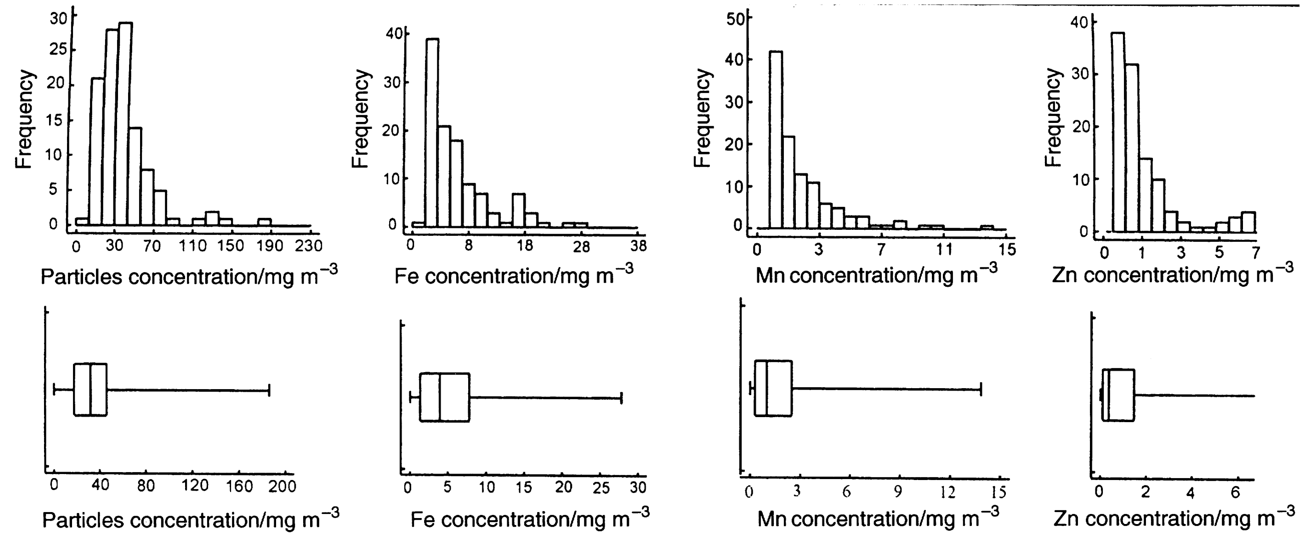

Fig. 1 Frequency histograms and Box–Whisker plots for particles, Fe, Mn and Zn.

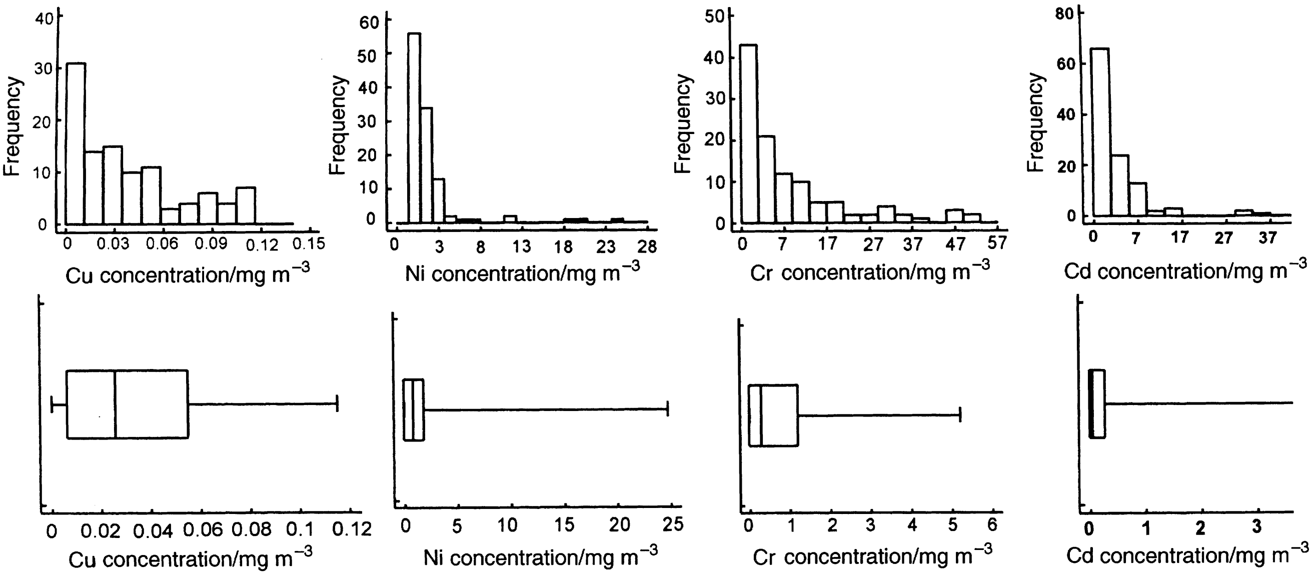

Fig. 2 Frequency histograms and Box–Whisker plots for Cu, Ni, Cr and Cd.

In general, all distributions are leptocurtic, which means having a more acute peak than usual. The skewness (a measure of the dispersion) and the histograms of Figs. 1 and 2 show that the shape of the distributions have an acute tendency to positive asymmetry; for this reason the superior tail of the distribution is more prolonged than the one of a normal distribution. That is due to unusual high values since superior outliers have not been eliminated.

The different sensitivities of the average of the centralization measurements and the median to the presence of outliers is revealed by the different values on the distribution centre. The centralization measurements are relatively closer for the more concentrated metals (Fe and Mn) and for particles. The coefficient of variation is a comparative index of the homogeneity of the concentrations. Therefore, the average and the median are more representative when the coefficient of variation is smaller.

Particles, Fe, Mn and Cu show more homogeneous distributions. It is worth commenting on the Zn, which has a high concentration but disperse results. The lack of homogeneity for the less concentrated metals could be due to the fact that the very low concentrations are near the detection limit of the technique used (ETAAS).

The interquartile ranges (*IQR*) and standard deviations (*s*) show that the dispersion is proportional to the analyte concentration:

$IQR_{\text{Particles}} > IQR_{\text{Fe}} > IQR_{\text{Zn}} > IQR_{\text{Mn}} > IQR_{\text{Cu}} > IQR_{\text{Cr}} > IQR_{\text{Ni}} > IQR_{\text{Cd}}$; $s_{\text{Particles}} > s_{\text{Fe}} > s_{\text{Mn}} > s_{\text{Zn}} > s_{\text{Cu}} > s_{\text{Cr}} > s_{\text{Ni}} > s_{\text{Cd}}$.

The mode values for Cu, Cr, Ni and Cd are 0.00 and the way these affect the corresponding centralization measurements should be noted.

Evaluation of Sources of Variations: ANOVA

ANOVA has been applied previously in interlaboratory statistical evaluations[9] and for the interpretation of data from collaborative trials.[10] In the present work it has been used with a different purpose, the aim being to establish the different factors that have a simultaneous influence on the results.

The factors described under Experimental have several categories, which are called levels; these are shown in Table 2.

The metal or particle concentrations have been taken as dependent variables and the factors mentioned above as explanatory variables. The number of explanatory variables did not allow the application of an ANOVA model with nine factors. Examples have not been found in the literature that

Table 2 Levels and code

Factors	Level	
Area	CB curve block	M modules
	FB flat block	S superestructure
	D dock	P preassambly
	B basin	
Confinement grade	O open	
	S semiclosed	
	C closed	
Welder's posture	0 standing	
	1 squatted	
	2 sitting	
Welding position	C ceiling	V vertical
	L ledge	H horizontal
Extractors	G general	
	L located	
	N none	
Type of welding	M manual	
	S semiautomatic	
	A automatic	
Type of electrode	R rutile	S solid
	B basic	BT basic tubular
	H high efficiency	RT rutile tubular
Electrode model	1 Fluxofil 12	5 SEO 68
	2 Filarc PZ6113	6 Ansa 48
	3 Dual shield 7100 Ultra	7 UZ 26
	4 Trafil 52	8 Oerlikon
Shop-primer painting and/or coating	1 iron oxide	5 galvanized
	2 zinc silicate	6 zinc silicate/painting
	3 none	7 zinc silicate/epoxy
	4 iron oxide/zinc silicate	8 galvanized/painting

can be explained by models with so many factors. Therefore, the factors were divided into two groups. The first group comprises the factors: area, confinement grade, welder's posture and welding position, and the second group comprises extractors, type of welding, type of electrode, electrode trade mark and shop-primer painting or coating. A four-way ANOVA model was applied to the first group of factors. When the more homogeneous conditions were established by fixing the first group of factors (which implies the physical elimination of the influence of these factors) a one-way ANOVA model was applied for each secondary factor that had not been considered.

Application of the Four-way ANOVA Model

The four-way ANOVA model applied was unbalanced because there were a different number of data for each level. A value of $p = 0.05$ was established as critical.

The p-values associated with the ANOVA are shown in Table 3.

The calculation of the p-value for Mn is given as an illustration in Table 4.

From the seven metals determined only Fe, Mn, Zn and Cu appear in Table 3 because only these four metals and the particles have normal distributions after Box–Cox transformations.[7] The only one having a mode value equal to zero and a normal distribution is Cu. The type of transformations used are the square root (SQRT) and fourth root. They are detailed in Table 3. This type of transformation does not give normality in the distributions for the other elements (Cd, Ni and Cr). Therefore, they had to be studied by applying nonparametric tests.

It can be observed in Table 3 that there are differences between the levels of each factor for all the metals (p-values < 0.05) except for Cu and for particles except for the welding position.

The ANOVA model simply informs us that there are differences among the levels of a factor. The Tukey homogeneity test was applied to establish these differences. The results are given in Table 5.

For the factor 'confinement grade' the concentrations are lower when the workplace is open than when it is closed or semiclosed, as is to be expected.

When the 'welder's posture' is standing (code 0) less fumes are collected. When the welder is sitting (code 2) more fumes are collected because the respiratory tract is closer to the welding fumes. The squatting posture (code 1) is an intermediate case.

The results for 'welding position' indicate that when a ledge is welded (code L) the amounts of Fe, Mn and Zn collected are smaller than for other types of welding.

The results obtained for the factor 'area' show that there are significant differences for the levels in the cases of Mn, Zn and particles. The Tukey test has not detected differences for Fe (p value $= 0.031$ near 0.05). The Mn originates mainly from the electrodes. Its concentration is higher at the dock and preassambly locations because the welding is more often carried out with semiautomatic equipment, which implies the use of electrodes containing Mn. The Zn concentration at the basin and superstructure locations is higher than in preassambly. This is explained because the panels welded at these areas have shop-primer that contains zinc silicate and painting would also introduce Zn. At preassambly, the panels are still not painted and the shop-primer during sampling was of iron oxide. The particle concentration is higher on superstructure, because the welding was carried out without fume extractors.

Validation of the four-ways ANOVA model

The differences between the experimental values and the model value are included in a term called residue. The four-ways ANOVA model was validated verifying the hypothesis of randomness, normality and homoscedasticity of the residues.

To verify the hypothesis of randomness and normality of the residues the test of the runs and the test of Kolmogorov–Smirnov were applied (Table 6).[11] As can be observed the tests applied establish the normality and randomness of the dependent variables with a significance level > 0.05. This implies that the randomness and the normality of the dependent variables are acceptable.

Graphic analysis of the residues for all metals and for particles has been carried out with the aim of verifying the hypothesis of homocedasticity. Only the graphics for Mn are

Table 3 p-Values of four-way ANOVA and transformation type. Values in bold type have p-values greater than 0.05

Analyte	Transformation (Box–Cox)	Area	Confinement grade	Welder's posture	Welding position
Fe	SQRT* (Fe)	0.031	0.000	0.031	0.005
Mn	SQRT (Mn)	0.000	0.000	0.003	0.016
Zn	SQRT [SQRT (Zn)]	0.003	0.037	0.008	0.006
Cu	SQRT (Cu)	**0.174**	0.000	**0.346**	**0.802**
Particles	SQRT (Prt)	0.006	0.000	0.002	**0.249**

* SQRT = square root.

Table 4 Four-way ANOVA model for Mn

Source of variation	Sum of squares	Degrees of freedom	Mean square	*F*	*p* value
Area	8.815	5	1.763	4.562	0.000
Welding position	4.216	3	1.405	3.636	0.016
Welder's posture	4.866	2	2.433	6.295	0.003
Confinement grade	9.824	2	4.912	12.710	0.000
Residual	37.102	99	0.386	—	—

Table 5 Tukey test results; the codes are those described in Table 2

Analyte	Area	Confinement grade	Welder's posture	Welding position
Fe	—	O<S	0<2	L<C
	O<C	L<H		
Mn	B<D	O<S	0<2	
	B<P	O<C	1<2	L<C
	CB<P			
Zn	P<B	—	0<1	L<H
	P<S		0<2	
Cu	—	O<S	—	—
		O<C		
Particles	B<S	O<S	0<2	—
	FB<S	O<C	1<2	

Table 6 Test results

Analyte	Kolmogorov–Smirnov test	Test of the runs
Fe	0.471	0.624
Mn	0.125	0.850
Zn	0.272	0.969
Cu	0.582	0.850
Particles	0.440	0.346

shown as an example because the behaviour of the other metals and of the particles is similar. In Fig. 3 a graphic representation of residues *versus* the mean for the model is shown. As can be observed the variability does not increase with the response level.

In Fig. 4 the residues *versus* the sampling order are represented. The residues are observed according to a temporal sequence, to identify possible changes in the experimental conditions with time. The graphic representation shows that there is neither a tendency to increase or decrease nor change from a specified instant.

In Figs. 5 and 6 the residues *versus* area and confinement grade are represented. The figures for welder's posture and welding position are similar. In all cases the variability is constant.

The model for particles and metals can thus be validated.

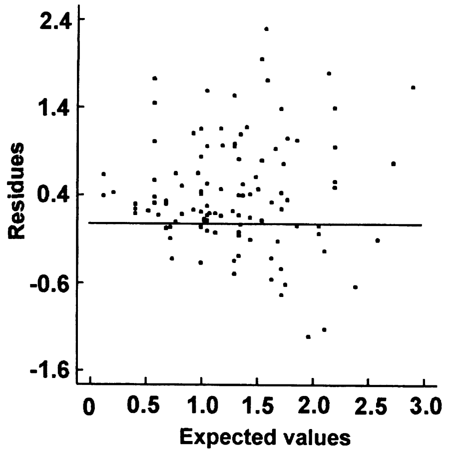

Fig. 3 Residues *versus* expected values for Mn.

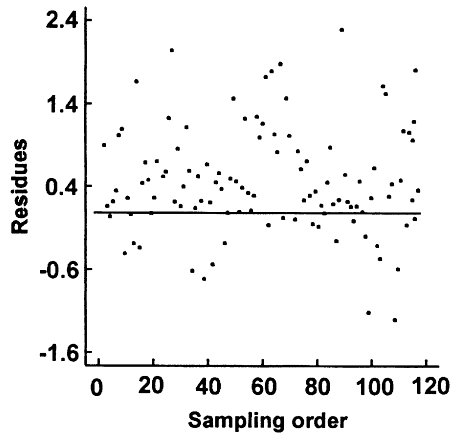

Fig. 4 Residues *versus* sampling order for Mn.

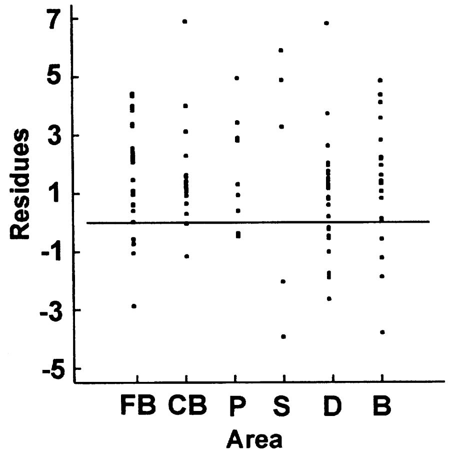

Fig. 5 Residues *versus* area for Mn.

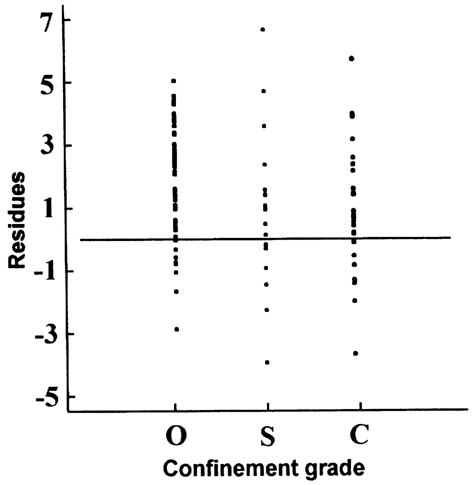

Fig. 6 Residues *versus* confinement grade for Mn.

Table 7 One-way ANOVA and Tukey test results; the codes are those described in Table 2. Values in bold type have p-values greater than 0.05

Factor	Fe	Mn	Cu	Zn	Particles
Extraction	0.496	0.372	0.555	0.827	0.270
Type of welding	**0.016** M < A M < S	**0.004** M < A M < S	0.462	0.632	0.107
Shop-primer painting	0.314	0.171	0.126	0.058	0.302
Type of electrode	**0.012** R < RT	**0.005** R < RT	0.359	0.479	**0.037** R < RT
Electrode trade mark	0.054	**0.043** 8 < 1	0.097	0.248	0.256

Table 8 Bartlett test results

Factor	Fe	Mn	Cu	Zn	Particles
Extraction	0.664	0.796	0.887	0.714	0.007
Type of welding	0.424	0.219	0.847	0.363	0.740
Shop-primer painting	0.584	0.577	0.432	0.150	0.715
Type of electrode	0.393	0.188	0.832	0.338	0.774
Electrode trade mark	0.819	0.735	0.539	0.777	0.956

Application of the One-way ANOVA Model

The ANOVA model was applied to the second group of factors (extractors, type of welding, type of electrode, electrode trade mark, shop-primer painting and/or coating). The conditions that give a higher number of data and that are more homogeneous are fixed. These conditions are as follows: confinement grade, closed (C) and semiclosed (S); welder's posture, squatting (1); and welding position, horizontal (H).

From all the samples analysed, 17 qualify for the conditions mentioned above. The one-way ANOVA model was applied to this group of samples.

The p-values resulting from the application of the ANOVA model are detailed in Table 7. When significant differences were obtained (p-value < 0.05) the differences among the levels were determined. The Tukey test gave the significant differences.

For the factor 'extraction' there is no difference among its levels (located extraction, general extraction and no extraction). These results were not those expected, particularly in the case of located extraction. However, it can be explained because the welder locates the extraction system near the place where he begins to work, but he moves during welding. Therefore the extraction system is insufficient.

Considering the factor 'type of welding' it is observed that there are significant differences among the levels for Fe and Mn. The automatic and semiautomatic weldings give a higher concentration than the manual welding. These results ratify one of the conclusions deduced from the application of the four-ways ANOVA model to the first group of factors on 'area'. It was concluded that in basin and curve blocks the Mn concentrations were smaller than on dock and preassambly. This is because in the former cases more welding tasks are performed with manual equipment. Each 'type of welding' implies the use of a specific electrode. The manual welding with a rutile electrode gives less Fe and Mn than the semiautomatic welding with a rutile tubular (RT) electrode.

The results for the factor 'electrode model' confirm the above paragraph. The manual electrode used gives less Mn than the semiautomatic electrode used.

For the factor 'shop-primer painting' it is observed that there are no significant differences amongst its levels, only for Zn the where p-value is about 0.05.

Validation of the one-way ANOVA model

The normality and randomness hypotheses were studied previously for the four-ways ANOVA model. In the present case the graphic study of the residues has been replaced by the homoscedasticity test of Bartlett, because the number of samples is relatively small and the model is unbalanced. In addition a graphic study could cause confusion because there are few data in the distributions. The p-values obtained for the Bartlett test are given in Table 8.

As the p-values are higher than 0.05 (except in one case) the homoscedasticity with a 0.05 significance level is accepted.

CONCLUSIONS

The main objective of this study was achieved by determining only Fe, Mn, Zn and particles. The statistical methods based on multivariate analysis normally applied in analytical chemistry were not appropriate to attaining the objective of the study. In contrast, using ANOVA the factors that affect the metal content could be clearly deduced. Therefore ANOVA must be regarded as a powerful tool to study the factors that can simultaneously affect the metal inhaled by welders or any other results influenced by many factors.

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