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MODELLING AND OPTIMIZATION OF METALS (As, Ca, Cd, Cr, Cu, Fe, Mg, AND Pb) AND ETHYLENE GLYCOL BUTYL ETHER IN PAINTS USING RESPONSE SURFACE METHOD

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ABSTRACT

Response surface methodology (RSM) and principal component analyses (PCA) modelling tools have been used in this study to quantitatively describe the interaction effects of more than one factor on system response for the modelling and optimization of experimental data. In Nigeria, there are no stringent policies in place by the government on paint production and this has led to unregulated paint products by producers in the commercial markets. Water-based paints currently available in Nigerian market were sampled. Experimental data of Metals (As, Ca, Cd, Cr, Cu, Fe, Mg, and Pb) and Ethylene glycol butyl ether (Volatile organic compounds (VOC)) measured using Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) and Gas Chromatography-Flame Ionisation Detector (GC-FID), respectively was used to develop a mathematical model. The principal component analyses were explained with a cumulative variance of 82% for the VOC and 76% for metals based on manufacturers. Estimated responses were compared with the experimentally determined responses and prediction capabilities of Response Surface Methodology. In the RSM, the developed model had R^2 value of 0.9569, with optimized value at 0.10 % (1000ppm) of Ethylene glycol butyl ether and concentration (ppm) ranges of As (383.0-1,930.0), Ca (614.0-10,400.0), Cd (98.0-2,000.0), Cr (10.3-225.0), Cu (133.0-1,840.0), Fe 742.0-2,910.0, Mg (4,000.0-99,510.0), Pb (170.0-3,230.0). The correlation and optimization study employed are applicable for assessing the impact of hazardous air pollutants on indoor air quality and a good applicability in paint industries to produce products within the set limit of international standards. For the purpose of reducing sick building syndrome and protecting public health, it was important to investigate paints and sealers extensively.

Keywords: VOCs; Paint; metals; Ethylene glycol butyl ether; Response Surface Method

Introduction

Indoor air pollution has become a serious public health issue due to increase in airtight nature of houses in recent times (ILO, 2011). Volatile organic compounds (VOCs) emitted from various consumer products (Han *et al*., 2010; Jia *et al*., 2010;(Kwon *et al*., 2008; (CDC, 2009; (Fromme *et al*., 2009; Kabir and Kim, 2011). They cause nonspecific health problems in congested indoor environment (Apanpa-Qasim *et al*., 2018a,b).

Health effects associated with migraine (Silva-Néto *et al*. 2014; Steinemann and Nematollahi 2020), asthma attacks, exacerbations (Zock *et al*., 2007; Weinberg *et al*., 2017; Steinemann and Goodman 2019), childhood wheeze (Sherriff *et al*. 2005; Parks *et al*., 2020), neurological, respiratory, gastrointestinal, dermatological, and immune systems disorder (Steinemann 2019). VOCs emitted by building materials are suspected cause of Sick building syndrome (SBS) (Herberth *et al*. 2009; Mori and Todaka 2011; Heinrich 2011; Kim *et al*. 2012; Azuma *et al*. 2016).

Paints release significant amounts of VOCs into the atmosphere during the painting process. Some components in these emissions are highly reactive and have contributed to photochemical smog (Movassaghi *et al*., 2012; Qi *et al*., 2018). The primary VOCs in water-based paints are alcohols and esters (Chang *et al*., 2011) and they include among others film-forming agents (texanol and cellosolve) and anti-freezing agents (glycols) (Nakashima et al., 2007). These two agents control flow and application properties, affects the stability of the paint, while in the liquid state and are carrier for the non-volatile components (Nakashima *et al*, 2007).

Ethylene glycol butyl ether (EGBE) also known as

(2-butoxyethanol) is a film forming agent in paints. Glycol ether produced in volumes exceeds 335 million pounds/year for industrial and domestic uses (USEPA, 2010). It is a colourless liquid with a characteristic odour, miscible with water and soluble in most organic solvents. It is used extensively as a solvent in surface coatings such as lacquers, enamels, varnishes, and latex paints; in paint thinners, paint stripping formulations, and inks; and in degreasers and industrial and household cleaners (NTP, 2000; USEPA, 2010). EGBE irritates the eyes and skin, affects the central nervous system, kidneys and the liver (Ching-Hui *et al.*, 2008). Industrial and indoor exposure of the general population to EGBE is most likely from inhalation and dermal absorption from products that contains them. Susceptible individuals are adversely affected at chronic low levels of exposure over time (Suzuki 2019; Tran *et al.*, 2020; Manisalidis *et al.*, 2021). It can also contaminate the environment because of its high solubility and low volatility (ATSDR, 1998).

Non-volatile components of paints are the pigments which contains metals. These pigments are incorporated into the paints to contribute colour, toughness, texture (European Solvents Industry, 2015). Metals are of public health concern for many years due to their persistence in the environment. Cadmium and lead have biological half-lives of more than ten years ((Nduka *et al.*, 2008; Health Canada, 2010). Non adherence to manufacturing standard, inefficient storage, handling and transportation has led to the introduction of metals into the environment (Apanpa-Qasim *et al.*, 2016). Metals such as arsenic, cadmium and lead are thought to have estrogenic activity and, as such, are classified as endocrine disrupting chemicals (EDCs). Anthropogenic activities such as mining and various industrial processes largely contribute to human exposure to metals (Tchounwou *et al.*, 2012). Though, small amounts of these elements such as copper, zinc and iron are needed in diet and are actually necessary for good health but large amounts in the body may cause acute or chronic toxicity (poisoning) (WHO, 1996). The most susceptible to their exposure are children among others (Jaishankar *et al.*, 2014).

Multivariate statistical techniques reduce the number of experiments, and the impact of the independent variables (individually or in combination) in the process (Amini *et al.*, 2009; Witek-Krowiak *et al.*, 2014; Ghoniem *et al.*, 2020). Response Surface Method (RSM) and Principal Component Analysis (PCA) are common methods used in the prediction and optimization on experimental data (Deniz Bas., 2007; Bezerra *et al.*, 2008; Nabil *et al.*, 2015; Fatimah and Wiharto., 2020). RSM and PCA provide an alternative for systems where the mathematical relationship between the parameters and the responses is unknown. They are powerful data modelling tools for capturing and representing complex nonlinear relationships between independent variables and responses of the system (Bezerra *et al.*, 2008).

Hence, the objective of this study is to correlate, predict and optimize As, Ca, Cd, Cr, Cu, Fe, Mg, and Pb and EGBE using RSM as a modelling tool thereby reducing impact of hazardous air pollutant in indoor air quality and to serve as a good applicability in paint industries to produce products within the limit of international standards.

METHODOLOGY

Sample collection and Metals determination

Commercial paint markets in Ibadan and Lagos, Nigeria were surveyed and paint samples based on colour availability and most commonly used purchased. A total of 174 paint samples were purchased from 14 different manufacturers with at least 2 samples per colour. Paint samples were kept in tightly packed sterilised plastic containers and subsequently analysed at the Council of Scientific and Industrial Research- National Environmental Engineering Research Institute Laboratory, Nagpur – Maharashtra, India.

A known amount of 5.0 g of paint sample was spread on glass slides using different brushes for all samples. The glass slides were dried in an oven at 120 ºC for 2 hrs. Dried paint chips of 1.0 g were weighed into closed Teflon vessels and subsequently digested in a closed micro-wave digestion system using 10 mL of 70 % nitric acid and 3 mL of 98 % sulphuric acid.

The determination of measurements of metals was carried out with Thermo Scientific Inductively Coupled Plasma-Optical Emission Spectrometer (ICPOES- iCAP 6300 Duo) coupled with an auto sampler CETAC ASX-52, spectrophotometer (Echelle type), equipped with a simultaneous charge injection device (CID) and detector. Recovery studies for selected metals (mg/kg) were 85.3-106.0 % and Ethylene glycol butyl ether (ppm) was 92.2 %.

VOCs

Wet paint samples of approximately 0.5 g carefully weighed into 15 ml polypropylene radiation sterilized centrifuge tubes and was adjusted with Milli-Q water to a total volume of 15 mL. The tubes were placed on a cyclo mixer at 50 cycles/min to homogenize them and then centrifuged at 5000 rpm at 20 °C. The water phase was filtered with PTFE micro-fibre syringe filter of 13 mm diameter and 0.22micron pore size. The sample extracts were stored in 2 mL maxipense plastic vials and analyzed using Gas Chromatography equipped with Flame Ionization Detector (GC/FID, Perkin Elmer Packard Clarus 500) (Apanpa-Qasim *et al.*, 2018a,b). Agilent JW DB 624UI polar column which is designed for the analysis of volatile priority pollutants (length: 30m, diameter 320µm, 1.80µm; -20°C - 260°C) was used. Operating conditions are: carrier gas flow of hydrogen 45ml/min; injection temperature of 250ºC, FID temperature of 280ºC and an oven temperature program: initial temperature of 50ºC for 3.00mins- (ramp 1):6ºC/min to 100ºC; holding for 0.00min- (ramp 2):10ºC/min to 250ºC, holding for 3.00min. Samples are injected manually with an injection volume of 1µl and at a sampling rate of 12.50000pts/sec. The detector attenuation is of -3 and the equilibrating time is of 0.5min. Experiment run time was 29.33mins. Samples were injected manually and the injection volume was 1 µL. The quantification of target VOCs was accomplished by multi-point external standard calibration curve.

Multivariate optimization strategy

Multivariate statistical methods were applied on these set of data as mentioned above using Minitab 19 software. Principal Component Analysis (PCA) involves the reduction of large number of random variables into a smaller set (into principal components that explains utmost of the variance in the experimental variables) assumed to be certain groups of the random variables representing the variability of the same factors with the random variables dependent on each other (Witek-Krowiak *et al.*, 2014). PCA technique is simple to use, non-parametric method of plummeting the multifaceted data sets to lower dimensions. PCA involves four major steps – pre-treatment of data (scaling, calculation covariance of the matrix, calculation of eigenvalues and eigenvectors) of the covariance matrix and computation of the score. PCA was applied to identify the VOCs in the samples with respect to the manufacturers.

Response surface methodology is a collection of statistical and mathematical techniques used for the development of satisfactory relationship between the response of interest and the parameters influencing the response of interest and further optimize the parameter (response) that is influenced by another dependent variable.

The second order polynomial equation was expressed using the relationship of the independent variable (ethylene glycol butyl ether) and dependent variable (metals) as shown below

$$y = \beta_0 + \sum_{i=1}^{i=n} \beta_i X_i + \sum_{i=1}^{i=n} \beta_{ii} X_i^2 + \sum\sum_{i<j} \beta_{ij} X_i X_j \quad (1)$$

Where, y is the predicted response; β_0 is a constant; β_i is the linear coefficient; β_{ii} is the squared coefficient; and β_{ij} is the product-coefficient, and n is the number of factors (Deshmukh *et al.*, 2012; Gadhe *et al.*, 2013; Sahu *et al.*, 2017; Engidayehu and Sahu, 2020). The response of the independent variable, (i.e., ethylene glycol butyl ether) was determined by the dependent variables (i.e., As, Ca, Cd, Cr, Cu, Fe, Mg, Pb).

The P values checks the significance of each of the coefficients, in order to understand the pattern of mutual interactions between the test variables. A smaller magnitude of P value, the more significant is the corresponding coefficient. The model adequacy was checked by R^2 and predictive error sum of squares (PRESS). The R^2 value of the model represents how successfully the model can fit the data, whereas R^2_{pred} represents the ability of the derived model to predict the output for unknown samples. A model with large R^2 and low PRESS values is considered to be a good model (Montgomery, 2011). PRESS is used to calculate R^2_{pred} which predicts the response of the model for unknown observations. PRESS and R^2_{pred} together help prevent over fitting of the model since it is calculated using observation and not included during model development. PRESS differs from SSE (sum of square error) in that PRESS is obtained by excluding the i^{th} observation from the data set, estimating the regression equation from the remaining n - 1 observations and then using the fitted regression function to obtain the predicted value for the ith observation.

RESULTS AND DISCUSSION

Reported concentrations in VOC and metals

Table 1 shows the range concentrations of **EGBE** and metals (dry weight, mg/kg) in paint samples with respect to manufacturers. Table 2 reports the recovery studies for As, Ca, Cd, Cr, Cu, Fe, Mg, Pb and EGBE. The VOC (EGBE) which is film forming agents is present in all samples except in manufacturer.

Table 1: Range concentrations of VOCs (ppm) and metals (dry weight, mg/kg) in paint samples with respect to manufacturers

	EGBE	As	Cd	Cr	Cu	Fe	Mg	Pb	Ca
A	1020-1550	383-873	377-1230	10-17	711-1330	1000-1580	76200-91700	503-832	3010-4350
B	1000-1620	449-921	509-2000	11-25	600-797	1050-2220	77700-93300	402-1780	2800-4980
C	1050-1600	1068-1290	1010-1820	11-22	133-182	1850-2730	4000-5580	863-1470	614-826
D	1090-1450	740-910	848-969	11-19	542-784	742-999	28300-33000	361-531	1650-2130
E	1010-1520	733-855	901-1560	11-19	620-739	1000-1440	30000-38700	643-820	1510-2220
F	1050-1340	795-898	781-1730	12-19	419-657	1310-1530	20000-29800	173-863	1710-2210
G	ND	1116-1720	781-880	117-225	636-849	1760-1960	80200-84000	813-1770	5580-6970
H	1060-1380	1572-1780	734-902	54-75	613-796	1010-1880	70200-90500	489-1590	5390-7660
I	1100-1560	1759-1930	764-1890	90-147	1550-1840	1020-1290	87700-95300	442-3020	9060-9630
J	1070-1190	1679-1800	448-952	35-53	568-793	1100-2150	75000-84200	229-3230	6820-9960
K	1030-1560	1680-1860	98-857	23-30	638-880	2050-2330	19800-32200	170-1380	4200-6140
L	1030-1300	1523-1680	790-1040	27-44	622-934	1070-1850	77700-99500	568-849	5890-7990
M	1010-1390	1110-1570	745-1240	28-40	721-991	1610-2910	27200-49000	433-1500	5680-7980
N	1360-1860	1340-1480	1579-1830	100-127	1580-1790	1890-2150	69012-94890	417-1390	9256-10420

*ND-not determined

Table 2: Recovery studies for selected metals (mg/kg) and Ethylene glycol butyl ether (ppm)

	Paint samples		
Parameters	**MS**	**MSD**	**MEAN±SD**
As	80.5	85.3	82.9±3.4
Ca	99.2	95.4	97.3±2.7
Cd	96.3	91.3	93.8±3.5
Cr	95.3	97.8	96.5±1.7
Cu	94.1	97.7	95.9±2.5
Fe	94.0	95.1	94.6±0.8
Mg	101	110	105±6.6
Pb	101	106	104±3.6
EGBE	93	92.2	92.6±0.6

MS= Matrix spike; MSD= Matrix spike duplicate; EGBE= Ethylene glycol butyl ether

Principal Component Analysis

The PCA was used as a predictive and optimization tool to identify different clusters based as shown in Fig. 1. The cumulative variations among them could be explained by three principal components, together accounting for 76 % of variations in the samples. Different clusters were formed based on the brands. Similarly, when PCA was applied to VOCs dataset it also resulted in various clusters based on the colour of the paint. Four components explained the variations up to 82 % in the datasets.

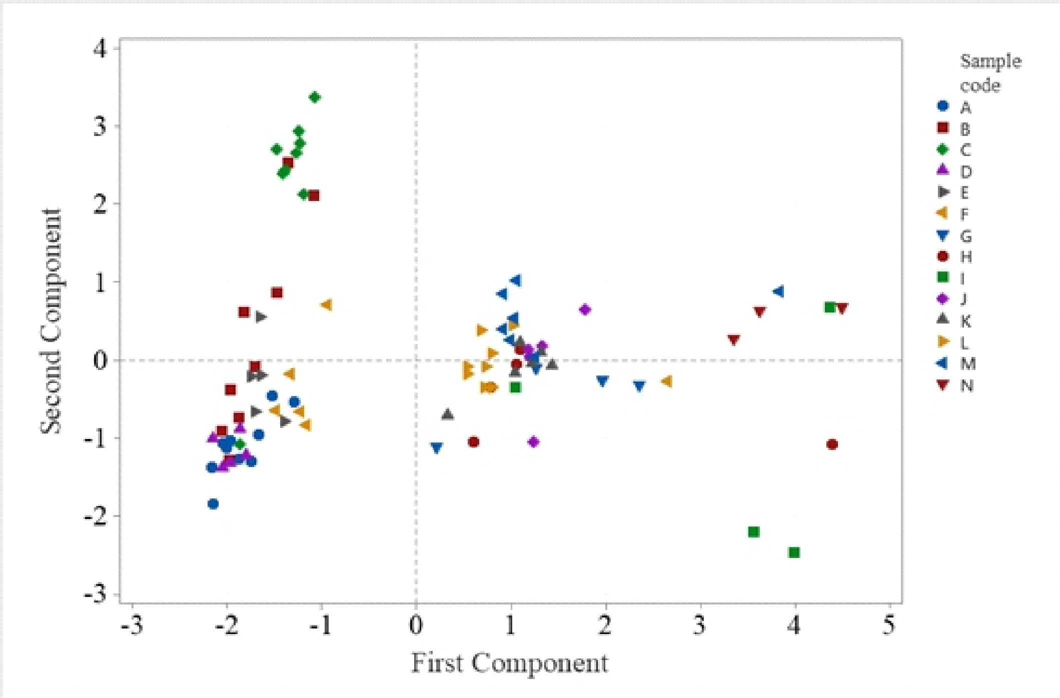


Fig. 1 (a): Principal Component analysis of variation in metal concentrations based on manufacturers

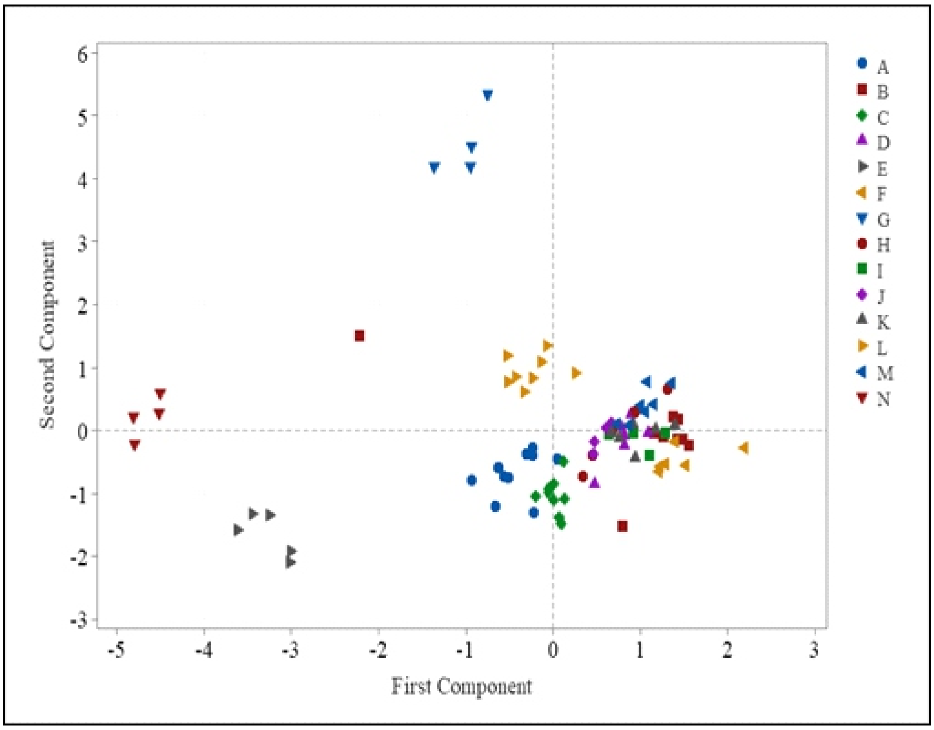


Fig. 1 (b): Principal Component analysis of Ethylene glycol butyl ether concentrations based on Manufacturers

Mathematical Modelling of VOCs Performance Prediction and Optimization in paints by Response Surface Method

The application of Response Surface Method (RSM) for optimization showed the following empirical relationship between the metals (i.e., As, Ca, Cd, Cr, Cu, Fe, Mg, and Pb) and the independent variable (i.e., Ethylene glycol butyl ether):

$$EGBE = 884 + 1.183 * As + 0.805 * Cd + 30.73 * Cr + 0.089 * Cu - 1.337 * Fe - 37.44 * Ni - 0.146 * Pb + 6.20 * Zn + 0.000357 * Fe * Fe + 0.000114 * Pb * Pb - 0.0365 * Zn * Zn - 0.000397 * As * Cd - 0.00674 * As * Cr - 0.000901 * As * Cu + 0.01843 * As * Ni - 0.00444 * As * Zn - 0.000579 * Cd * Cu + 0.00339 * Cd * Ni - 0.000136 * \mathrm{Cd} * \mathrm{Pb} - 0.00514 * \mathrm{Cr} * \mathrm{Fe} - 0.00753 * \mathrm{Cr} * \mathrm{Pb} - 0.00514 * \mathrm{Cr} * \mathrm{FE} - 0.00753 * \mathrm{Cr} * \mathrm{Pb} - 0.0404 * \mathrm{Cr} * \mathrm{Zn} + 0.000365 * \mathrm{Cu} * \mathrm{Fe} + 0.00788 * \mathrm{Cu} * \mathrm{Ni} + 0.000672 * \mathrm{Cu} * \mathrm{Pb} + 00776 * \mathrm{Cu} * \mathrm{Zn} - 0.0003808 * \mathrm{Ni} * \mathrm{Pb}$$

Stepwise method with backward elimination having alpha as 0.1 was used to perform the analysis. Stepwise method removes and adds terms to the model for the purpose of identifying a useful subset of the terms. Backward elimination method starts with all potential terms in the model and removes the least significant term for each step. A better result is obtained from the Minitab when all variables in the model have p-values that are less than or equal to the specified Alpha to remove value. The adequacy of the developed model indicating the relationship between response (EGBE) and the predictors in the form of eight metals was analysed using the Analysis of variances (ANOVA) as shown in Table 3. Table 3 indicates that the overall model was significant with p -value < 0.01. Fisher's variance ratio *F*-value was also considered. It is calculated as a ratio of mean square regression and mean square residual. It is a measure of variance in the data about the mean. The high *F*-value and very low *P*-value confirms the high significance of the developed models. The developed model indicated that linear, 2- way effect and interaction effect were significant. Out of the metals linear effect of Cu, Fe, Ni, Pb, Zn, were having prominent effect on the VOC and the same could be observed from the pareto chart i.e. EGBE. The developed model had R^2value of 0.9569 and R^2_{pred} value of 0.8620 as shown in Table 4, the model summary.

Table 3: Analysis of Variance of selected metals

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	27	4143562	153465	45.21	0.000
Linear	8	1036598	129575	38.17	0.000
As	1	4800	4800	1.41	0.240
Cd	1	3478	3478	1.02	0.316
Cr	1	6645	6645	1.96	0.167
Cu	1	257779	257779	75.94	0.000
Fe	1	33950	33950	10.00	0.003
Ni	1	212509	212509	62.60	0.000
Pb	1	182953	182953	53.90	0.000
Zn	1	37823	37823	11.14	0.002
Square	3	230134	76711	22.60	0.000
Fe*Fe	1	146181	146181	43.06	0.000
Pb*Pb	1	40992	40992	12.08	0.001
Zn*Zn	1	20414	20414	6.01	0.017
2-Way Interaction	16	2400643	150040	44.20	0.000
As*Cd	1	19914	19914	5.87	0.019
As*Cr	1	13225	13225	3.90	0.053
As*Cu	1	87132	87132	25.67	0.000
As*Ni	1	155087	155087	45.69	0.000
As*Zn	1	30787	30787	9.07	0.004
Cd*Cu	1	42250	42250	12.45	0.001
Cd*Ni	1	10708	10708	3.15	0.081
Cd*Pb	1	13980	13980	4.12	0.047
Cr*Fe	1	56310	56310	16.59	0.000
Cr*Pb	1	136248	136248	40.14	0.000
Cr*Zn	1	14025	14025	4.13	0.047
Cu*Fe	1	16324	16324	4.81	0.033
Cu*Ni	1	63822	63822	18.80	0.000
Cu*Pb	1	96289	96289	28.37	0.000
Cu*Zn	1	93328	93328	27.49	0.000
Ni*Pb	1	80870	80870	23.82	0.000
Error	55	186702	3395		
Total	82	4330264			

Table 4: Model Summary of the RSM

S	R-sq	R-sq(adj)	R-sq(pred)
58.2630	95.69%	93.57%	86.20%

The high R^2 for all the four models shows that the developed models could explain the variations present in the independent variables.

The contour graphs of metals having maximum effect based on the ANOVA table and Pareto chart on the EGBE are presented below in Fig. 2. The contour graphs are shown in Fig. 3. Fig. 3a- d wherein X -axis is Cu on Y Axis and this suggests that when Cu concentration is limited below 1000 ppm the VOC content restricts to 1000 ppm irrespective of which metal is present on the Y axis. Furthermore, the graphs (e, h and i) inferred that Ni was restricted below 100 ppm to have the VOC concentration around 1000 ppm.

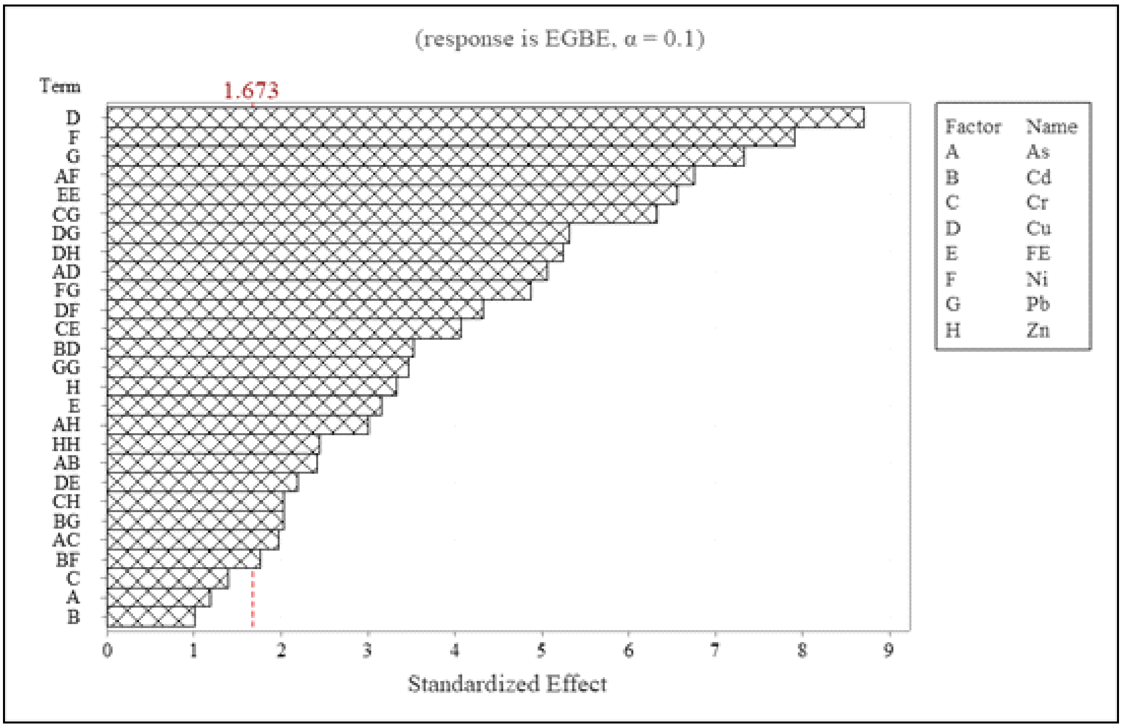
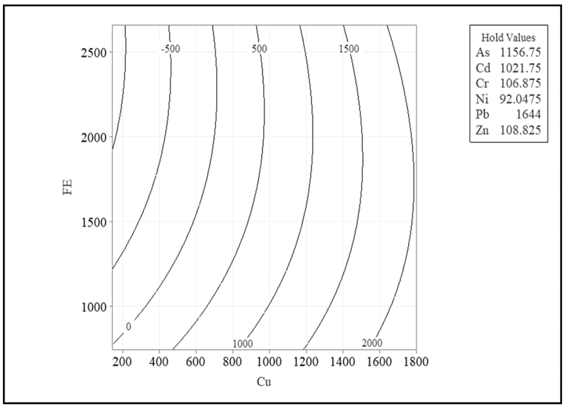
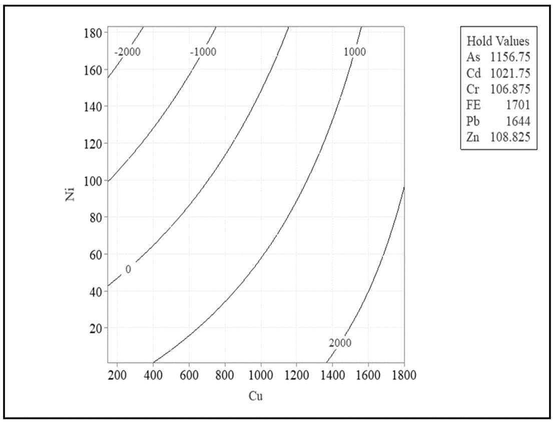


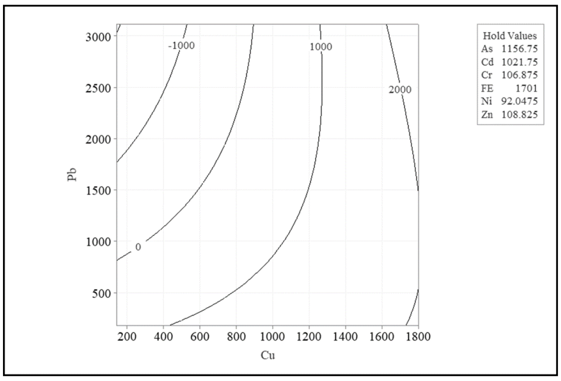
Fig. 2: Pareto Chart of significant metals analysed



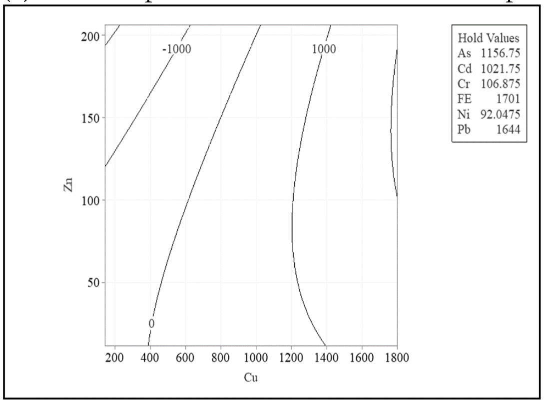
(a) Contour plot of Cu vs Fe on **EGBE** output



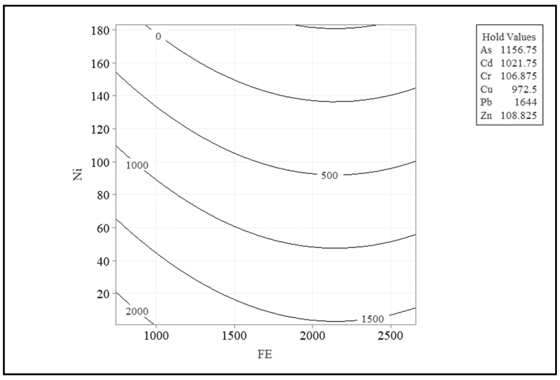
(b) Contour plot of Cu vs Ni on **EGBE** output



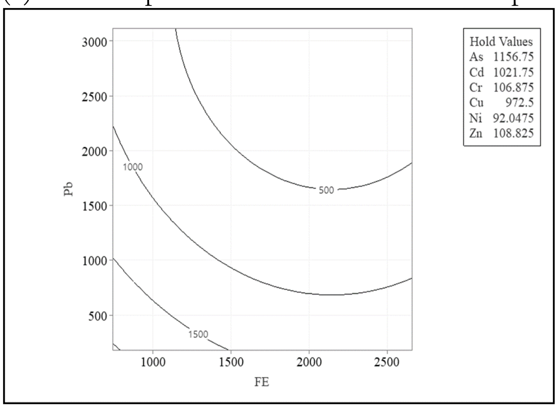
(c) Contour plot of Cu vs Pb on **EGBE** output



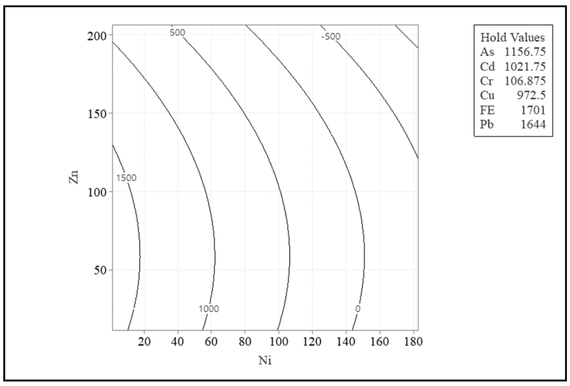
(d) Contour plot of Cu vs Zn on **EGBE** output



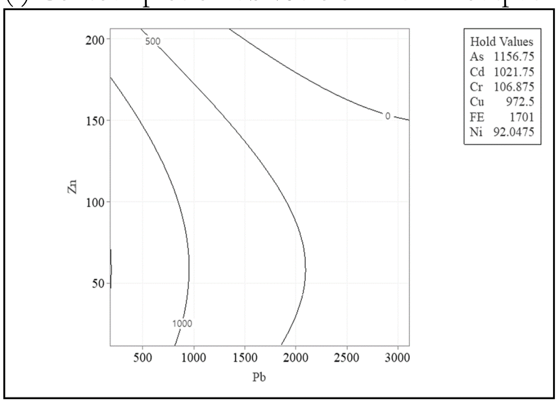
(e) Contour plot of Fe vs Ni on **EGBE** output



(f) Contour plot of Pb vs Fe on **EGBE** output



(i) Contour plot of Ni vs Zn on **EGBE output**



(j) Contour plot of Pb vs Zn on **EGBE** output

Fig. 3: Contour plots of selected metals vs EGBE (VOC)

To assess the prediction competence of the established model using RSM, an inverse range scaling was executed on all the experimental outputs (VOC output) to return predicted response (VOC predicted output) for its subsequent comparison with experimental response. **Fig.4** shows a comparison between values obtained as a result of experimental VOC analysis and predicted response using RSM. The prediction competence of the developed model is shown by two lines: one line represents an ideal model wherein experimental data is equal to predicted data; while the other line is obtained by plotting data obtained using developed RSM models and experimental responses.

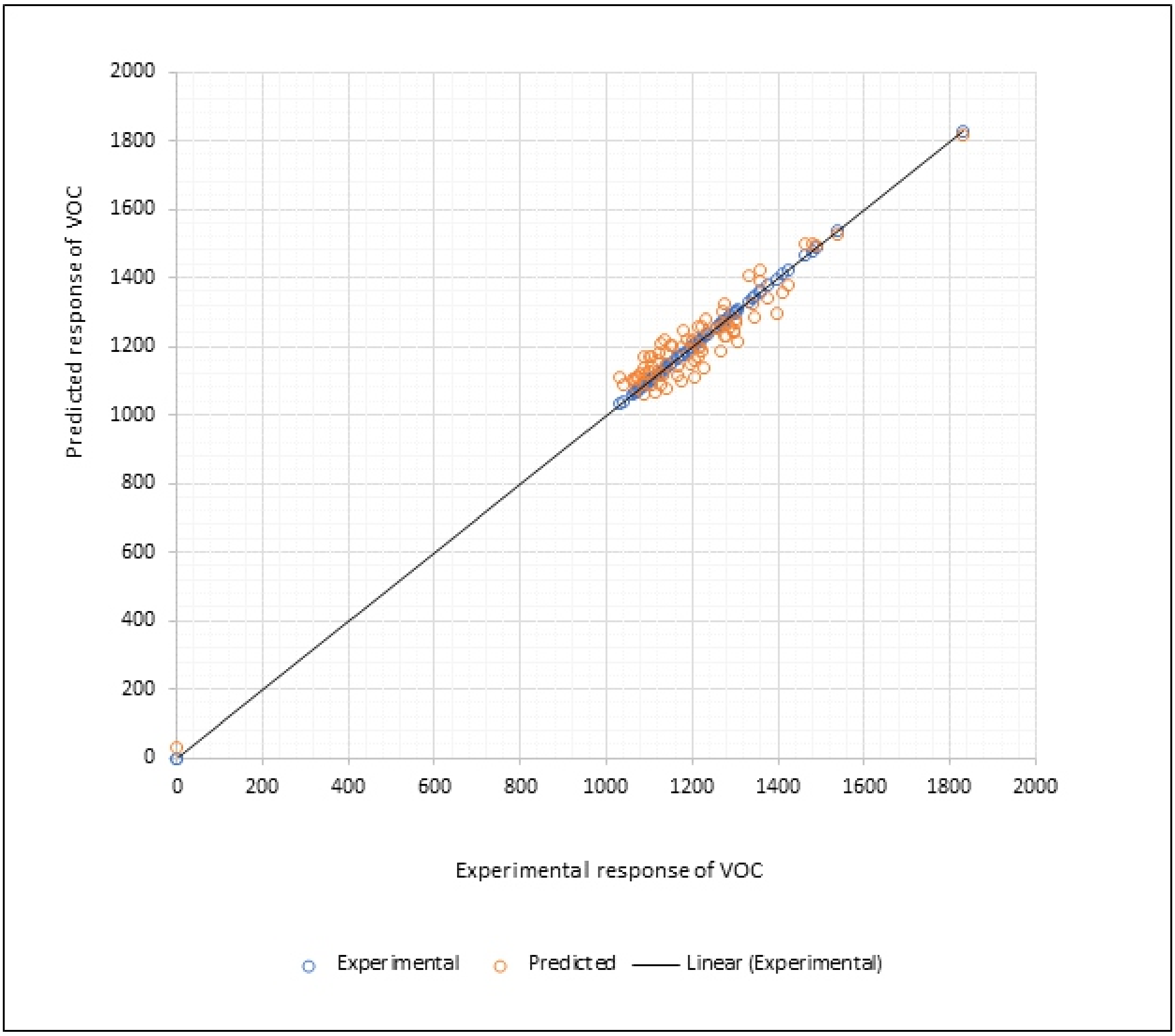


Fig. 4: Experimental and predicted Optimization of ethylene glycol butyl ether using Response Surface Methodology

Further optimization was carried out with the target to minimize the EGBE concentration. During the optimization, the minimum concentration of EGBE set at 900 ppm (with a target set at 1100 ppm and upper limit at 1300 ppm). The values were set based on the range of concentration of EGBE found to be present in the tested samples. The multi response optimization was carried out using desirability function approach. The best optimization condition having EGBE concentration as 1100 ppm was found to have metal concentrations (ppm) as As (499.116), Cd (198.819), Cr (59.093), Cu (145), Fe (2659.20), Ni (8.36887), Pb (300) and

Zn (11.15). The composite desirability y was 1. However, the above conditions of metals could not be tested experimentally. The results propose a way to minimize VOC content in the paints.

CONCLUSION

RSM and PCA modelling tools have been used in this study to quantitatively describe the interaction effects of more than one factor on system response and have proven especially useful in the modelling and optimization of experimental data. The PCA identified the VOCs present in all the samples and categorize samples based on different VOCs present in a cluster. The RSM provided a relationship between the independent variables (ethylene glycol butyl ether) and the response of the system which had a significant effect on experimental results. The RSM also established a correlation between the metals and the ethylene glycol butyl ether. Furthermore, optimization of the process was carried out to maintain an acceptable range of metals during the production of low emission VOC (ethylene glycol butyl ether) in paints for household uses. The optimization of the data set shows that metal contents in the purchased samples were very high and therefore the value of metals changes based as VOC content changes. The use of response surface method to optimize and predict the metals and targeted VOC can be applied to other VOCs to maintain the metal concentrations within the established permissible limits. The results can be very useful in assessing the impact of hazardous air pollutant in indoor air quality and a good applicability in paint industries to produce products within the limit of international standards. The use of RSM to predict and optimize EGBE can be applied to other anti-freezing and film-forming agents to retain the metal concentrations within the regulated permissible limits.

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