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A Multivariate Statistical Approach To Detecting Adulteration Of Cement, Using Gamma Spectroscopy And Instrumental Nuclear Activation Analysis (INAA) Data

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ABSTRACT

This study is considered as an attempt for employing multivariate statistical analysis, such as multiple linear correlations, principal component analysis and cluster analysis, to infer the spatial distribution of elements in cement samples through which we can detect possible adulteration of the samples based on measured radioactivity and elemental levels. It was estimated on the bases of data from five types of cements produced and or used in Ghana. The study results showed that the adapted classification rule leads to the classification of all CM I, CM II and CM III, about 60% of the total cements sampled, to the group which they belong. From the classification of the remaining 40%, it is highly probable that CM IV and CM V are from the same product but packaged under different names, whilst the CM IV and CM V from Accra and Kumasi are adulterated forms of this product. The analysis adopted was found to be effective in classifying the cement samples into their true statutes. This shows that multivariate statistical analysis of data from gamma spectroscopy and INAA may be an efficient and useful tool for predicting adulteration of cement.

Keywords: *Multivariate statistical analysis, Adulteration, Gamma spectroscopy, Instrumental nuclear activation analysis*

1. INTRODUCTION

Cement is one of the important and expensive materials used by the building industry in Ghana. Most buildings in Ghana are constructed from cement blocks and cement concrete. Cement is used for making blocks, concrete, and for plastering the buildings made of bricks, blocks or concrete. The development of a strong physical infrastructural base is cardinal in achieving the millennium development goals of the country to attain a middle income status by 2015, as this will aid industrialization and consequently promote a sound economic growth. Ghana's housing deficit currently stands at more than 1 million with an annual delivery of only 40,000 being provided. The country's cement industry is estimated to grow by over 8% every year for the next 20 years. According to Ministry of Water resources, Works and Housing, Ghana, report 2010 [1] demand for cement in the country is expected to increase as a result of increasing population and expansion of infrastructure.

Potential for buying and using adulterated cement is high in Ghana, this is particularly high in rural housing development as unscrupulous persons open, adulterate and re-package cement and sell the products to unsuspecting customers. Cement is easy to adulterate with flour, rock dust, etc.. The products made from such cement will be inferior. Concrete is defined by its properties in the hardened state. However, these properties are known to depend strongly on the chemical make-up created by the tens of chemical hydration reactions that take place when cement clinker phases react to form this cohesive liquid stone.

Such concrete, made from adulterated cement, may withstand initial loads but is likely to collapse over time and under unusual loads, especially during hurricanes, typhoons, tsunamis, floods, etc. Poorly consolidated concrete is common in columns and slabs. It leaves voids and exposes reinforcement bars, leading to water penetration and invisible but potentially disastrous corrosion. Entrapped air, often the result of poor mixture and/or lack of effort in consolidating a mixture, also weakens the structure. Beam and column joints are prone to poor detailing and faulty casting leading to poor coverage of the reinforcing steel.

The identification, adulteration detection and estimation of different types of crime exhibits such as cement, drugs, petroleum product and their residues, liquor, vegetable oil and fats, dyes, gold, chemicals etc. in forensic science laboratories required high degree of skill and expertise. Forensic scientists are following various methods for the chemical analysis of these substances in the laboratories. In this study, Gamma spectroscopy in conjunction with Instrumental nuclear activation analysis (INAA) was used to determine natural radioactivity levels and the elemental composition of the five main types of cement manufactured and used in building construction in Ghana. Multivariate statistical methods were then applied to the data obtained, to detect possible adulteration of the cement samples.

2. MATERIALS AND METHODS

The study was carried out at the Radiation and Waste Safety Department of the Radiation Protection

institute, Ghana Atomic Energy Commission from October, 2009 to September, 2010.

Sampling and sample preparation

A total of 25 cement samples representing the five main types of cement manufactured and or used in building construction in Ghana were sampled from different cement suppliers and retailers. The samples were dried in a temperature-controlled furnace at 110ºC for 24h to remove moisture. After moisture removal, these samples were cooled in moisture-free atmosphere and pulverized into powdered form.

The samples codes for cement samples and sampling towns are shown in Table 1. Sample preparation was done in the A. Chatt Chemical Laboratory at the Ghana Research Reactor-1 (GHARR-1) Centre.

Table 1: Sample codes for cement samples and sampling towns

Cement type	Sample code	Towns	Sample code
Portland limestone cement	CM I	Accra	a
Portland limestone cement	CM II	Kumasi	b
Ordinary portland cement	CM III	Ho	c
Tile adhesive cement cole	CM IV	Takoradi	d
Tile adhesive cement	CMV	Cape Coast	e

Gamma Spectroscopy

The prepared samples were packed into a plastic 1litre Marinelli beaker, weighed and hermetically sealed. These sample containers were same in size and geometry of the reference materials (RG-set) used for calibrations. The sealed samples and the reference materials were stored for 6-8 weeks before counting so as to allow ^{224}Ra and ^{226}Ra to reach the secular equilibrium with their short-lived decay products.

The activity concentrations of natural radionuclides were determined by high-resolution gamma-ray spectrometry using n-type HPGe detector Model GR 2518-7500SL (Canberra Industries Inc.) coupled to a computer based PCA-MR 8192 Multi-Channel Analyser (MCA) mounted in a cylindrical lead shield (100 mm thick) and cooled in liquid nitrogen. The detector has a relative efficiency of 25% to NaI detector, 1.8 keV energy resolutions at the energy peak of 1333 keV of 60Co isotope, and a peak-to-Compton ratio of 55:1. The radionuclides were identified using gamma ray spectrum analysis software, ORTEC MAESTRO-32.

The absolute efficiency calibration of the gamma spectrometry system was carried out using the radionuclide specific efficiency method in order to reduce the uncertainty in gamma-ray intensities, as well as the influence of coincidence summation and self-absorption effects of the emitting gamma rays [2-5]. The IAEA reference materials RGU-1(U-ore), RGTh-1 (Th-ore) and RGK-1 (K2SO4), with densities similar to the cement samples to be measured after pulverization, were employed for the efficiency calibration of the system. The sample containers were placed on top of the detector for counting. The same geometry was used to determine peak area of samples and references. Each sample was measured during an accumulating time between 36,000 and 80,000s. Background measurements were taken and subtracted in order to get net counts for the sample. The specific radioactivity of ^{40}K was measured directly by its own gamma ray at 1460.8 keV (10.7), while activities of ^{226}Ra and ^{232}Th were calculated based on the weighted mean value of their respective decay products in equilibrium.

The specific radioactivity of ^{226}Ra was measured using the 295.2 (18.2), 351.9 (35.1) keV gamma rays from ^{214}Pb and the 609.3 (44.6), 1764.5 (15.1) keV from ^{214}Bi. The specific radioactivity of ^{232}Th was measured using the 911.2 (26.6) keV from ^{228}Ac, and the 583.2 (30.6) keV from 208Tl. The values inside the parentheses following gamma-ray energy indicate the absolute emission probability of the gamma decay.

The specific activities in Bq/kg of the radionuclides in the samples were calculated after decay correction using the expression:

$$A = \frac{N_{sam}}{f_E.\eta(E).T_C.M_{sam}} \quad \text{.....(1)}$$

Where, A is the activity concentration of the radionuclides in Bqkg^{-1} in the samples, M_{sam} is the mass of sample (kg), N_{sam} is the sample net counts in the peak range, f_E is the gamma emission probability, T_c is the counting time and η(E) is the photopeak efficiency.

INAA

About 200 mg of each sample and standard reference material were weighed into pre-cleaned irradiation plastic vials. The standard reference materials namely, NIST 1566b oyster tissue, and certified reference materials (CRM) were used for quantification and validations of results.

Samples and the standards were irradiated using the Ghana Research Reactor-1(GHARR-1) facility, operating at half power of 15.0 kW and at a thermal neutron flux of 5.0 9 1011 cm^{-2} s^{-1}. Irradiation times ranged from 2 min to 3 h depending on the half-life of elements of interest. The experimental conditions for the determination of short lived nuclides using thermal neutrons and counting system were 2 min irradiation and 2

min counting time. For the medium lived radionuclides, samples were subjected to 1-h irradiation with 1–2 days decay time and 10 min counting time. For the long lived radionuclides, the samples were irradiated for 3 h, allowed a decay time of 3–7 days and counted for 10 h. The detector used in this work was an n-type high purity germanium (HPGe) detector Model GR 2518 (Canberra Industries Inc.) with a resolution of 1.8 keV (FWHM) for ^{60}Co gamma-ray energies of 1332 keV. The detector operated at a bias voltage of (-ve) 3000 V with relative efficiency of 25% to NaI detector. MAESTRO was used for the spectrum analysis.

3. RESULTS AND DISCUSSION

The data obtained for this work consisted of 20 elements analyzed for five cements which were sampled from five towns making a total of 500 data points.

Statistical data analysis was performed on the logarithmically-transformed data variables (Table 2) using Euclidean distance and the Ward's linkage method. The data was then standardized by Z-score approach. Data evaluation such as multiple linear correlations, principal component analysis and cluster analysis were applied to infer the spatial distribution of elements in the analyzed cement samples.

Table 2: Descriptive statistics of logarithmically-transformed data of elements in cements produced and or used in Ghana

Element	N	Min	Max	Mean	STDV	Var
^{226}Ra	25	1.40	1.74	1.5489	.11301	.013
^{232}Th	25	1.24	1.71	1.4027	.14381	.021
^{40}K	25	1.81	2.83	2.2551	.32249	.104
Ti	25	-1.00	.22	-.4011	.31977	.102
Si	25	3.52	4.98	4.6306	.42586	.181
V	25	1.36	1.94	1.6633	.19091	.036
Al	25	4.59	4.70	4.6423	.04424	.002
Mn	25	2.30	2.68	2.5099	.12557	.016
Ca	25	4.50	5.08	4.8409	.17259	.030
La	25	2.60	2.98	2.7765	.12867	.017
Cd	25	-1.05	.00	-.5334	.31542	.099
As	25	-.70	.35	.0380	.26471	.070
Na	25	3.10	3.66	3.3735	.21280	.045
K	25	3.81	4.40	4.0949	.16450	.027
Sc	25	1.32	1.60	1.4744	.08739	.008
Fe	25	3.25	4.60	3.5865	.47201	.223
Co	25	.97	1.53	1.3328	.18561	.034
Cr	25	.11	.92	.5862	.25768	.066
Hg	25	-1.05	.10	-.4763	.37695	.142
Zn	25	.60	1.35	1.0456	.17323	.030

In order to identify patterns in the data and to reduce its dimensionality for easy interpretation, the principal component analysis was employed for this task [6-10]. Table 3 shows the varimax-rotated components matrix. The first three principal components of this study accounted for 84.643% of the total variance in the data set (PCA 1, PCA 2 and PCA 3 accounted for 60.643%, 13.799 and 10.146%, respectively).

Figure 1, depicts how each element is distributed spatially and how each element relates with the others. Two main groups for elements can be observed. Mercury (Hg) and Ti formed one group while the remaining 18 elements formed the second. Cluster analysis is one of multivariate techniques used to identify and classify groups with similar characters in a new group of observations. Each observation in a cluster is most like others in the same cluster. Cluster analysis was carried out through two axes; the first was to identify cements with similar characters. The other axis was to identify similar characteristics among elements.

Table 3: Varimax-rotated components matrix for samples data

Element	Component			
	1	2	3	Communalities
^{226}Ra	0.721	-0.330	0.359	0.758
^{232}Th	0.948	-0.180	0.042	0.932
^{40}K	0.865	0.070	-0.331	0.863
Ti	0.129	0.920	-0.053	0.866
Si	0.757	0.331	-0.015	0.683
V	0.973	0.000	-0.138	0.966
Al	0.930	-0.175	0.287	0.977
Mn	0.852	0.066	-0.036	0.732
Ca	0.932	-0.011	0.138	0.888
La	0.829	-0.477	0.083	0.922
Cd	0.642	0.456	0.346	0.741
As	0.758	0.407	-0.020	0.740

Na	0.904	-0.390	-0.063	0.974
K	0.936	0.242	-0.055	0.939
Sc	0.621	-0.103	-0.731	0.930
Fe	0.860	-0.075	0.035	0.746
Co	0.410	-0.164	0.858	0.931
Cr	0.784	-0.242	-0.499	0.922
Hg	0.173	0.775	0.076	0.636
Zn	0.812	0.328	0.072	0.772
Eigenvalues	12.129	2.760	2.029	
% of Variance	60.643	13.799	10.146	
Cumulative %	60.643	74.442	84.588	

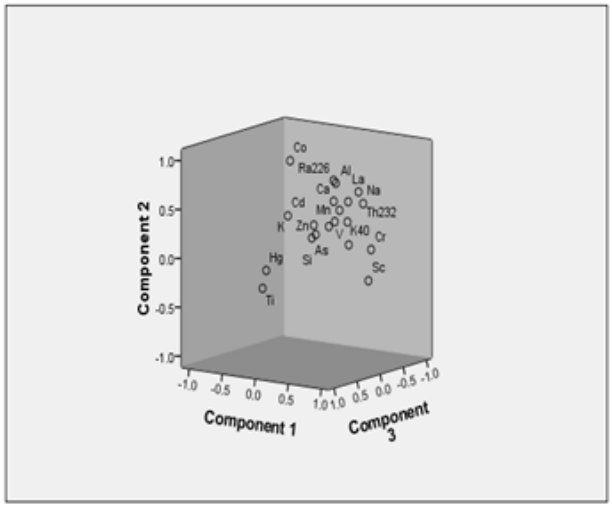

Figure 1: Principal component plot in rotated space for elements

Figure 2. shows a dendrogram of classification of the Ghanaian cements as groups according to the radioactive isotope concentrations and physicochemical parameters in their samples. Five (5) main groups can be observed in which three are well defined while the other two are not. The first group consisted of the entire CM I samples linked at a relatively short distance to all five CM II samples in group two. This may be due to the fact that both CM I and CM II are Portland cements, hence having almost the same elemental composition. Group three is made up of CM III samples collected from the five towns. The fourth and fifth groups are not well defined. Group four contains two CM IV samples from Accra and Kumasi while the other two members are CM V samples also from Accra and Kumasi. The last group has three samples of CM IV and CM V from Ho, Takoradi and Cape Coast respectively. From the composition of groups four and five, it is probable that CM IV and CM V are from the same product but packaged under different names, whilst the CM IV and CM V from Accra and Kumasi are adulterated forms of this product.

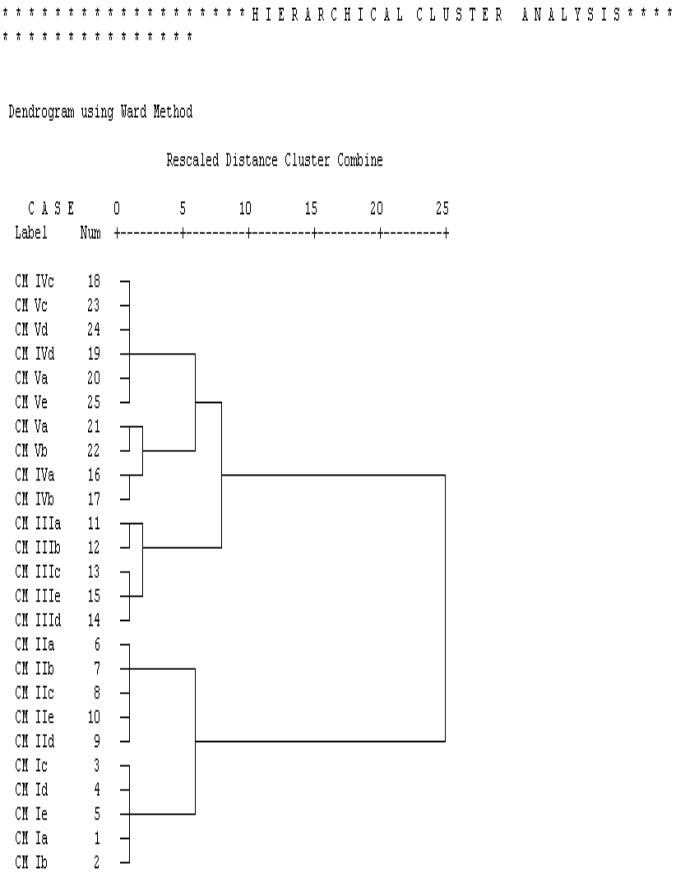

Figure 2: Dendrogram for Ghanaian cements concerning radioactive isotope concentrations and elemental levels in the cement samples.

4. CONCLUSION

Gamma spectroscopy analysis in conjunction with Instrumental neutron activation analysis has been utilised for multi-elemental analysis of cements produced and or used in Ghana. In all, 20 elements were identified and quantified. The activity and elemental concentration values were used in a multivariate statistical analysis methodology. Statistically, all the cement samples present similar radiological and elemental signatures. This suggests that a similar type of raw material was used in the manufacturing of the cements. The results from the study raised some concerns about the authenticity of some of these cements.

In this study, Cluster analysis was used as a statistical tool for statistical analysis. The analysis adopted was found to be effective in classifying the cement samples into their true statutes. This shows that multivariate statistical analysis of data from gamma spectroscopy and INAA analysis may be an efficient and useful tool for predicting adulteration of cement.

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