

Determination of some metal contaminants from industrial effluents in North-West Nigeria using k_0 -NAA Standardization Method

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ABSTRACT

The k_0 -NAA standardization method has been applied to investigate the metal contents of industrial effluents collected at several sites in North-Western part of Nigeria. Ten elements (Cr, Co, Ca, Na, Eu, Hf, Th, Dy, Sb and Cs) were determined from 10 samples from the leather, textile and petrochemical industries. The enrichment factors were determined by comparison of the elemental concentration with that of a typical soil from non-industrial area within the same locality of the survey. Some of the industrial effluents had high elevated concentration for chromium, calcium, cobalt, sodium, antimony and dysprosium.

Keywords: k_0 -standardization, k_0 -IAEA program, Neutron activation analysis, Industrial effluents, Metal contaminants.

INTRODUCTION

The adoption and implementation of k_0 -NAA standardization method is a culmination of several efforts in recent years geared towards the optimization [9] of the Nigeria Research Reactor-1 (NIRR-1) installed and commissioned at the Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria, Nigeria, for training and research. One of the strategic development plans for the optimum utilization of the Nigeria Research Reactor-1 (NIRR-1) [24] is the adoption and implementation of the most widely accepted single comparator NAA technique termed the " k_0 -standardized method" for routine analysis in NIRR-1 laboratory. Several efforts have been directed towards this goal since it was installed and commissioned in 2004. Some of the preliminary works done include the characterization of the neutron flux parameters in the irradiation channels, development of the experimental protocols for the facilities and calibration of the detectors at different source-detector geometries, the development of a relative quantitative NAA method for routine analysis of over 30 elements using NIRR-1 as well as the installation and testing of the k_0 -IAEA program for elemental analysis in NIRR-1 NAA laboratory. The details of all these previous works are described in separate papers [13, 14, 15]. In recent times, Nigeria like many other developing nations has witnessed rapid industrialization with its attendant problem of generation of wastes. This study was partly motivated by the fact that some metal contaminants from industrial effluents constitute a serious threat to human health. In extreme cases, leading to failure of vital organs such as liver, kidneys or causing cancer of the lungs [1, 2, 4, 12, 18, 21, 25].

MATERIALS AND METHODS

A random survey of the various industries that is potentially capable of causing metal contamination of the environment via industrial effluents was carried out in three industrial cities of Kano, Kaduna and Zaria, North-Western part of Nigeria. The choice of this location was informed by the fact that there is a large concentration of leather and textile industries in this area due to the abundance of the raw materials – hides & skin for leather and

cotton for textile. A total of ten samples of solid effluents were collected consisting of six samples from tannery, two samples from textile, one sample each from petrochemical refinery and soil for background values of elements using polythene bags. Industrial waste in this study collectively refers to useless, unwanted, undesirable or discarded materials that arise out of industrial activities. This excludes dumps within the plant premises from being classified as wastes even though some poses damages to the environment.

Observations during the field survey shows the wastes collected vary in composition and in colour depending on the industry and the stage of production. A typical example is waste from tanneries which contains more sulphur when they are unhairing and more chromium when tanning the skin and hides. So two different samples were sometimes taken from the same company. This is responsible for the non-normal distribution in the data leading to the large standard deviations in Table 4.

The sludge were collected directly from the effluent discharge point within the vicinity of the plant before they are mixed together as they empty into a common drainage canal that channels the effluents into the Challawa river in Kano Challawa industrial layout. Similarly the sediments from industrial effluents are emptied into the Kaduna river basin environment in Kaduna [10].

It is noteworthy that the effluents from the textile industries are semi-solid dyes flushed out after colour fixing so the sediments collected required drying.

The samples were air-dried and then oven-dried at a temperature of 60°C to 80°C for few hours depending on the moisture contents after which the dried samples were grinded to fine powder and homogenized with agate mortar and pestle. Sieve with aperture 125µm was used to obtain fine particle size for nine of the samples except the crude oil sludge which was oily. The sieving was carried out to remove the chaff or extraneous materials inadvertently collected along with the samples.

The samples were weighed into polythene bags using digital balance. Between 150 and 200 mg of each sample was added into the polythene bag and heat-sealed with the sample identity on it. The sample is then placed into a cylindrical vial 5 cm high and 1.5 cm diameter, the top stocked with cotton wool, vials cap snapped closed, sealed with cello tape and the ID number of the sample written on the vial. For long irradiation, 6 – 8 samples were packed together in the same vial and the job card number is written on the vial.

For the INAA process, both short and long irradiation were carried out with NIRR-1 reactor, operating at a nominal thermal power rating of 15.5 KW with control console thermal neutron flux setting of $5 \times 10^{11} \text{ n.cm}^{-2}.\text{s}^{-1}$. The samples were irradiated with the neutrons in inner and outer channels of NIRR-1, according to the protocols developed. By monitoring the subsequent decay of these radioisotopes using their well known decay schemes, the elements present in each analyte were identified and precisely quantified. The polythene vials were transferred by the pneumatic (rabbit) system into the reactor for irradiation using NIRR-1 irradiation regime and counting protocols [14]. The short and long irradiations were carried out for 1 minute and 6 hours respectively.

The first count for short irradiation was carried out immediately (approximately 10 minutes) after irradiation at a detector-source distance of 15 cm for 600 seconds for the short-lived nuclides. The second count was carried out at a detector-source distance of 2 cm for 600 seconds after allowing the samples to decay for 3 hours for medium-lived nuclides. The first count after the long irradiation was carried out after allowing the samples to decay for 3-4 days at a detector-source distance of 2 cm for 1800 seconds. The second count was carried out at a detector-source distance of 2 cm for 3600 seconds one week after first count. (12 – 14 days after irradiation) All the measurements were done using high-purity coaxial germanium detector (HPGe) 30195 with relative efficiency of 30% and a resolution of 1.95 keV (FWHM) for the 1.33 MeV gamma line of ^{60}Co . Samples were placed on plexi-glass sample holders for the two counting geometries used in this work.

Prior to the measurements, the detector was calibrated for use with the k_0 -IAEA spectral analysis software to establish the relationship between the peak energy and the probability of the detector recording a count in the full energy peak. The efficiency calibration was done from measurement using two spectra from two separate standard calibration sources, Cs-137 for peak-to-total ratio curve and Eu-152 for full-energy peak efficiency curves at the two source-detector positions [8].

Theoretically, flux monitor was not necessary because NIRR-1 like all Miniature Neutron Source Reactor (MNSR) facilities has a stable neutron flux profile during steady state operation and has a burn-up of less than 1% for the entire life time of core, as such the neutron spectrum parameters remain constant for the entire period [15]. However, just to be double sure, the determination of the neutron flux parameters of NIRR-1 was carried out again

to ascertain neutron flux stability after the recent installation of the Cd-lined irradiation channel for the implementation of epithermal and fast NAA procedures [17,19]. The results confirmed again the neutron flux stability as one of the hallmarks of MNSRs. The blank also was not necessary because the sample was removed from the vial before counting and the polythene bag used as recipient has insignificant elemental composition hence negligible blank values [14].

Table 1. Routine irradiation and measuring regimes developed for NIRR-1 facilities

Neutron flux/irradiation channel	Procedure	T _{irr}	T _d	T _m	Activation products
2.5 x 10 ¹¹ n/cm ² s/outer irradiation channels (B4)	S1	1 min	10 – 15 min	10 min	²⁷ Mg, ²⁸ Al, ³⁸ Cl, ⁴⁹ Ca, ⁵¹ Ti, ⁵² V, ⁶⁶ Cu
2.5 x 10 ¹¹ n/cm ² s/outer irradiation channels (B4)	S2	1 min	3 - 4 h	10 min	⁴² K, ⁵⁶ Mn, ¹⁶⁵ Dy
5 x 10 ¹¹ n/cm ² s/inner irradiation channels (B2 and B3)	L1	6 h	4 – 5 d	30 min	²⁴ Na, ⁷² Ga, ⁷⁶ As, ⁸² Br, ¹²² Sb, ¹⁴⁰ La, ¹⁵³ Sm, ¹⁹⁸ Au, ²³⁸ U
5 x 10 ¹¹ n/cm ² s/inner irradiation channels (B2 and B3)	L2	6h	11 – 12 d	60 min	⁴⁶ Sc, ⁵¹ Cr, ⁵⁹ Fe, ⁶⁰ Co, ⁶⁵ Zn, ⁸⁶ Rb, ¹³¹ Ba, ¹³⁴ Cs, ¹⁴¹ Ce, ¹⁵² Eu, ¹⁶⁰ Tb, ¹⁷⁵ Yb, ¹⁷⁷ Lu, ¹⁸¹ Hf, ¹⁸² Ta, ²³² Th

T_{irr} = Irradiation time

T_d = Decay time

T_m = Measurement time

The detailed theory, methodology, recommended k_0 values and related nuclear data used for computations of elemental concentrations of samples in k_0 -standardization method applied in this study has been described in numerous publications [5,11,16,23]. The k_0 -INAA standardization proved to be the method of choice because it can determine several elements simultaneously in the same sample, with a high sensitivity or low detection limit and without any chemical separation. Apart from the ten listed elements of interest (metals), other non-metallic elements were detected and determined. Version 5.00 of the k_0 -IAEA spectral analysis software developed to assist users of the k_0 -approach in NAA to harmonize their results from nuclear analytical laboratories was used in this study to calculate the concentration of the respective elements of interest in each sample [23].

Validation of the analytical procedure is done by irradiating, measuring and analyzing a Certified Reference Material (CRM) Lake Sediment IAEA-SL-3 under the same experimental conditions as the real samples.

RESULTS AND DISCUSSION

The result obtained for the CRM analysed is in good agreement with certified values for the elements determined. The results of the analysis of the CRM is in Table 2.

Results of elemental concentrations in the ten samples are displayed in Table 3 with the summary in Table 4. For comparison, ordinary soil was also analysed and local normalization was then carried out. Taking into consideration the fact that the elemental concentration of soil could vary greatly at different places and also with time, due to a change in physical state and chemical composition. The soil used for this work was taken from an uninhabited, uncultivated and non-industrial area within the same locality of the survey, to ensure little or no impact of man's activities on the soil, the data is also displayed in Table 3.

High concentration or Background Loading Factor (BLF) was obtained for chromium in the effluent from the tanneries while the petrochemical industries' effluents have the least metal concentration elevation.

Comparison of the results with previous data obtained for the metal levels in the same study area, Kaduna river basin, by Ewa et al., in 2002 using the same method of Neutron Activation Analysis, [10] showed that the level of contamination of some of the metals have increased by many folds over the years, notably chromium and cobalt. Even for those with fairly constant BLF, a BLF > 1 implies there is still some measure of contamination no matter how little. Also the results of the study conducted by Akan et al., in determining pollutant levels in effluents from different industries within the same industrial areas of Kano metropolis between 2007 and 2008 using Atomic Absorption Spectroscopy shows that the concentrations of heavy metals, nitrate, nitrite, sulphate, phosphate and chloride were higher than the limits set by WHO for the discharged of tanneries and textile effluents into river [3].

In this study the environmental impact of element levels from the effluents on the background was assessed via a background-loading factor defined as:

$$\text{Background-Loading Factor (BLF)} = \frac{\langle C_i \rangle_{\text{eff}}}{\langle C_i \rangle_{\text{soil}}}$$

Where

$\langle C_i \rangle_{\text{eff}}$ = mean concentration of the i-th element in the industrial effluent.

$\langle C_i \rangle_{\text{soil}}$ = mean concentration of the i-th element in the soil (assumed to be the background level for the environment)

From the BLF expression, the threshold level for the loading of these elements from industrial effluents on the environment will then be unity [10,20,22].

So the enrichment factors were determined by comparison of the elemental concentration in the effluents with that of the soil.

Table 2. Comparison of certified values for Lake Sediment IAEA-SL-3 with our results based on the k_0 -Standardization

ELEMENT	This work	C.V. (Range)
	IAEA-SL-3 Lake Sediment [mg/kg]	
Al	24500 ± 953	23300 – 25700
As	3.03 ± 0.41	3.0 – 3.4
Ba	256 ± 64	-----
Br	5.27 ± 0.43	4.8 – 6.4
Ca	116700 ± 13887	107200 – 115000
Ce	-----	43.8 – 47.2
Co	4.21 ± 0.40	-----
Cr	-----	-----
Cs	BDL	1.24 – 1.52
Dy	1.66 ± 0.47	1.65 – 2.79
Eu	BDL	0.64 – 0.68
Fe	14660 ± 733	-----
Hf	8.8 ± 0.58	8.5 – 9.7
K	9031 ± 1117	7910 – 9570
La	20.0 ± 1.0	21.5 – 23.5
Lu	-----	0.27 – 0.33
Mg	24910 ± 5206	24600 – 29400
Mn	539 ± 28	-----
Na	6550 ± 263	6360 – 7020
Rb	-----	36.9 – 40.7
Sb	0.72 ± 0.09	0.46 – 0.66
Sc	3.92 ± 0.31	3.64 – 4.18
Sm	3.58 ± 0.50	3.53 – 4.13
Ta	0.71 ± 0.23	0.65 – 0.75
Tb	0.51 ± 0.15	0.44 – 0.54
Th	7.94 ± 0.65	6.5 – 7.5
Ti	2731 ± 489	2300 – 2920
U	1.41 ± 0.40	2.08 – 2.52
V	21.4 ± 4.5	-----
Yb	1.84 ± 0.49	1.77 – 2.01
Zn	-----	-----

BDL = Below Detection Limit

Table 5. Background Loading Factors (BLF) for elements from different effluents

Element	Leather Industries	Textile Industries	Petrochemical Industry
Ca	10.15	27.32	-----
Dy	0.93	0.32	10.05
Na	3.64	2.97	2.80
Cr	520.23	0.79	1.72
Co	0.58	12.17	2.28
Sb	9.14	1.05	-----
Cs	2.93	1.17	-----
Eu	0.50	1.14	5.14
Hf	2.68	0.41	-----
Th	3.35	0.57	0.72

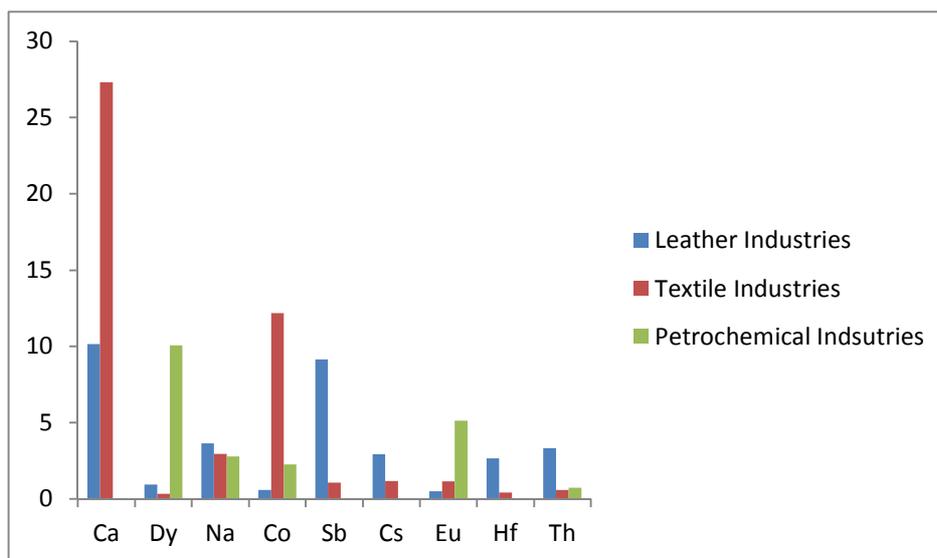


Fig. 1 Metal concentrations in industrial effluents normalized to background soil elemental abundance (Chromium expunged for convenience of good scale)

Table 3. Analytical results for the elements of interest in the industrial effluents in µg/g

Element	Multitan Limited 1	West African Tannery 1	Fata Tanning Limited 1	Zaria Industries Limited	African Textile Manufacturers	Kaduna Refinery Crude Oil Sludge	Background Soil
Ca	28010 ± 2101	61570 ± 3632	1877 ± 516	133900 ± 6159	7955 ± 1352	BDL	2596 ± 626
Dy	7.42 ± 0.96	1.9 ± 0.5	4.59 ± 1.23	0.81 ± 0.19	2.79 ± 1.23	56 ± 1	5.57 ± 1.54
Na	2328 ± 95	12540 ± 514	1559 ± 62	1156 ± 47	6680 ± 267	3703 ± 41	1321 ± 53
Cr	35870 ± 5560	87060 ± 3482	6443 ± 258	27.7 ± 4.3	97.7 ± 4.0	136 ± 10	79.1 ± 3.2
Co	2.82 ± 1.25	2.28 ± 0.22	6.41 ± 1.43	0.99 ± 0.16	476 ± 21	44.7 ± 2.9	19.6 ± 2.9
Sb	0.38 ± 0.08	BDL	1.64 ± 0.14	BDL	0.63 ± 0.17	BDL	0.57 ± 0.08
Cs	1.11 ± 0.25	BDL	2.12 ± 0.45	BDL	3.45 ± 0.56	BDL	3.0 ± 0.4
Eu	0.72 ± 0.15	BDL	0.57 ± 0.14	BDL	1.57 ± 0.20	7.19 ± 0.84	1.4 ± 0.2
Hf	68.1 ± 10.6	7.93 ± 0.77	63.5 ± 7.0	0.81 ± 0.16	16.7 ± 1.5	BDL	21.6 ± 3.8
Th	21.3 ± 4.1	50.9 ± 1.0	26.5 ± 1.9	1.16 ± 0.12	10.4 ± 0.7	7.23 ± 0.90	10.1 ± 1.2

Element	Multitan Limited 2	West African Tannery 2	Fata Tanning Limited 2
Ca	42260 ± 3296	22290 ± 1850	2158 ± 563
Dy	6.2 ± 0.6	9.2 ± 0.7	2.15 ± 0.74
Na	6492 ± 13	1712 ± 69	4247 ± 174
Cr	28360 ± 1134	22420 ± 897	66750 ± 2670
Co	2.49 ± 0.51	3.42 ± 0.13	50.2 ± 2.9
Sb	BDL	BDL	13.7 ± 0.9
Cs	1.14 ± 0.39	25.3 ± 1.4	14.2 ± 3.7
Eu	0.55 ± 0.13	1.0 ± 0.1	0.7 ± 0.1
Hf	25.5 ± 1.7	64.5 ± 2.9	117 ± 9
Th	20.8 ± 0.5	34.1 ± 1.8	48.9 ± 5.7

BDL = Below Detection Limit

Table 4. Concentration summary for the elements determined in the industrial effluents in µg/g

Element	Leather Industries		Textile Industries		Petrochemical Industry	Background Soil
	Average	Standard Deviation	Average	Standard Deviation		
Ca	26361	23225	70927.5	89057	BDL	2596
Dy	5.2	2.9	1.8	1.4	56	5.6
Na	4813	4224	3918	3906	3703	1321
Cr	41151	30033	62.7	49.5	136	79.1
Co	11.3	19.1	239	336	44.7	19.6
Sb	5.2	7.4	0.6	---	BDL	0.6
Cs	8.8	10.8	3.5	---	BDL	3
Eu	0.7	0.2	1.6	---	7.19	1.4
Hf	57.8	38	8.8	11.2	BDL	21.6
Th	33.8	13.4	5.8	6.5	7.23	10.1

BDL = Below Detection Limit

CONCLUSION

The study revealed some of the metals had high elevated concentration which could be attributed to the industrial activities. The highest levels are Cr > Ca > Sb > Na > Th > Cs > Hf in the leather processing effluents (tanneries) and Ca > Co > Na in the textile industries. The most distinct being Cr from the tanneries. The data shows it is an outlier and this high concentration or BLF of chromium observed could be explained as due to the chemical processing stage of leather products involving tanning with chrome. The petrochemical industries' effluents have the least BLF with highest elevated concentration of Dy, Eu, Na and Co respectively. Some of the elements such as Na, Ca and Cr also vary over a wide range by as much as an order of magnitude.

On the other hand, it is believed that the industrial processes also led to reduction in concentration of some of the elements such as Dy with Background Loading Factors < 1 in the textile industries. With the exception of the soil, all the samples were collected the same day as they were produced; this precludes leaching or other processes as being responsible for this depressed concentration of the elements with BLF < 1.

There are plans for further studies to include samples from other industries and geographical locations spread across the country after this preliminary investigation.

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