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ENVIRONMENTAL AIR DEGRADATION IN DAR ES SALAAM BY X-RAY FLUORESCENCE

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ABSTRACT

In Dar es Salaam a study of the aerosol contents was conducted and particulate matter on the filters were collected using an Andersen™ PM10 impactor to determine the environmental air pollution. The contents were determined by X-ray fluorescence analysis. In this study sources of environmental degradation and the concentrations were named as follows: Combustion processes with range of Br from 10 to 800 ng/m^3, Pb from 30 to 790 ng/m^3. Industrial processes with range of Fe from 37 to 883 ng/m^3, Cu from 14 to 310 ng/m^3, Zn from 6 to 820 ng/m^3. Top soil activities with range of K from 20 to 540 ng/m^3, Ca from 24 to 3805 ng/m^3, Ti from 2 to 59 ng/m^3, Mn from 10 to 386 ng/m^3. Marine processes with range of Cl from 20 to 310 ng/m^3, S from 72 to 134 ng/m^3.

Key Words: Environment; Aerosol; X-ray fluorescence; Impactor

INTRODUCTION

Environmental degradation is a wide subject, which involves all the factors that contribute to the change of the environment from its clean living to pollute disastrous conditions.

The environmental pollution may be a result of natural processes like soil erosion, change of weather, effects of earthquakes, marine activities, etc.

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It may as well be a result of anthropogenic activities such as industrial development, that produce unwanted particles in the air, unwanted chemicals to the rivers, ocean and streams. Human activities like overpopulation, overgrazing may also be causes of environmental degradation.

Agricultural activities like tilling of soil followed by planting trees and crops during the rainy season help to control pollution resulting from erosion. However, when these activities are conducted in the wrong times and in the wrong areas they amount to sources of pollution. Leaded gasoline is the source of elements such as Br and Pb which are known to be introduce to the atmosphere in large quantities of these elements through exhaust. In order to control pollution there is a need to identify the sources. It is also important to quantify the levels of pollution, which are produced by these sources, then design the ways and means to control pollution. In developed countries where pollution is dominated by man-made sources, a number of monitoring facilities is used. These are concurrently evaluating the pollution levels. This means many of the industries have small laboratories or are attached to laboratories, which give advice on the levels of pollution at every particular interval of time. By doing so, the production process of the industry may be expanded or reduced depending on the environmental impact they cause.

Many of the laboratories making pollution assessment are mainly concerned on analyzing samples like water, air, contaminated food, hair from affected humans, affected living organism etc. In such laboratories these work may be done as consultancy work for particular incidents. This is however, a temporary solution to environmental monitoring research since a need to know the rate at which the polluting source is increasing or diminishing. Also critical points may be spotted immediately as they occur.

The problems that faces the monitoring activities includes, lack of expertise in the subject, lack of equipment, lack of cooperation between scientists and the administrators, lack of knowledge on the subject even when the facilities and expertise are present.

The aim of this presentation is to highlight on the X-ray fluorescence method in analyzing air, water and solid samples with emphasis on aerosol collection methodologies. Some results of samples collected at Tanzania oxygen limited (TOL) Dar es Salaam will be presented.

MATERIALS AND METHODS

X-Ray Fluorescence Analysis System in Dar es Salaam

The EDXRF system comprising of X-ray tube, Si(Li) detector and associated electronics appears as shown in the block diagram in Figure 1 was used in the analysis of this work in Dar es Salaam.

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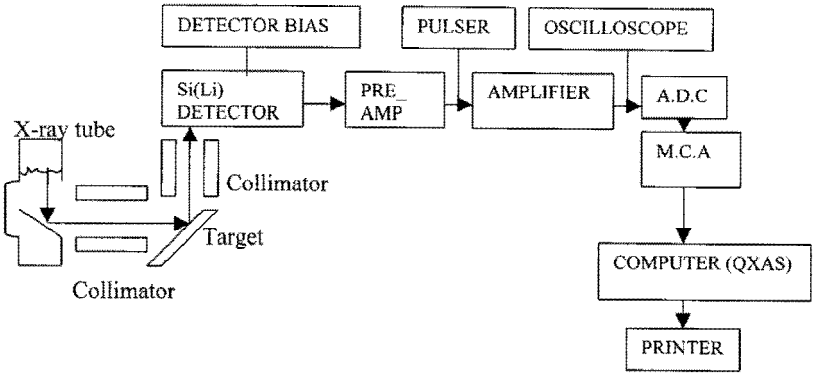


Figure 1. Block diagram of X-ray fluorescence spectrometer.

The X-ray tube provides polychromatic radiation exciting the secondary target. The secondary target of metallic Mo provides a monochromatic Mo line 17.4 KeV radiation exciting the sample. The sample placed on a holder which was newly designed to have both vertical and horizontal movement whereby the radiation from strikes the sample at 45° from which characteristic X-rays are directed towards the detector. The Si(Li) detector was modified to fit in a vertical orientation position with pre amplifier, amplifier, ADC, MCA-S100 card and a computer analyzing facility with QXAS software (1,2) are used for measurements. Out of this facility a quantitative and qualitative evaluation of samples is possible for air, water or solid materials (3–6). The relation used to calculate sensitivity (1) is

$$I_j = K_j m_j C_j$$

where

$$K_j = I_o G \csc\phi_1 \tau_j (1 - 1/j_{kj}) w_{kj} f_{\alpha j} A_b \varepsilon(E_j)$$
$$m_j = \rho_i d$$
$$C_j = \{1 - \exp(-a\rho d)\}/a\rho d$$

K_j values can be obtained using the physical constants μ_1, μ_2; τ_i, J_K, w_K, and f available in the literature or can be obtained from experiments when standard samples of known concentration are used; m_j is the mass concentration of the element j; C_j is the absorption correction factor for element j, which may also be calculated when the thickness of the sample is known and the coefficients obtained from tables. In order to calculate C_j correctly, the concentrations have to be known; ρ is the density (g/cm^3) of the sample; ρ_j is the density of element j within the sample; τ_j is the photoelectric mass absorption coefficient for element j for the primary radiation; J_k is the ratio between the photoelectric mass absorption coefficients at the top and

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the bottom of the K absorption edge; $\{1-1/j_k\}$ is the function of photoelectric events, which occur in the K-shell; w_{kj} is the fluorescence yield for the X-rays from element j; $f_{\alpha j}$ is the fraction of the K_α X-rays of energy E_j with respect to the K X-rays emitted; A_b is the absorption for the air path, if present, plus the absorption of the detector window, both of which can be calculated; $\varepsilon(E_j)$ is the detector efficiency for X-ray of energy E_j. When $a\rho d \ll 1$; $e^{-a\rho d} \approx 1 - a\rho d$ (by Taylor expansion); The relation reduces to $I_j = K_j m_j$ (for infinitely thin sample criterion); The sensitivities K_j of the element j is calculated in the calibration as $K_j = I_j/(m_j C_j)$ where $I_j C_j$ are obtained from irradiation of Standard material.

Sampling Equipment

The filters used were 37 mm diameter and 0.8 μm pore size enclosed in a disc with possibility of being weighed in microbalance. The sampling period could be varied between 1 h and more than 24 h. The sampling was set at 24 h collection time. However in several cases electricity was interrupted, the time-keeping function was stopped and extended to compensate for the lost time later.

The sampling module of the equipment was used interconnected by tube, 15 m long. This allowed flexibility of the two separate modules is placed on the point of monitoring, or the sampling module placed at the monitoring point with control module is inside close to the power supply. Alternatively, they can operate side by side with sampling module. The sampling module weighs 20.5 kg; the control module weighs 25 kg and are both portable to allow easy movement during sampling. In the sacking mechanism of the air through the filters, the aerosols were deposited on the filters. The aerosol enters the inlet at a height of 1.2 m and is sampled at a flow rate of 1 cm/h or 16.7 l/m. Adjustments were made such that 0.9 m^3/h go via the 2.5 μm size filter and 0.1 m^3/h via the coarse determined by the top wire mesh. The aerosol inlet has a particle size cut-point of 15 microns (Figure 2).

In PM 10^{TM} Sierra medium flow air sampler (7,8), suspended particles enter the medium flow 15 l/m inlet at a flow rate of 1 m^3/h. The particles are then accelerated through multiple impactor nozzles. By virtue of their momentum, particles greater than 2.5 μm cut-point impact out and are retained in the impaction chamber. The particle fraction smaller than 2.5 μm is carried vertically upward by the airflow and down the vent tube to 37 mm diameter Teflon filter where it is uniformly collected.

Cleaning Procedure in XRF

The sample preparation begins with the cleaning procedure to ensure that there is no contamination. This involved application of soap with soft

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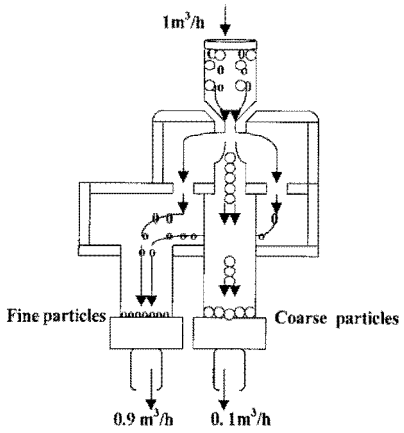


Figure 2. Design and operation of the dichotomous impactor.

tissue to rub the preparation surfaces. This is followed by rinsing with double distilled water and then transferred to a clean beaker. The 10% volume of the high quality nitric acid is added into this and then boiled for 15 min. The tools are then transferred to a clean beaker with double distilled water using Teflon™ pincers. Then the sample is weighed in a clean balance. The digestion of the sample when necessary is conducted in a clean vessel. Internal standard is added to the sample. A clean blank and sample are prepared and their spectra obtained. QXAS is used for evaluation of spectra and the correct results are obtained by subtracting the blank results (9).

RESULTS AND DISCUSSION

The results presented here are for total particulate matter and elemental concentration for Tanzania oxygen limited (TOL) station in Dar es Salaam over the period of three months. The gravimetric measurement of the total suspended particulate matter are shown in Figure 3 for the month of August 1996 with an average of $400 \pm 2.443\,\mu g$ for fine and $491.067 \pm 14.135\,\mu g$ for coarse particles.

The relationship between the coarse and the fine particles is shown in Figure 4 with the equation $y = 1.12x + 42$ and a good correlation between them with coefficient of $r^2 = 0.925$.

The particles may be from different sources caused daily variations of amounts collected in the sample. Wind speed has been changing from 150 to 300° which could be a contributing factor to the rise of particulate matter between the 20th and 30th days of the month of August. The change in the wind direction between 100 and 200° may have contributed to the

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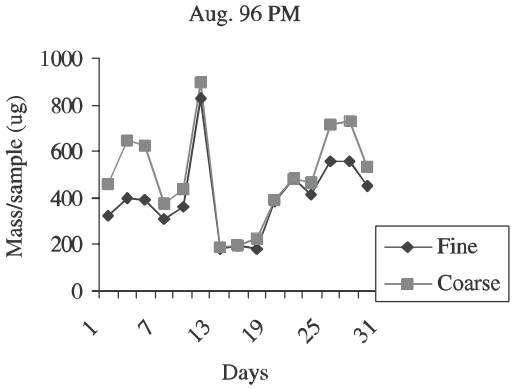


Figure 3. Total particulate matter (μg) for the month of August 1996.

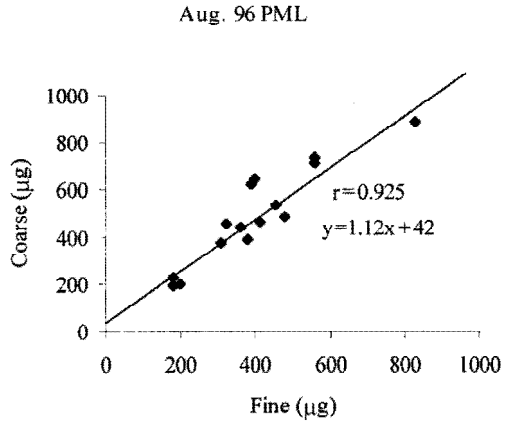


Figure 4. Relationship between coarse and fine particulate matter (μg) for the month of August 1996.

fluctuations of the fine and coarse total suspended particulate matter between the 15th and 20th day. In these two days the monthly wind speed has been rising to the maximum values of 10 and 15 m/s (Figures 5 and 6). This is a dry season while its counterpart-wet season of May 1997 has wind direction changing between 0–250° starting from North and speed raising from 0 to 15 m/s.

The average particulate matter for the month of May 1997 was 218 μg for fine and 267 μg for coarse (Figure 7). The equation relating the coarse and the fine particles is given by $y=0.8x+0.007$ with correlation coefficient of $r=0.9$ (Figure 8). The total particulate matter in the dry season of August 1996 is about twice that of the wet rainy season of May 1997 (Figure 8).

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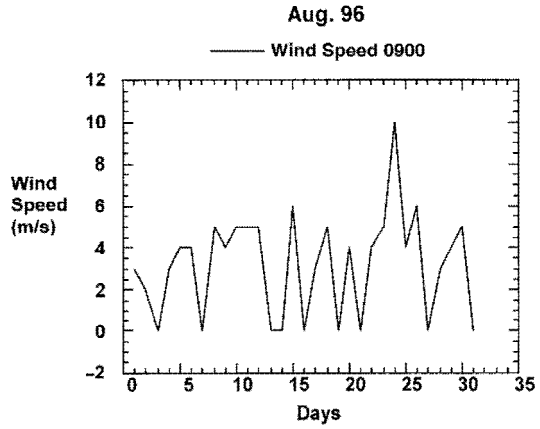


Figure 5. The daily wind speed for the month of August 1996, 900 h.

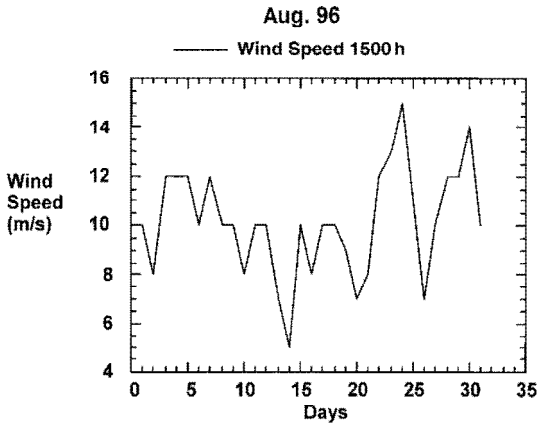


Figure 6. The daily wind speed for the month of August 1996, 1500 h.

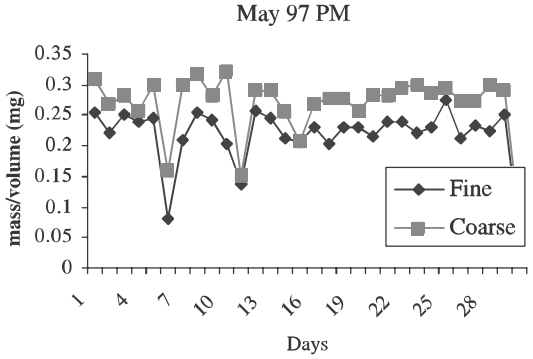


Figure 7. The total particulate matter for the month of May 1997.

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The February total particulate matter starts from a high value of just below 1 mg and drops drastically to below 0.1 mg for the first seven days as in Figure 9. The variation is increasingly fluctuating between 0.1 and 1 mg from 10th to the end of the month of February. The mean value of total particulate matter for May 1997 was 230 μg for fine and 293 μg for coarse particles. The correlation between the two has coefficient $r = 0.90$ and with the linear equation $y = 0.69x + 0.057$ (Figure 10).

The particulate monthly variations could be due to changes in wind speed and wind direction from different polluting sources. The variations may be contributed to the monthly wind direction sharp rise and drops for February 1997 (Figures 11 and 12). A similar phenomenon was also observed by threshold wind speed values by Oblad and Selin 1986 (11), El-Shobokshy et al., 1990 (12) where he comments on the wind speed necessary to pick up the soil particles. The same explanation could also be applicable for the total particulate matter of May 1997 (Figure 13).

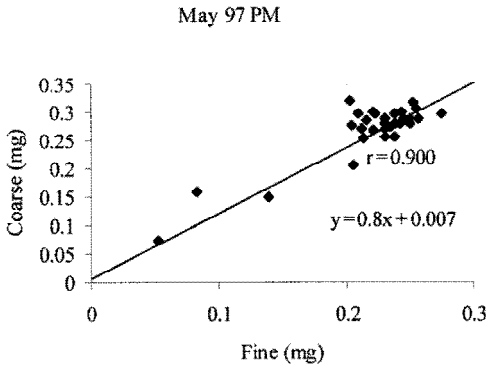


Figure 8. Relationship between coarse and fine particulate matter (μg) for the month of May 1997.

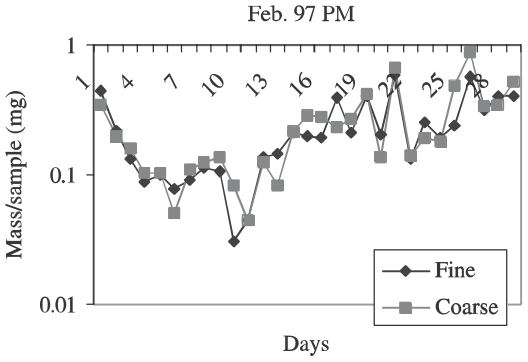


Figure 9. Total particulate matter (mg) for the month of February 1997.

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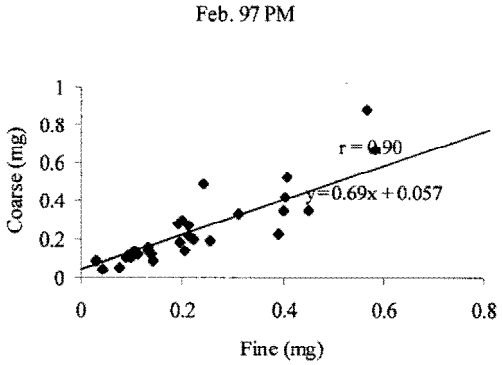


Figure 10. Relationship between coarse and fine particulate matter (mg) for the month of February 1997.

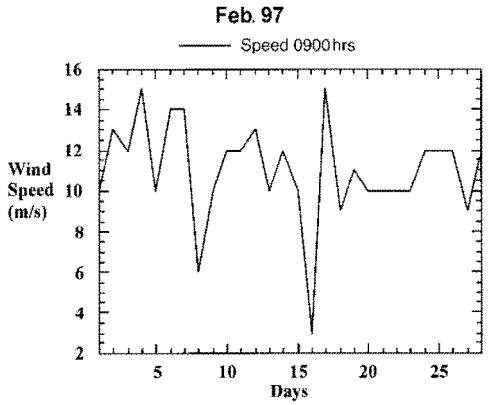


Figure 11. The daily wind speed for the month of February 1997, 0900 h.

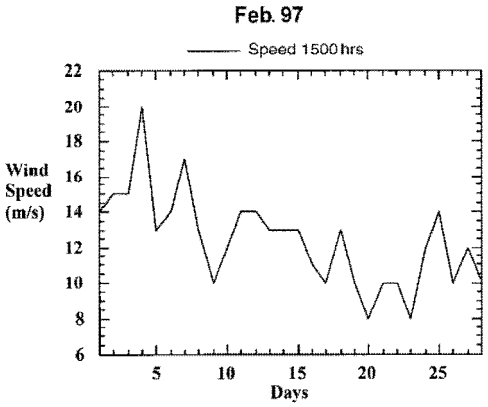


Figure 12. The daily wind speed for the month of February 1997, 1500 h.

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For the same station Table 1 provides the summary of the range of concentration of elements in aerosol (ng/m^3) for the collection months of August 1996, February 1997 and May 1997. The grouping of the elements is that originating from combustion such as Pb and Br (Alves et al., 1998 (13); Bouland et al., 1978 (14); Sturges et al., 1985 (15); Lannerfors and Hansson 1981 (16); Nriagu 1990 (17); Oblad and Selin 1986 (11)), industrial such as Mn, Fe, Cu and Zn (Parekh 1990) (18), top soil such as K, Ca, Ti and Mn (Alves et al., 1998) (13), Maenhaut and Akilimali 1987 (19) and marine

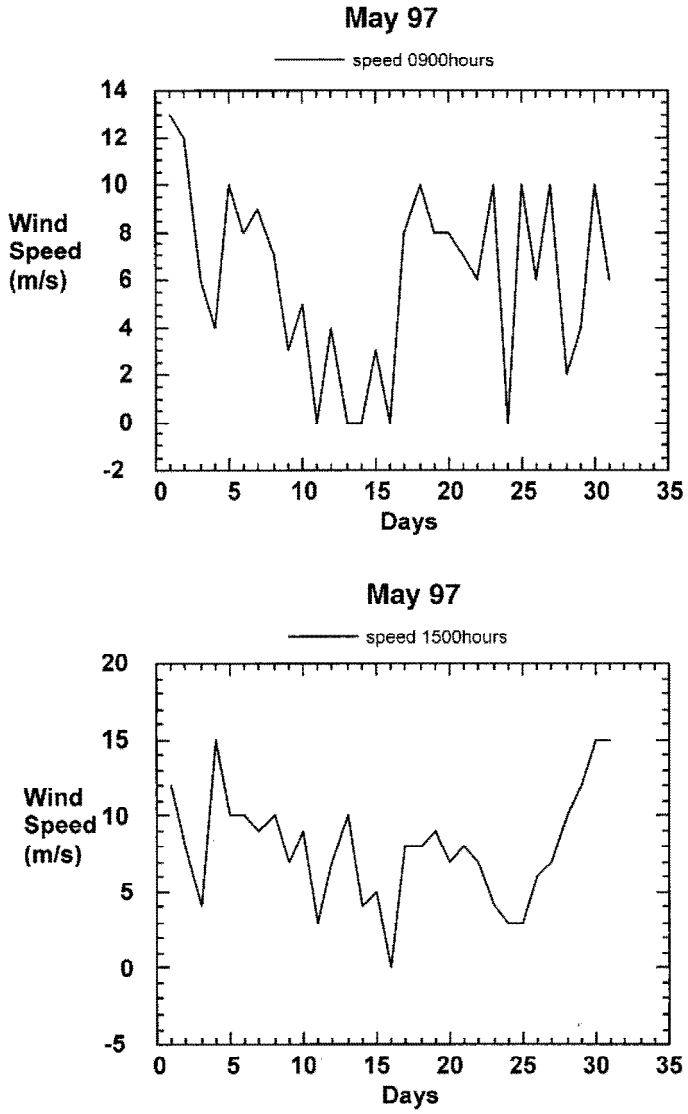


Figure 13. The daily wind speed for the month of May 1997.

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Table 1. The Range of Concentration of Elements for August, February, and May 1997 (TOL) (ng/m^3)

TOL	Fine/Coarse Range	August Range	Feb Range	May Range
Combustion	Br Fine	13–32	13–43	7–100
	Br Coarse	10–42	13–42	6–800
	Pb Fine	37–94	34–194	18–790
	Pb Coarse	30–105	22–974	27–340
Industrial	Fe Fine	37–499	238–827	3–488
	Fe Coarse	37–703	244–883	3–322
	Cu Fine	14–163	70–214	30–298
	Cu Coarse	14–134	74–218	80–310
	Zn Fine	6–166	30–236	20–820
	Zn Coarse	6–139	32–236	10–410
Top soil	K Fine	63–260	52–193	160–368
	K Coarse	50–540	55–322	20–379
	Ca Fine	24–521	106–423	30–140
	Ca Coarse	24–3805	487–546	250–187
	Ti Fine	2–21	8–56	—
	Ti Coarse	2–37	9–59	—
	Mn Fine	23–259	153–305	10–180
	Mn Coarse	23–386	143–312	10–260
Marine	Cl Fine	—	—	20–221
	Cl Coarse	—	—	61–310
	S Fine	—	—	95–134
	S Coarse	—	—	72–107
Other sources	Sr Fine	2–15	7–29	—
	Sr Coarse	2–16	6–32	—
	Zr Fine	1–17	5–22	—
	Zr Coarse	1–26	5–20	—
	Nb Fine	2–7	—	—
	Nb coarse	1–6	—	—
	Se Fine	5–13	8–15	—
	Se Coarse	5–11	8–14	—

activities such as Cl and S (Alves et al., 1998 (13); Frieslander 1973 (20); Alpert and Hopke 1980 (21); Steen et al., 1984 (22)). However, the grouping may overlap having one element belonging to more than one origin. Morales et al., 1990 (23); Weisel et al., 1984 (24) reported on element in marine aerosols for which the ocean is the primary source of atmospheric Na, K and Mg for seacoast areas. There are other cases in non-industrial areas where Fe and Mn are associated with natural composition of soil origin which are introduced to the atmosphere by soil erosion (Parekh and Hussain 1981 (25); Viskina et al., 1999 (26)). The typical aerosol spectra are shown in Figures 14a–b.

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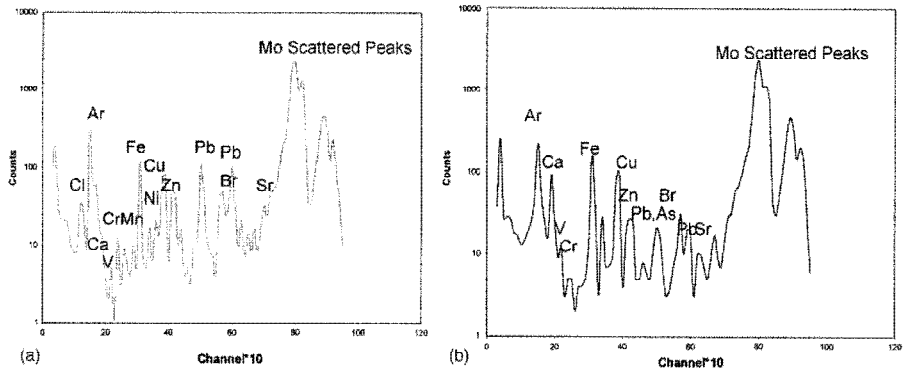


Figure 14. (a) Typical fine aerosol sample spectrum and (b) typical coarse aerosol sample spectrum.

CONCLUSION

The results have shown the significance of environmental monitoring research. The typical natural and artificial sources of pollution have been sighted. Among a number of techniques used for quantification X-ray fluorescence analysis has been explained to be suitable for air, water and solid samples. For the air sampling purposes the aerosol impactor system were explained with typical results of aerosol collected along Nyerere road. The results are grouped in terms of the probable source. Br and Pb resulting from combustion process, Fe, Cu and Zn from industrial activities, K, Ca, Ti and Mn from soil, Cl and S from marine activities, Sr, Zr, Nb and Se from other sources yet to be established. Some of the elements are sometimes from more than one source.

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