



Elemental characterization of $PM_{10-2.5}$ and $PM_{2.5}$ in aerosols collected in town Antsirabe by TXRF

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Abstract: This work was carried out at the laboratory Techniques of X-ray Fluorescence and Environment, INSTN-Madagascar. The aim of this study is to determine the elemental composition of $PM_{2.5}$ and $PM_{10-2.5}$ in the aerosols collected in town Antsirabe and to determine their sources. The aerosols samples were collected at seven sites: Miaramasoandro, Ambohimena, STAR, COTONA-SACIMEN, Tsenan'Asabotsy, Hopital-Andranomafana and Ambavahady Mangatsiaka located in town Antsirabe. GENT sampler stacked filter unit (SFU) was used during the sampling campaign. This air sampler is suitable to collect the aerosols samples in two fractions: coarse particles noted $PM_{10-2.5}$ and fine particles called $PM_{2.5}$. Total reflection X-ray Fluorescence (TXRF) was used for quantification of the elements presents in the aerosols samples. Before the analysis, all filters must be mineralized with acid digestion bomb in closed system. Then, the obtained solution was prepared and analyzed directly with TXRF spectrometer with molybdenum (Mo) anode. The results showed that the elements such as K, Ca, Ti, Cr, Mn, Fe, Ni, Zn, Se, Br, Rb, Sr and Pb were analyzed in the aerosols samples at seven sites. The calculation of the enrichment factor (EF) based on Mason's method showed that the elements such as Zn, Br and Pb are from anthropogenic sources and K, Ca, Cr, Mn, Fe, Ni and Sr are from natural sources.

Keywords: Total Reflection X-ray Fluorescence, air pollution, enrichment factor, $PM_{2.5}$, $PM_{10-2.5}$

I. Introduction

Antsirabe is one of the largest cities in Madagascar and it is classified as an industrialized areas. Antsirabe is belong to Vakinankaratra region and his population is about 238 478 in 2013. It is situated at an altitude about 1500m. During the winter season, the temperature could be down around 0°C at night. In term of air pollution research in Madagascar, this work was the first study related in aerosols particularly in $PM_{10-2.5}$ and $PM_{2.5}$ in town Antsirabe. Air pollution studies are one of great concern in many countries due to its significant negative impact as well as in human health than in the environment. In addition, the knowledge of the properties of aerosols such as size distribution, chemical or elemental compositions and source apportionment are important for the management of air pollution. In term of elemental composition, numerous techniques can be used such as Inductive Coupled Plasma-Mass Spectrometry (ICP-MS) and Inductive Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Norhayati Mohd Tahir et al., 2013), Particle Induced X-Ray Emission (PIXE) (Mkoma S. L. et al., 2010), Total Reflection X-ray Fluorescence (TXRF) (I. Durukan et al., 2013), neutron activation analysis (NAA) (YANG Shao-jin et al., 2000).

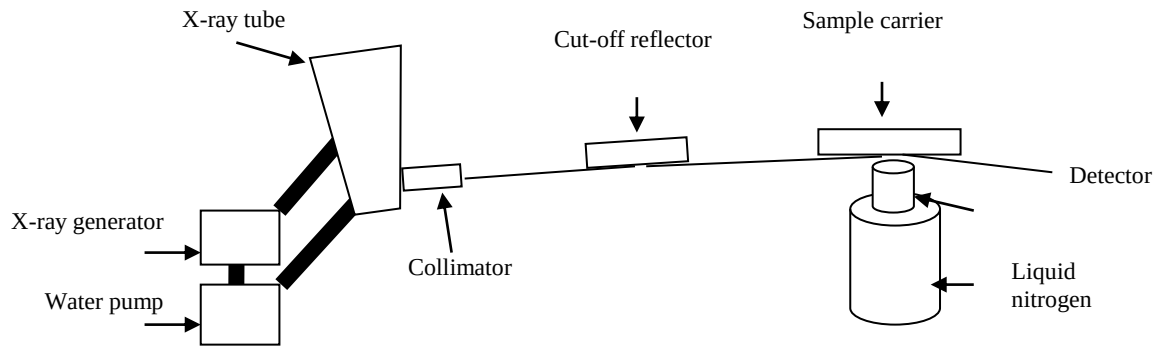
In our case, Total reflection X-ray Fluorescence (TXRF) was used for the elemental analysis in the collected aerosols samples taken at the areas study.

The aim of this study was to determine the elemental composition both in $PM_{2.5}$ and $PM_{10-2.5}$ in the aerosols collected in town Antsirabe and to determine their sources using the method developed by Mason.

II. Analytical methods

Total Reflection X-ray Fluorescence (TXRF) was used for the analysis of aerosol samples. It was composed by X-ray generator, X-ray tube with molybdenum (Mo) anode, water pump for cooling the system, Si(Li) detector, pre-amplifier produced by CANBERRA, inspector and a computer containing both AXIL and QXAS program. Figure 1 illustrated the general setup of TXRF spectrometry.

Figure 1. General setup of TXRF spectrometer



II.1. Calibration and quality control

II.1.1. Experimental conditions

The following experimental conditions were applied:

- Power of the X-ray generator: 45Kv
- Current of the X-ray generator: 12mA
- X-ray tube with molybdenum (Mo) anode

II.1.2. Calibration

The calibration of the Total Reflection X-ray Fluorescence is based on the determination of the sensitivity of the element j . Then, knowing this sensitivity, the determination of the concentration for element j in unknown sample is possible. The intensity of element j in the sample is given by the following relation:

$$I_j = G_0 K_j C_j$$

where

G_0 : geometrical factor

K_j : relative efficiency excitation-detection for j element

C_j : Concentration of j element

In TXRF technique, the quantitative analysis is based on the use of internal standard. In fact, the calibration of system must be the same. The equation before is also valid for the intensity of the internal standard. So, the expression becomes

$$I_{IS} = G_0 K_{IS} C_{IS}$$

where

the subscript "IS" designed Internal Standard

The ratio of the two equations gives the next equation

$$C_j = \frac{I_j}{I_{IS}} \frac{1}{S_j} C_{IS}$$

with

$$S_j = \frac{K_j}{K_{IS}}$$

S_j : relative sensitivity of j element compared to internal standard

Finally,

$$S_j = \frac{I_j}{I_{IS}} \frac{C_{IS}}{C_j}$$

To perform the calibration of the spectrometer, five (05) standard solutions were prepared from standard produced by Merck product. Each standard contained K, Ca, Ti, Mn, Zn, Br and Sr for K-lines and contained Ba, Yb, W, Pb, and U for L-lines. Then, 5 μ L of cobalt (1000ppm) was used as internal standard for each 995 μ L

of prepared solution. Table 1 and 2 give the details of the standard to be used for the calibration for K-lines and L-lines respectively.

Element	Concentration in ng.mL ⁻¹				
	Std-K1	Std-K2	Std-K3	Std-K4	Std-K5
K	1000	2000	3000	4000	5000
Ca	1000	2000	3000	4000	5000
Ti	100	250	500	750	1000
Mn	10	30	50	80	100
Zn	100	250	500	750	1000
Br	50	100	250	350	500
Sr	10	30	50	80	100

Table 1. Standard solution for K-lines

Element	Concentration in ng.mL ⁻¹				
	Std-L1	Std-L2	Std-L3	Std-L4	Std-L5
Ba	1000	2000	3000	4000	5000
Yb	1000	2000	3000	4000	5000
W	100	250	500	750	1000
Pb	10	30	50	80	100
U	100	250	500	750	1000

Table 2. Standard solution for L-lines

II.1.3. Quality control

To check the accuracy and precision of the method, the control of the analytical method must be done. Multi elements synthetic standard were prepared from analytical grade reagents. Three aliquots independent of 5μL are taken from the prepared solution standard using micro pipette and are deposited on quartz carrier with respect of the sample preparation applied during the calibration. Then, they are measured three times and the average concentrations are reported on table 3.

Elements	Unit	Synthetic standard solution	INSTN-Madagascar results	Percent difference (%)
K	ng.mL ⁻¹	3500	3488 ± 125*	0.34
Ca	ng.mL ⁻¹	3500	3491 ± 107	0.25
Ti	ng.mL ⁻¹	400	406 ± 52	1.50
Mn	ng.mL ⁻¹	50	49 ± 5	2.00
Ni	ng.mL ⁻¹	50	50 ± 6	0.00
Cu	ng.mL ⁻¹	100	98 ± 4	2.00
Zn	ng.mL ⁻¹	600	596 ± 53	0.66
Se	ng.mL ⁻¹	200	205 ± 17	2.50
Br	ng.mL ⁻¹	300	303 ± 20	1.00
Sr	ng.mL ⁻¹	50	49 ± 5	2.00
Ba	ng.mL ⁻¹	200	192 ± 16	4.00
Yb	ng.mL ⁻¹	200	205 ± 17	2.50
W	ng.mL ⁻¹	200	201 ± 18	0.50
Pb	ng.mL ⁻¹	200	201 ± 19	0.50

Table 3 : Comparison of synthetic standard and measured values at INSTN-Madagascar

*: standard deviation

The results showed that the experimental and the theoretical values are with good agreement. The calculated percent differences are smaller than five (05) percent. In fact, we can conclude that the calibration of the TXRF spectrometer is suitable for the analysis of the aerosols sample.

II.2. Detection limit

The detection limit was calculated using the following relation:

$$(C_{LMD})_j = 3C_j \frac{\sqrt{(N_B)_j}}{N_j}$$

where

C_j : Concentration of the interest element in the standard

$(C_{LMD})_j$: Concentration of the limit detection

The values of the minimal concentration to be analyzed both for K-lines and L-lines were reported in the table 4

Element	K	Ca	Ti	Cr	Mn	Fe	Ni	Zn	Se	Br	Rb	Sr	Pb
Detection limit in ng.mL ⁻¹	20	17	13	10	9	8.5	7	6.5	6.7	6	5.92	5.86	5

Table 4. Detection limit for some elements

II.3. Sampling and sample preparation

II.3.1 Sampling

The selection of sampling site was based on the following criteria: frequented areas by the population such as town, market place, terminal of transportation, school, residential zone, high traffic road, industrial areas, zone having a potential air pollution sources like tunnel, rural areas. GENT sampler stacked filter unit (SFU) was used during sampling campaign (Maenhaut *et al.*, 1993). It was placed at 1.60 meters above the ground. This sampler is suitable to separate the aerosols samples in two fractions: coarse fraction noted PM_{10-2.5} (particles with aerodynamic diameters between 10µm and 2.5µm) and fine fraction called PM_{2.5} (particles with aerodynamic diameters less than 2.5µm). Nuclepore Polycarbonate membrane filters with diameter 47mm and pore size 8µm and 0.4µm were used to collect the coarse and fine particles aerosols, respectively. Filters are weighed before and after sampling using a precision balance Mettler Toledo with sensitivity 10µg for determination of the aerosol mass deposited on each filter. Aerosols samples were taken at seven sites and the duration of the sampling varied from eight (08) to nine (09) hours. Table 5 gives the details information during sampling campaign.

Site Code	Name of site	Geographic position	Starting time of sampling	End of sampling	Total air volume (m ³)
Site 1	Miaramasoandro	L=47°02'11" l=19°50'15"	09h05	17h00	6
Site 2	Ambohimena	L=47°02'28" l=19°53'27"	08h25	17h00	7
Site 3	STAR	L=47°00'55" l=19°51'44"	08h55	16h40	6
Site 4	COTONA-SACIMEN	L=47°02'29" l=19°52'54"	08h45	16h45	6
Site 5	Tsenan' Asabotsy	L=47°01'36" l=19°52'05"	08h35	17h00	6
Site 6	Hopital-Andranomafana	L=47°01'51" l=19°52'01"	08h30	17h00	7
Site 7	Ambavahady Mangatsiaka	L=47°02'08" l=19°52'34"	08h20	16h30	7

Table 5. Information during sampling campaign

II.3.2. Sample preparation

Aerosols samples must be transformed into liquid sample before to be analyzed with Total Reflection X-ray Fluorescence spectrometry (TXRF). Then, aerosols samples were mineralized in closed system using acid digestion bomb with the mixture of 600µL of CHCl₃, 3mL of HNO₃ (63%) and 1mL of H₂O₂ (30%) under temperature 165°C during four (04) hours (Marina Dargie *et al.*, 1996). Then, 995µL of prepared solution were taken and added 5µL of standard solution of cobalt (1000ppm) as internal standard. After, aliquots of 5µL were taken and were placed onto quartz carrier with micro pipette, dried in desiccators and measured directly by the TXRF spectrometer.

III. Analysis, results and discussion

The experimental conditions used during the calibration of the spectrometer must be applied during the analysis of the aerosols samples. The aerosols samples obtained after sample preparation are analyzed directly with TXRF spectrometer. The average concentrations of the analyzed elements in the aerosols from each sampling site are reported in table 6, table 7 and table 8.

Elements	Concentration in ng.m ⁻³								
	Site 1: Miaramasoandro			Site 2: Ambohimena			Site 3: STAR		
	PM _{10-2.5}	PM _{2.5}	PM ₁₀	PM _{10-2.5}	PM _{2.5}	PM ₁₀	PM _{10-2.5}	PM _{2.5}	PM ₁₀
K	339±84	505±54	844±138	318±78	375±62	693±140	483±71	439±28	922±39
Ca	3688±37	4375±43	8063±80	3054±31	3884±26	6938±57	4367±52	3714±21	8081±73
Ti	46±7	84±8	130±15	52±10	279±9	331±19	510±11	89±8	599±19
Cr	11±2	18±2	29±4	15±2	13±2	28±4	25±2	18±3	43±5
Mn	6±1	11±2	17±3	7±1	21±2	28±3	30±14	8±1	38±15
Fe	369±4	654±6	1023±10	357±5	775±10	1132±15	486±14	661±12	1147±26
Ni	15±2	18±3	33±5	15±2	47±3	62±5	22±5	19±2	41±7
Zn	82±3	98±3	180±6	86±2	44±6	130±8	99±4	73±2	172±6
Se	<6.7	<6.7	<6.7	<6.7	<6.7	<6.7	<6.7	<6.7	<6.7

Br	44±3	53±3	97±6	38±2	51±3	89±5	67±3	44±4	111±7
Rb	<5.92	<5.92	<5.92	6±2	<5.92	6±2	<5.92	<5.92	<5.92
Sr	17±3	26±4	43±7	16±2	15±3	31±5	33±4	23±2	56±6
Pb	21±2	25±3	46±5	42±3	60±3	102±6	56±3	51±2	107±5

Table 6. Results of aerosols from Miaramasoandro, Ambohimena and STAR

Elements	Concentration in ng.m ⁻³								
	Site 4: COTONA-SACIMEN-			Site 5: Tsenan'Asabotsy			Site 6: Hopital Andranomafana		
	PM _{10-2.5}	PM _{2.5}	PM ₁₀	PM _{10-2.5}	PM _{2.5}	PM ₁₀	PM _{10-2.5}	PM _{2.5}	PM ₁₀
K	450±74	331±26	781±100	489±97	468±49	957±146	386±86	532±25	918±101
Ca	3907±38	3786±26	7693±64	1784±43	3782±28	5566±71	3925±41	2431±17	6356±58
Ti	122±9	39±6	161±15	136±15	103±9	239±23	306±12	133±7	439±19
Cr	22±3	20±2	42±5	18±2	26±2	44±4	17±2	<10	17±2
Mn	13±2	10±2	23±3	29±5	13±2	42±7	23±2	9±1	32±3
Fe	816±9	426±4	1242±13	947±18	793±7	1740±25	2010±9	837±2	2847±11
Ni	19±2	28±3	47±5	24±5	17±3	41±8	15±3	7±1	22±4
Zn	89±2	76±2	165±4	247±5	196±5	443±10	105±4	49±1	154±5
Se	<6.7	<6.7	<6.7	10±3	<6.7	10±3	8±3	7±2	15±5
Br	47±3	34±2	81±6	67±3	41±3	108±6	49±3	13±2	62±5
Rb	<5.92	<5.92	<5.92	19±4	10±3	29±7	10±3	<5.92	10±3
Sr	<5.86	14±2	14±2	39±3	24±3	63±6	49±3	<5.86	49±3
Pb	44±4	53±3	97±7	110±2	102±3	212±5	58±3	94±3	152±6

Table 7. Results of aerosols from COTONA-SACIMEN, Tsenan'Asabotsy and Hopital Andranomafana

Elements	Concentration in ng.m ⁻³		
	Site 7: COTONA-SACIMEN		
	PM _{10-2.5}	PM _{2.5}	PM ₁₀
K	380±85	402±19	782±104
Ca	3572±43	2677±17	6249±60
Ti	428±8	80±6	508±14
Cr	17±2	12±1	29±3
Mn	28±2	8±2	36±3
Fe	919±10	590±5	1509±15
Ni	12±3	13±2	25±5
Zn	92±2	77±2	169±4
Se	<6.7	5±1	5±1
Br	44±3	33±2	77±5
Rb	15±3	4±1	19±4
Sr	19±3	12±2	31±5
Pb	71±2	67±3	138±4

Table 8. Results of aerosols from Ambavahady Mangatsiaka

The results showed that the average concentration of potassium in the aerosols samples collected in town Antsirabe ranged from 331ng.m⁻³ to 532ng.m⁻³ in fine particles and varied from 318ng.m⁻³ to 489ng.m⁻³ in coarse particles. Figure 1 and 2 illustrated both the variation of the concentration of potassium collected at seven sampling sites in PM_{10-2.5} and PM_{2.5} respectively.

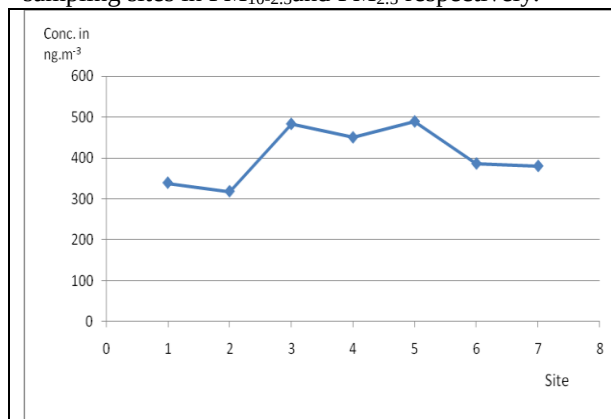


Figure 1. Variation of the average concentration of potassium in PM_{10-2.5} at sampling sites

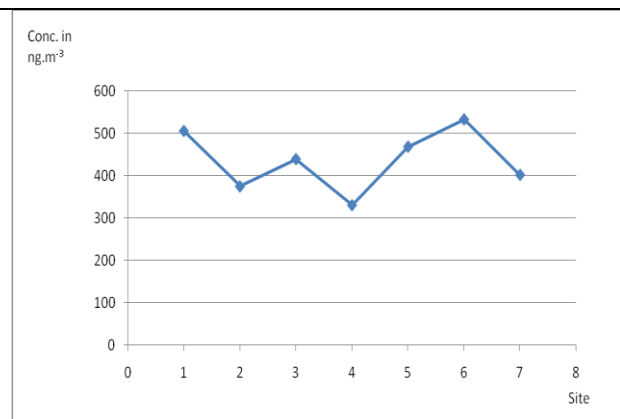


Figure 2. Variation of the average concentration of potassium in PM_{2.5} at sampling sites

The average concentration of calcium in the aerosols samples collected in town Antsirabe ranged from 2431 ng.m^{-3} to 4375 ng.m^{-3} in fine particles and varied from 1784 ng.m^{-3} to 4367 ng.m^{-3} in coarse particles. Figure 3 and 4 showed both the variation of the concentration of calcium collected at seven sampling sites in $\text{PM}_{10-2.5}$ and $\text{PM}_{2.5}$ respectively.

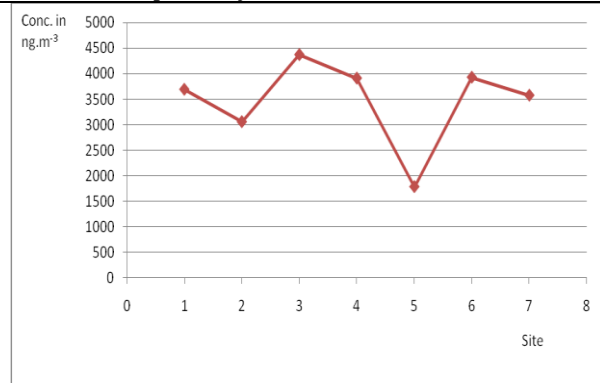


Figure 3. Variation of the average concentration of calcium in $\text{PM}_{10-2.5}$ at sampling sites

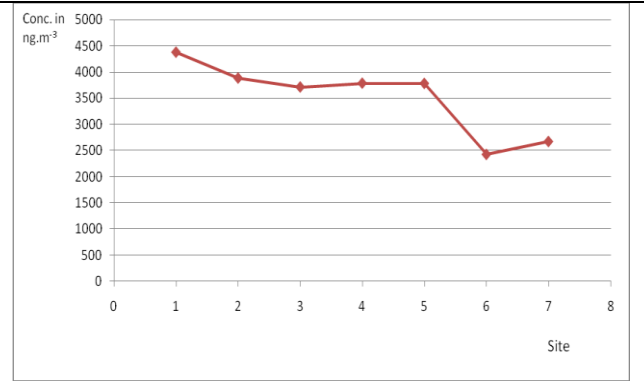


Figure 4. Variation of the average concentration of calcium in $\text{PM}_{2.5}$ at sampling sites

The average concentration of titanium in the aerosols samples taken at town Antsirabe ranged from 39 ng.m^{-3} to 279 ng.m^{-3} in fine particles and varied from 46 ng.m^{-3} to 510 ng.m^{-3} in coarse particles. Figure 5 and 6 showed both the variation of the concentration of titanium at seven sampling sites in $\text{PM}_{10-2.5}$ and $\text{PM}_{2.5}$ respectively

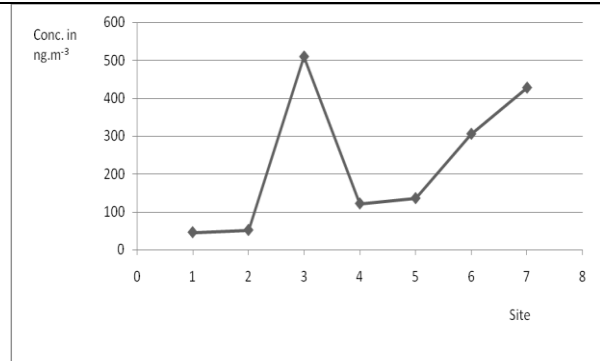


Figure 5. Variation of the average concentration of titanium $\text{PM}_{10-2.5}$ at sampling sites

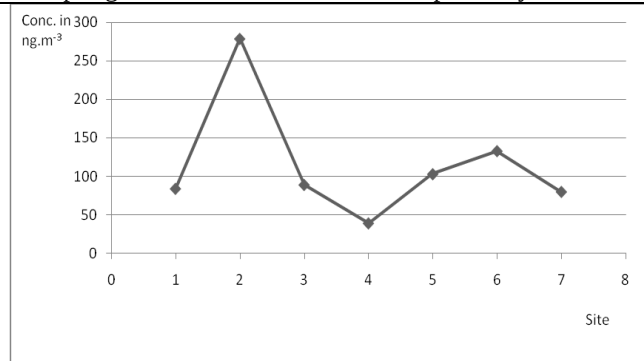


Figure 6. Variation of the average concentration of titanium in $\text{PM}_{2.5}$ at sampling sites

The concentration of chromium in site 6 was less than the detection limit (10 ng.mL^{-1}). For the other sites, the average concentration of chromium in the aerosols collected in town Antsirabe ranged from 12 ng.m^{-3} to 26 ng.m^{-3} in $\text{PM}_{2.5}$ and varied from 11 ng.m^{-3} to 25 ng.m^{-3} in $\text{PM}_{10-2.5}$. Figure 7 and 8 showed both the variation of the concentration of the potassium at seven sampling sites in $\text{PM}_{10-2.5}$ and $\text{PM}_{2.5}$ respectively.

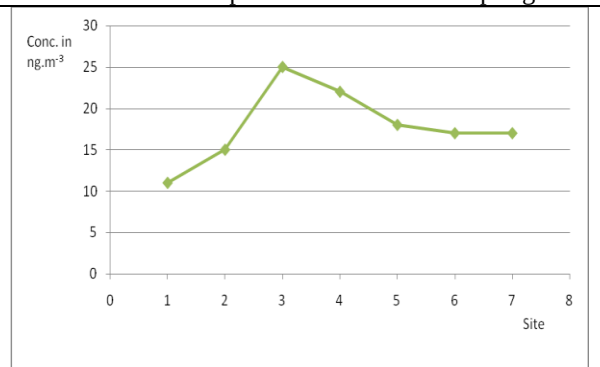


Figure 7. Variation of the average concentration of chromium in $\text{PM}_{10-2.5}$ at sampling sites

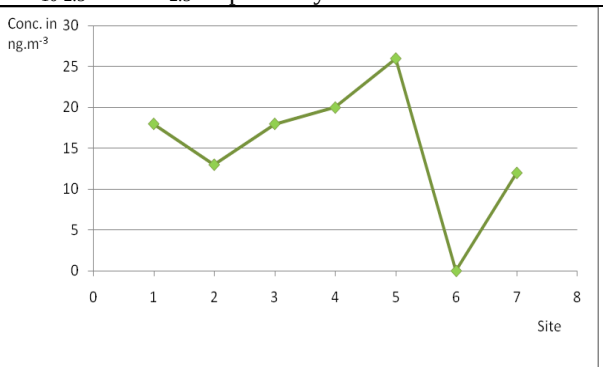


Figure 8. Variation of the average concentration of chromium in $\text{PM}_{2.5}$ at sampling sites

The average concentration of manganese in the aerosols taken at town Antsirabe ranged from 8 ng.m^{-3} to 21 ng.m^{-3} in fine particles and varied from 6 ng.m^{-3} to 30 ng.m^{-3} in coarse particles. Figure 9 and 10 showed both the variation of the concentration of manganese collected at seven sampling sites in $\text{PM}_{10-2.5}$ and $\text{PM}_{2.5}$ respectively.

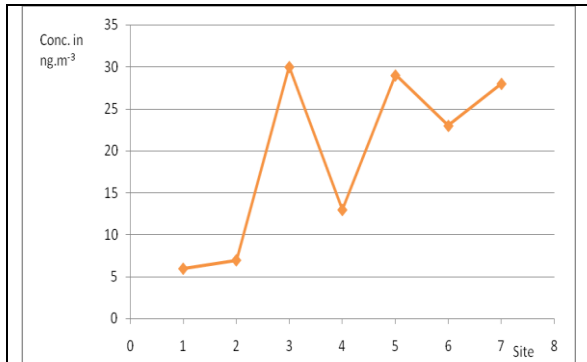


Figure 9. Variation of the average concentration of manganese in PM_{10-2.5} at sampling sites

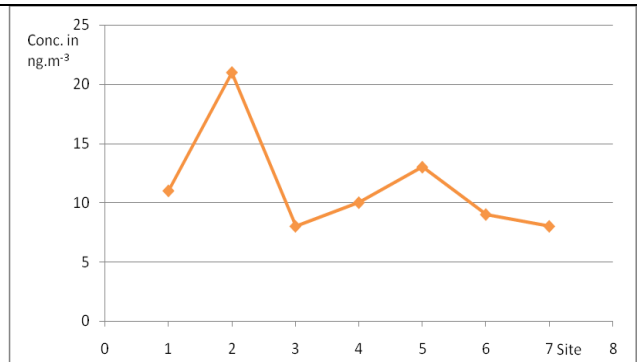


Figure 10. Variation of the average concentration of manganese in PM_{2.5} at sampling sites

The mean concentration of iron in the aerosols taken at town Antsirabe ranged from 426ng.m⁻³ to 837ng.m⁻³ in PM_{2.5} and varied from 357ng.m⁻³ to 2010ng.m⁻³ in PM_{10-2.5}. Figure 11 and 12 showed both the variation of the concentration of the potassium at seven sampling sites in PM_{10-2.5} and PM_{2.5}, respectively.

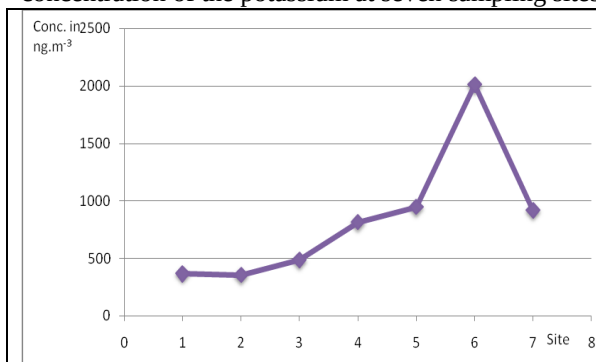


Figure 11. Variation of the average concentration of iron in PM_{10-2.5} at sampling sites

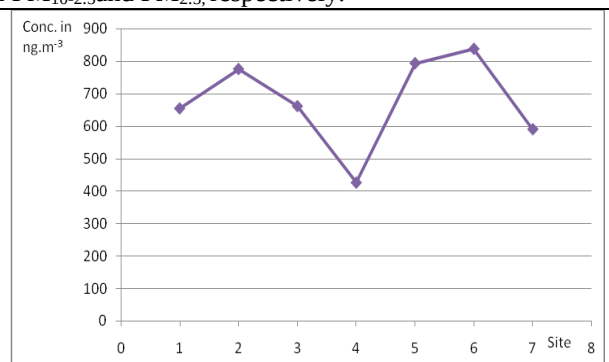


Figure 12. Variation of the average concentration of iron in PM_{2.5} at sampling sites

The average concentration of nickel in the aerosols samples taken at town Antsirabe ranged from 7ng.m⁻³ to 47ng.m⁻³ in fine particles and varied from 12ng.m⁻³ to 24ng.m⁻³ in coarse particles. Figure 3 and showed both the variation of the concentration of nickel collected at seven sampling sites in PM_{10-2.5} and PM_{2.5}, respectively.

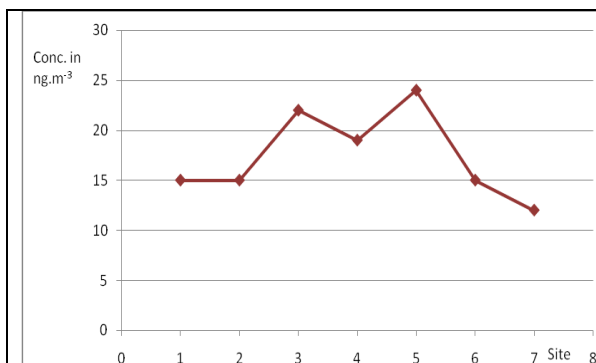


Figure 13. Variation of the average concentration of nickel in PM_{10-2.5} at sampling sites

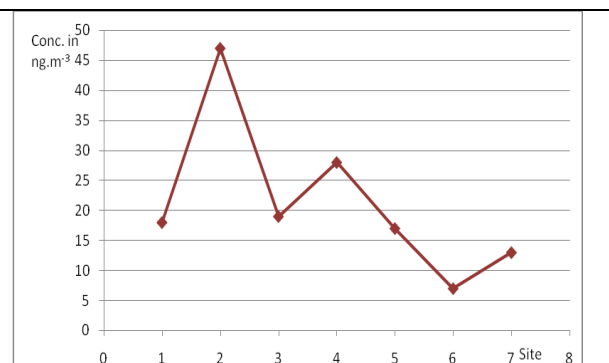


Figure 14. Variation of the average concentration of nickel in PM_{2.5} at sampling sites

The average concentration of zinc in the aerosols samples taken at town Antsirabe ranged from 44ng.m⁻³ to 196ng.m⁻³ in PM_{2.5} and varied from 82ng.m⁻³ to 247ng.m⁻³ in PM_{10-2.5}. Figure 15 and 16 showed both the variation of the concentration of zinc taken at seven sampling sites in PM_{10-2.5} and PM_{2.5}, respectively.

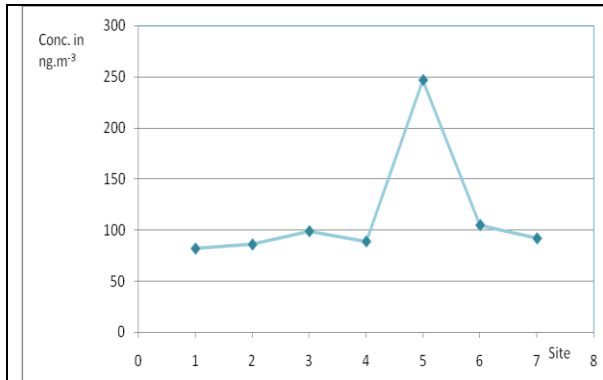


Figure 15. Variation of the average concentration of zinc in PM_{10-2.5} at sampling sites

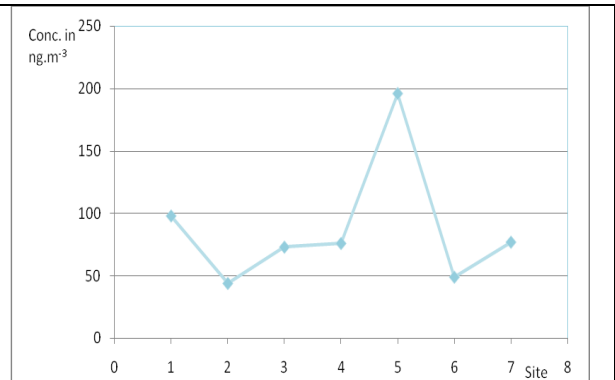


Figure 16. Variation of the average concentration of zinc in PM_{2.5} at sampling sites

The average concentration of selenium in the aerosols samples taken at town Antsirabe ranged from 5ng.m⁻³ to 7ng.m⁻³ in fine particles and varied from 8ng.m⁻³ to 10ng.m⁻³ in coarse particles. But for the sites 1, 2, 3, 4 and 7 the concentration of selenium were smaller than the detection limit (6.7ng.mL⁻¹) in PM_{10-2.5} and the same results for the sites 1, 2, 3, 4 and 5 in PM_{2.5}. Figure 17 and 18 showed both the variation of the concentration of selenium collected at seven sampling sites in PM_{10-2.5} and PM_{2.5}, respectively.

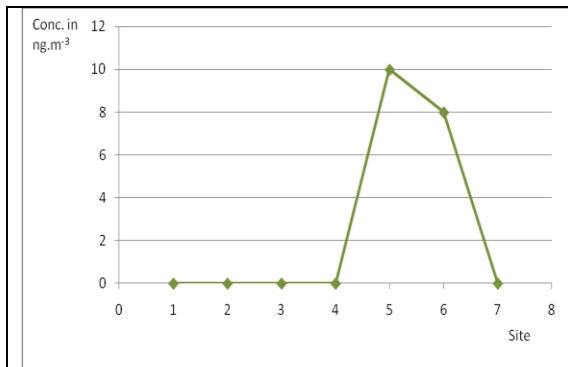


Figure 17. Variation of the average concentration of selenium in PM_{10-2.5} at sampling sites

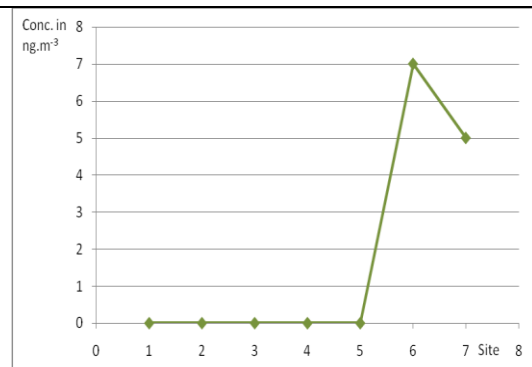


Figure 18. Variation of the average concentration of selenium in PM_{2.5} at sampling sites

The mean concentration of bromine in the aerosols samples taken at town Antsirabe ranged from 13ng.m⁻³ to 53ng.m⁻³ in fine particles and varied from 38ng.m⁻³ to 67ng.m⁻³ in coarse particles. Figure 19 and 20 showed both the variation of the concentration of bromine taken at seven sampling sites in PM_{10-2.5} and PM_{2.5}, respectively.

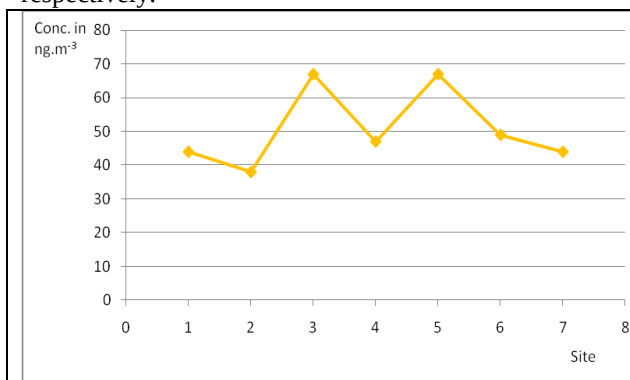


Figure 19. Variation of the average concentration of bromine in PM_{10-2.5} at sampling sites

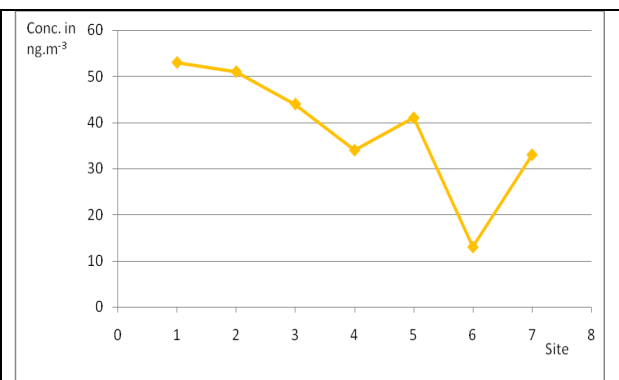


Figure 20. Variation of the average concentration of bromine in PM_{2.5} at sampling sites

The concentration of rubidium in PM_{2.5} at the sites 1, 2, 3, 4 and 6 were smaller than the detection limit (5.92ng.mL⁻¹). But, the average concentration of rubidium in the aerosols samples at sites 5 and 7 are 4ng.m⁻³ and 10 ng.m⁻³, respectively. In PM_{10-2.5}, the concentration of rubidium in sites 1, 3 and 4 are less than the detection limit (5.92ng.mL⁻¹) but for the other sites the concentration ranged from 6ng.m⁻³ to 19ng.m⁻³. Figure

21 and 22 showed both the variation of the concentration of rubidium collected at seven sampling sites in $PM_{10-2.5}$ and $PM_{2.5}$, respectively.

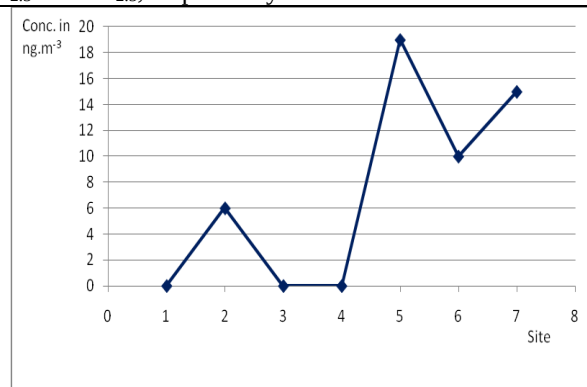


Figure 21. Variation of the average concentration of rubidium in $PM_{10-2.5}$ at sampling sites

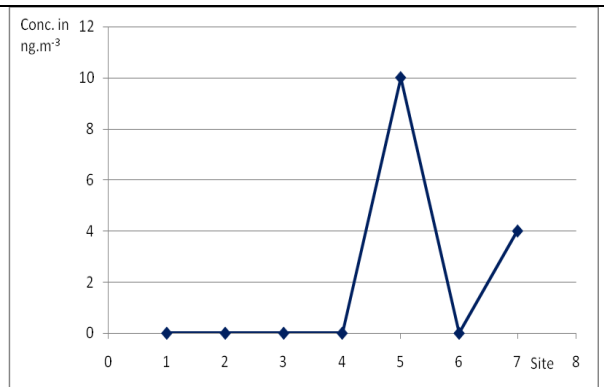


Figure 22. Variation of the average concentration of rubidium in $PM_{2.5}$ at sampling sites

In $PM_{2.5}$, the concentration of strontium at site 6 was less than the detection limit ($5.86ng.mL^{-1}$). For the other sites, the mean concentration varied from $12ng.m^{-3}$ to $26ng.m^{-3}$. In $PM_{10-2.5}$, the average concentration of strontium ranged from $16ng.m^{-3}$ to $49ng.m^{-3}$. But, the concentration of rubidium is less than the detection limit ($5.86ng.mL^{-1}$) at site 4. Figure 23 and 24 showed both the variation of the concentration of strontium collected at seven sampling sites in $PM_{10-2.5}$ and $PM_{2.5}$, respectively.

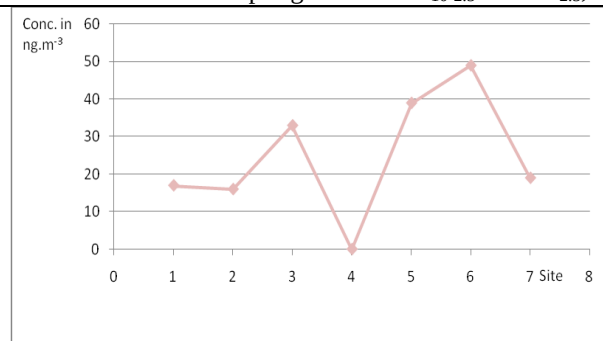


Figure 23. Variation of the average concentration of strontium in $PM_{10-2.5}$ at sampling sites

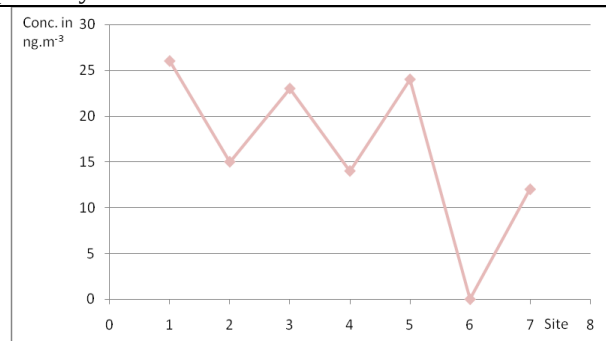


Figure 24. Variation of the average concentration of strontium in $PM_{2.5}$ at sampling sites

All aerosols samples collected in town Antsirabe contained lead as well as in $PM_{2.5}$ than in $PM_{2.5-10}$. The average concentration of lead in $PM_{2.5}$ varied from $25ng.m^{-3}$ to $102ng.m^{-3}$. But, for $PM_{10-2.5}$, $21ng.m^{-3}$ to $110ng.m^{-3}$. Figure 25 and 26 showed both the variation of the concentration of lead collected at seven sampling sites in $PM_{10-2.5}$ and $PM_{2.5}$, respectively.

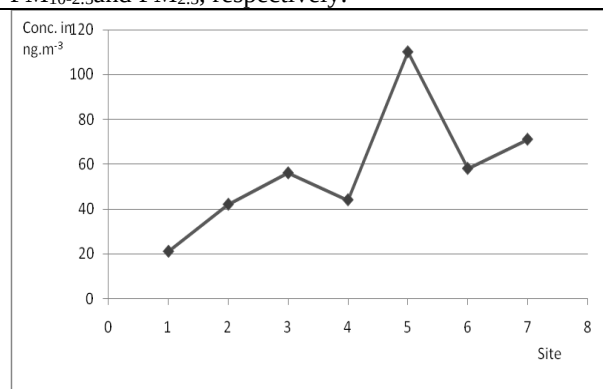


Figure 25. Variation of the average concentration of lead in $PM_{10-2.5}$ at sampling sites

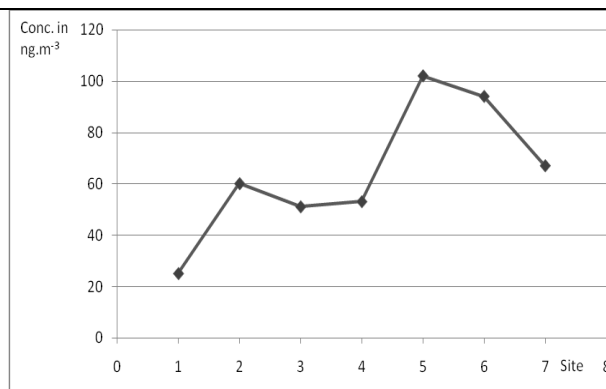


Figure 26. Variation of the average concentration of lead in $PM_{2.5}$ at sampling sites

The method developed by Mason was applied for the determination of the enrichment factor for all elements present in the aerosols samples. In fact, titanium was chosen as reference element (Mason, 1966). Table 9 gives the values of the enrichment factor for all elements.

Elements	PM _{10-2.5} (ng.m ⁻³)	PM _{2.5} (ng.m ⁻³)	Enrichement factor (EF)
K	436	406	1
Ca	3521	3471	2
Cr	15	18	4
Mn	11	19	1
Fe	677	843	1
Ni	21	17	7
Zn	88	114	37
Se	2	2	-
Br	33	51	379
Rb	2	7	-
Sr	16	25	1
Pb	65	57	29

Table 9 . Values of the enrichment factors for all elements

The values of enrichment factors (EF) in table 9 showed that the elements such as Zn, Br and Pb are from anthropogenic sources and K, Ca, Cr, Mn, Fe, Ni and Sr are from natural sources.

IV. Conclusion

The present work showed that TXRF techniques at the laboratory Techniques X-ray Fluorescence and Environment, INSTN-Madagascar was able to analyze the elemental composition in PM_{10-2.5} and PM_{2.5} by TXRF. The results showed that both PM_{10-2.5} and PM_{2.5} contained K, Ca, Ti, Cr, Mn, Fe, Ni, Zn, Se, Br, Rb, Sr and Pb. In addition, the source apportionment gives that the elements such as Zn, Br, and Pb are from anthropogenic sources and the other elements are from natural sources. Finally, it is advisable for the future work to compare the obtained results from TXRF to other analytical techniques like Atomic Absorption Spectrometry (AAS) or ICP-MS and to perform the source apportionment using receptor modeling or factor analysis, principal components Analysis.

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