BJRS

BRAZILIAN JOURNAL OF RADIATION SCIENCES
10-03B (2022) 01-16

Characterization of suspended particulate matter using cascade impactor and X-ray fluorescence

Costa[a] V.A., Pereira[a,c] J.L., Assis[b] J.T., Anjos[b] M.J.

[a] *Universidade do Estado do Rio de Janeiro – UERJ / Instituto de Física, CEP 20550900, Rio de Janeiro, RJ, Brasil*

[b] *Universidade do Estado do Rio de Janeiro – UERJ / Instituto Politécnico, CEP 28625570, Nova Friburgo, RJ, Brasil*

[c] Colégio Pedro II / *Departamento de Física, CEP 29921903, Rio de Janeiro, RJ, Brasil*

ABSTRACT

Atmospheric pollution has become one of the biggest environmental and public health problems in large urban centers. The process of industrialization and urbanization of large cities together with population growth and motorized transport has caused an increase in the level of air pollution in these places. Thus, this work approaches the characterization of suspended particulates in the surroundings of the Duque de Caxias Refinery (REDUC) from the identification of the chemical elements present using the X-ray fluorescence technique - XRF. A PIXE 8-stage impactor was used to collect the particulate material (aerodynamic diameters of 16 – 0.12 µm). On the other hand, the experimental measurements of XRF were performed using a commercial system ARTAX 200 (Bruker) and under the following conditions: voltage of 45 kV, current of 500 µA, acquisition time of 300 s and no filter in the incident X-ray beam. The study allowed estimating the dimensions of the particulate materials, identifying the chemical elements present and pointing out possible sources, from samples collected in three residential points that are in the surroundings of REDUC in the region of Campos Elísios. The X-ray fluorescence technique proved to be efficient and it was possible to detect the following chemical elements: Silicon, Sulfur, Chlorine, Potassium, Calcium, Titanium, Manganese, Iron, Nickel and Zinc. Correlations were observed between some elements making it possible to identify possible sources of pollution.

Keywords: **Atmospheric pollution, particulate matter, X-ray fluorescence.**

ISSN: 2319-0612
DOI: https://doi.org/10.15392/2319-0612.2022.1919
Submitted: 2022-01-30
Accepted: 2022-08-01

1. INTRODUCTION

Atmospheric pollution has become one of the biggest environmental and public health problems in large urban centers. The process of industrialization and urbanization of large cities together with population growth and motorized transport has caused an increase in the level of air pollution in these places [1,2].

There is a large amount of pollutants present in the air that are suspected of generating harmful effects to human health and the environment, including particulate matter (PM). PM can be understood as a complex mixture of solid and liquid components, which vary substantially in composition and size, depending on the emission source and weather conditions. The composition and size of these particles determine the potential for deposition in the respiratory tract and health effects, which are associated with an individual's exposure to this pollutant [3,4].

Therefore, the need to take measures to regulate the emitting sources and understand the profile of atmospheric pollution, as well as the types of pollutants and their respective characteristics, has become a necessity for the improvement of the conditions of the environment and public health, an since atmospheric pollutants have caused changes in the human respiratory system, in the medium and long term, directly influencing the health of the population in general. Children appear to be the most vulnerable to the harmful effects of ambient air pollutants because their defense mechanisms are still evolving and because they inhale a greater volume of air per body weight than adults. Air pollutants can also harm the fetus if the mother is exposed to high levels of air pollution during pregnancy. An increase in respiratory neonatal mortality was associated with environmental levels of air pollutants [5,6]. According to Pires (2005), oil refining activities are responsible for 42% of industrial air pollutant emissions in the Metropolitan Region of Rio de Janeiro. In Brazil, oil refining plays an important role in the economy, accounting for about 30% of the total energy consumed in the country, and practically all the energy consumed in the transport sector [7].

Located in the metropolitan region of Rio de Janeiro, the second district of the municipality of Duque de Caxias, Campos Elíseos, has a petrochemical complex, in which the Duque de Caxias refinery (REDUC) is located. The purpose of this work is to identify the chemical elements present in samples of particulates suspended in the air of this locality using the technique of X-ray fluorescence spectrometry (XRF) and to point out possible sources for the elements found. In addition, classify the suspended particulate by its aerodynamic diameter using a cascade impactor.

2. MATERIALS AND METHODS

The collection of suspended particulate matter was performed using a cascade impactor (PIXE International Corporation). The impactor consists of a set of concentric rings with 10 different particulate cutting diameters: 0.06 µm – 16 µm. The air-flow (1 L/min) was controlled by a flow meter. The impactor is operated 1.5 m above the ground in an inverted position, i.e. with the air inlet facing downwards so that rain or coarse debris does not obstruct the entrance.

Particulate matter samples were collected at three sampling points A, B and C (A: latitude 43°16'37.7" W, Longitude 43°15'51.5" W; B: latitude 22°42'13.0" S, Longitude 43°16'37.7" W and C: latitude 22°42'02.2" S, Longitude 43°14'20.0" W) in homes near REDUC using cellulose acetate membranes, smooth, Unifil brand, with a diameter of 25 mm and porosity of 0.2 µm. For each point, internal measurements (in), that is, inside the residence, and external measurements (out), outside the residence, were performed. At each point, the collection system was turned on in the morning at 9:00 am and turned off after 10 hours of collection, being monitored throughout the interval.

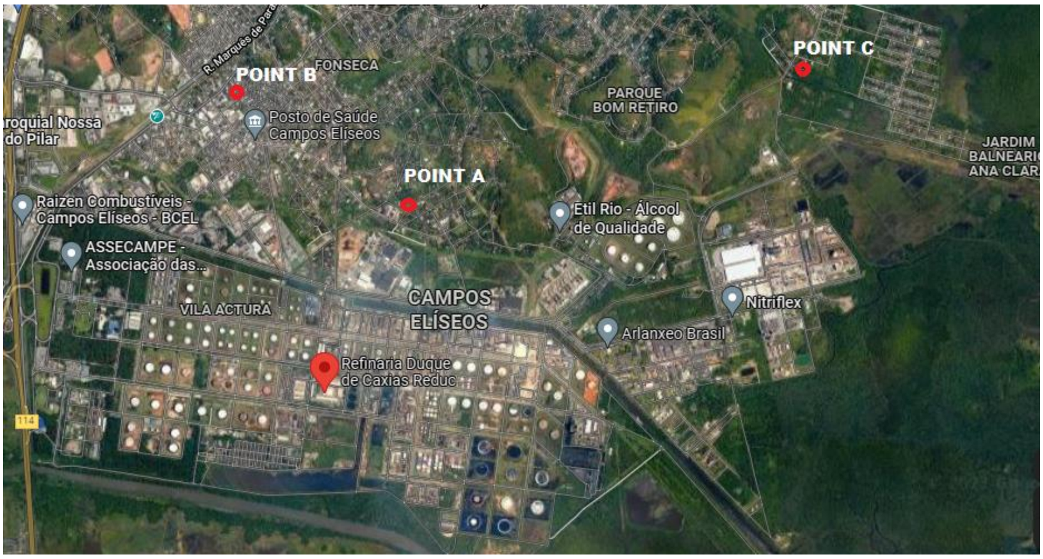

Figure 1: *Map of the Campos Elíseos region around the REDUC. Points A, B and C represent the locations where samples of atmospheric particulate matter were collected.*

X-ray fluorescence measurements were performed using the commercial XRF system (ARTAX 200). The X-ray tube has a fine focus (0.6 mm collimator) and a Molybdenum anode. The system uses an SDD type XFlash 3001 detector (Silicon Drift Detector) with an 8 µm thick beryllium window, 10 mm² detector sensitive area. The ARTAX 200 has a laser beam for alignment and a color CCD camera with a resolution of 500 x 582 pixels to observe the alignment of the measurement point. The XRF experimental measurements were performed under the following conditions: 45 kV, 500 µA, acquisition time of 300 s and no filter was used in the incident X-ray beam. The XRF spectra of each analysis performed are acquired and evaluated by the SPECTRA software, version 5.3, provided by the manufacturer.

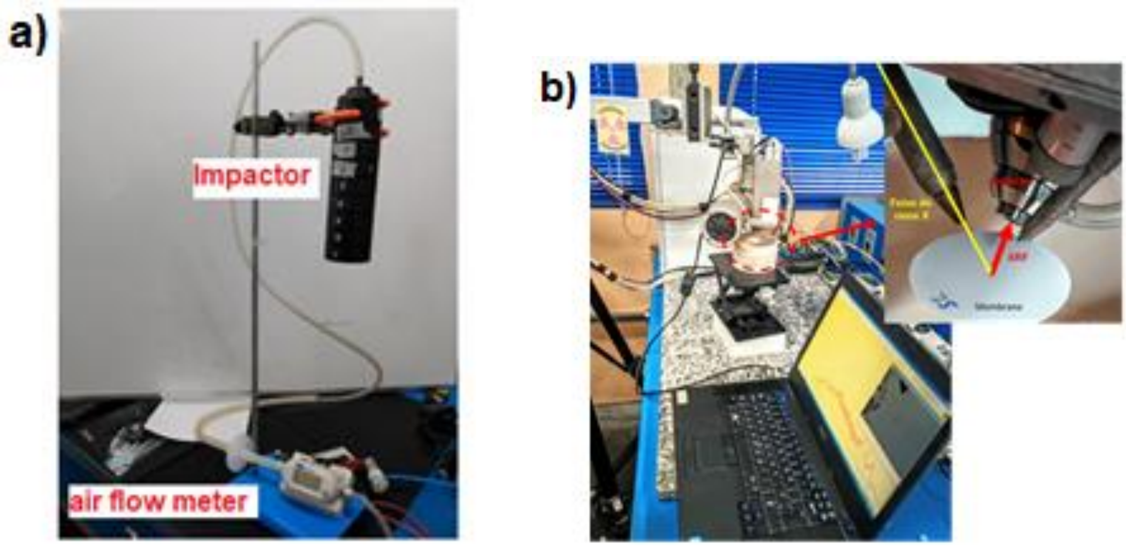

Figure 2: *a) Atmospheric particulate collection system and b) XRF system.*

3. RESULTS AND DISCUSSION

The elements detected in the XRF measurements were: Si, S, Cl, Ar, K, Ca, Ti, Mn, Fe, Zn and Mo. The chemical element Ar is one of the constituents of atmospheric air and molybdenum (elastic scattering) is from the target material of the anode of the X-ray tube, so they are not part of the particulate material sample despite being present in the spectrum.

The areas under the peaks (counts) for each of the sampling points (in and out) were obtained to determine the contribution of each element present in the particulate. To observe the formation of clusters by their similarity levels, we analyzed the results for each sampling point by dendrograms.

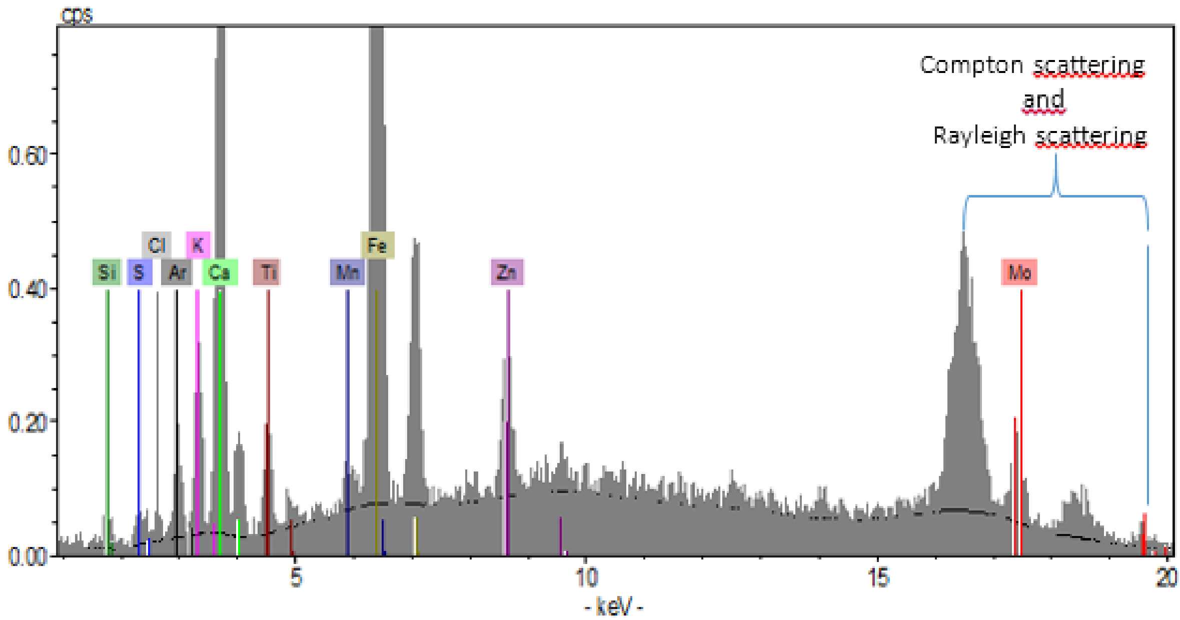

Figure 3: *XRF spectrum from point B out with aerodynamic cut-off diameter of 2.0 µm*

3.1. Sampling Point A

According to the data in table I, it can be seen that the elements Si, S, Cl, K, Ca, Ti, Fe and Zn were detected. The greatest contributions of these elements occurred in the aerodynamic cutoff diameter of 4 µm. It was observed that there was an expressive contribution of iron, which may be associated with dynamic processes of soil resuspension, due to the proximity to industrial sources and scrap company [8].

In figure 4 (A in), the dendrogram shows a strong correlation between all detected elements, Si, S, Cl, K, Ca, Ti, Mn, Fe and Zn, whose maximum difference was 0.15. However, Zn, Si, S and Cl were in the same grouping, which may show that they are from the same source, probably industrial. Ti was close to this cluster, with a slight difference.

Table I: Elements present in the samples from point A in (Counts - Area under the XRF peaks)

cut diameter (µm)	Elements (K$_\alpha$ lines)							
	Si	**S**	**Cl**	**K**	**Ca**	**Ti**	**Fe**	**Zn**
16	ND	ND	ND	ND	ND	ND	ND	ND
8.0	ND	ND	ND	ND	33	ND	ND	ND
4.0	69	57	823	243	962	173	5018	163
2.0	ND	ND	ND	55	327	ND	918	ND
1.0	ND	ND	ND	61	401	ND	1716	ND
0.5	ND	ND	ND	42	122	45	440	ND
0.25	ND	ND	ND	ND	ND	ND	ND	ND
0.12	ND	ND	ND	ND	ND	ND	185	ND

ND : non detected

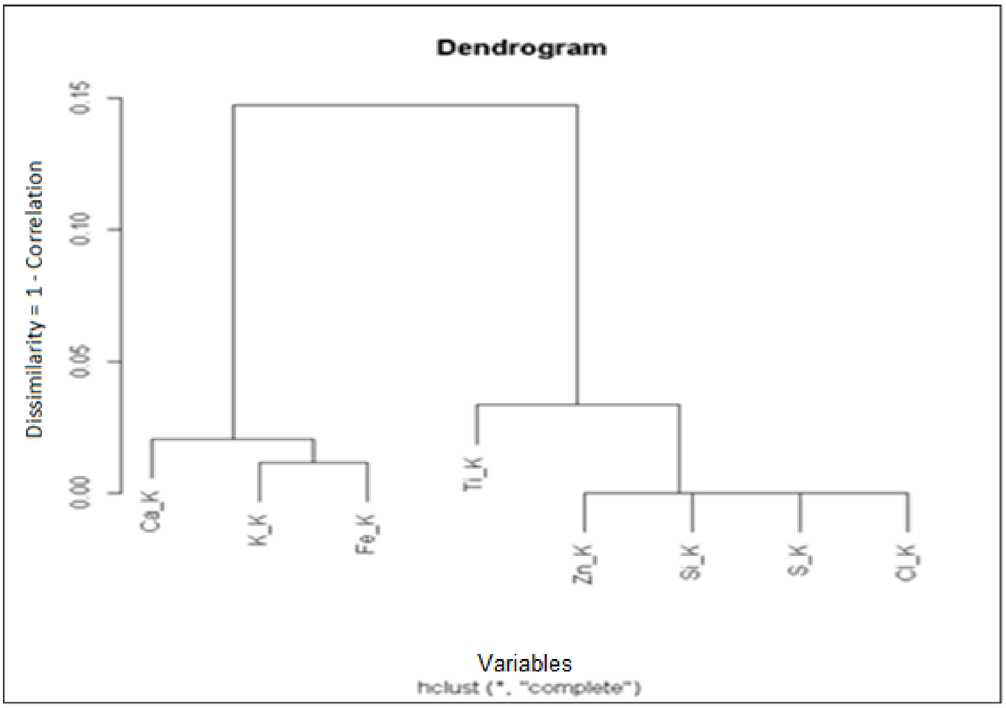

Figure 4: *Dendrogram of the elements at point A in*

The literature shows that this metal has been used in metal alloys and paints [9]. Besides that, the elements Ca, K and Fe have another important cluster, which may be due to resuspension of the soil close to point sampling [10], because close to the sampling point there is vehicle traffic on an unpaved street, this same pattern was found at the sampling point B in.

At point A out, as indicated in table II, the presence of the Ni element was verified, which had not been detected at sampling point A in. Ni is a metallic element because of its high resistance to corrosion and oxidation, it is applied in metal alloys, in the manufacture of stainless steel and in the coating of other metals. A possible source for the presence of this element at sampling point A is due to a scrap recycling company operating close to sampling point A.

It was verified a greater contribution of chemical elements in the aerodynamic diameter of cut of 4 μm and 1 μm, in addition it was detected S, Ca, Ti, Fe, Ni, Zn in the aerodynamic diameter of cut of 0.12 μm; particulates with this size can reach the alveoli and cause damage to health.

The dendrogram in Figure 5 shows a very strong correlation between Ni and Zn and, close to them, S, this may be evidence that these elements come from the same source, in this case, an anthropogenic source.

Table II: Elements present in the samples from point A out. (Counts - Area under the XRF peaks)

cut diameter (μm)	**Elements (K_α lines)**								
	Si	**S**	**Cl**	**K**	**Ca**	**Ti**	**Fe**	**Ni**	**Zn**
16	ND	ND	ND	ND	ND	ND	ND	ND	ND
8.0	ND	ND	91	ND	57	ND	268	ND	ND
4.0	66	75	783	347	977	235	4393	ND	ND
2.0	ND	ND	98	56	248	ND	1078	ND	ND
1.0	ND	32	81	33	231	40	681	ND	ND
0.5	ND	34	ND	ND	23	ND	ND	ND	ND
0.25	ND	ND	ND	ND	ND	ND	ND	ND	ND
0.12	ND	108	ND	ND	179	99	198	205	211

ND : non detected

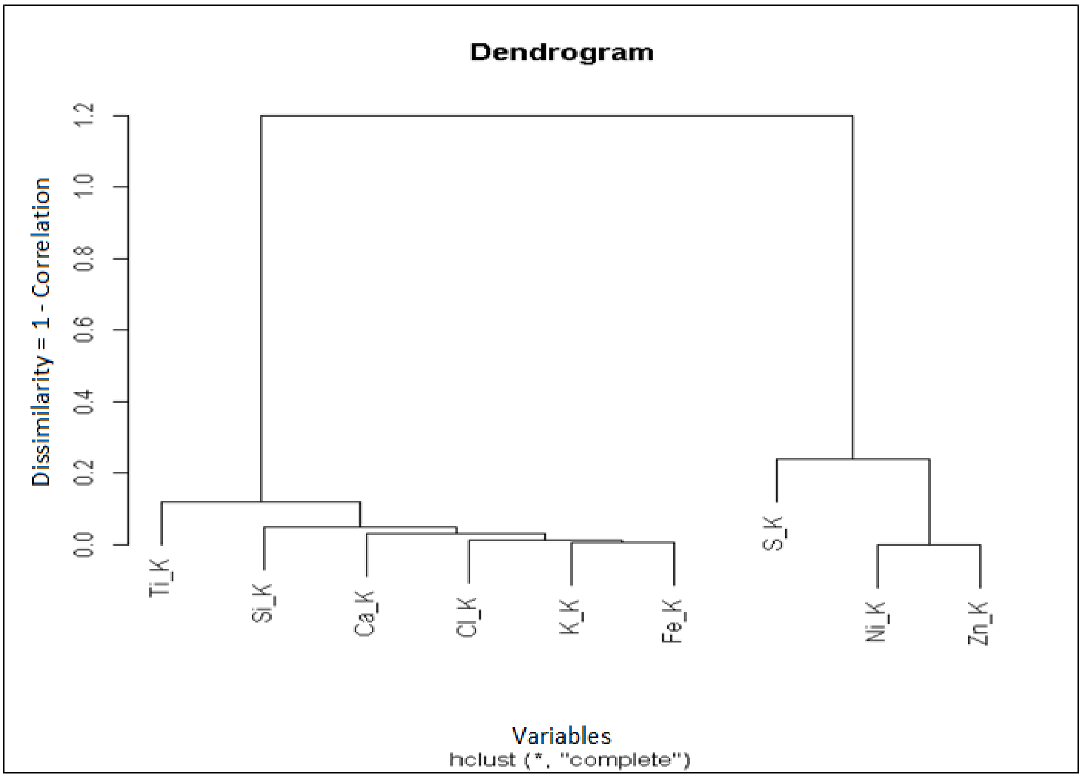

Figure 5: *Dendrogram of elements from point A out*

3.2. Sampling Point B

At point B (in), the elements Si, Cl, K, Ca, Ti and Fe were detected with the greatest contribution in the diameter of 2 **µ**m.

The dendrogram of Figure 6 shows a strong correlation between Si and Ti, which are possibly due to suspension of ceramic particles. At this sampling point, the floor was coated with white glazed ceramic (ceramic floor tiles). Si is the major element in the composition of ceramics and titanium oxide (TiO_2) is a white pigment widely used in the ceramic manufacturing industry [11]. The Cl was a little distant from the other two groups, as it was not identified a behavior similar to the other elements, indicating another source, in this case, it is very likely that it comes from the use of cleaning products that contain chlorine in its composition. for floor cleaning. As already discussed in A in, the Ca, K and Fe grouping may be due to soil resuspension.

Table III: Elements present in the samples from point B in. (Counts - Area under the XRF peaks)

cut diameter (µm)	Elements (K_α lines)					
	Si	**Cl**	**K**	**Ca**	**Ti**	**Fe**
16	ND	ND	ND	ND	ND	ND
8.0	ND	ND	ND	47	ND	ND
4.0	ND	91	104	390	ND	861
2.0	63	112	282	1595	261	3022
1.0	ND	ND	59	245	ND	402
0.5	ND	ND	ND	70	ND	ND
0.25	ND	ND	ND	ND	ND	ND
0.12	ND	ND	ND	37	ND	89

ND : non detected

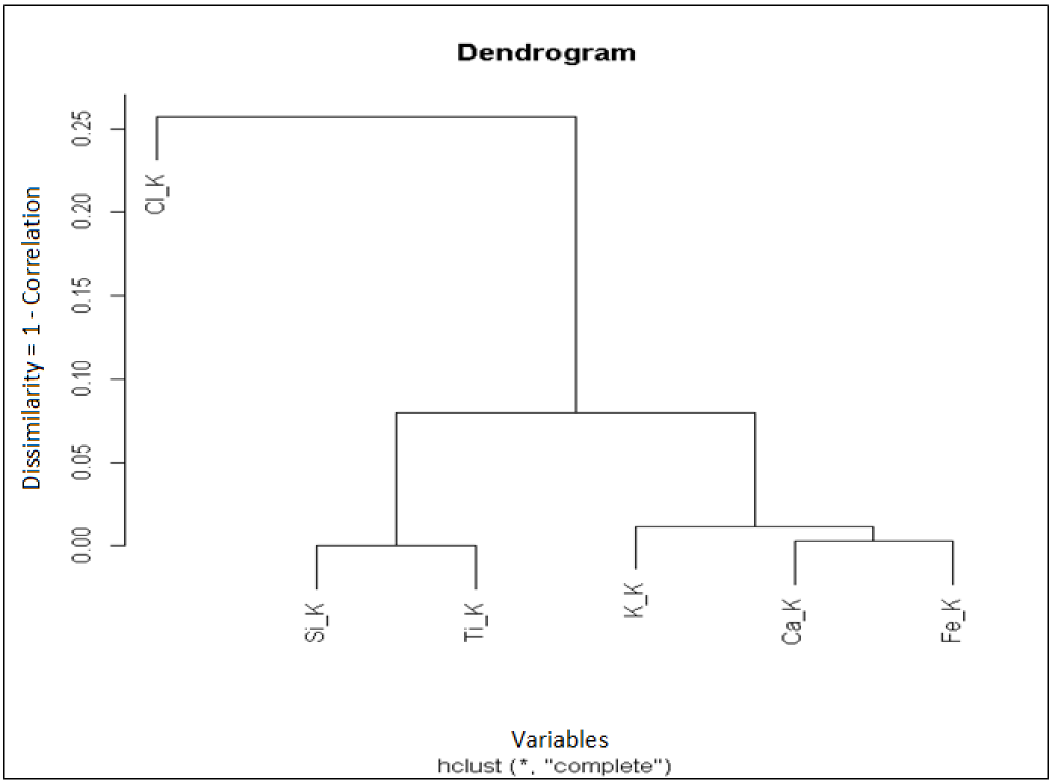

Figure 6: *Dendrogram of the elements of point B in*

In table 4 B (out), we observe the elements Si, S, Cl, K, Ca, Ti, Mn, Fe and Zn, being found in greater proportions between the aerodynamic cutting diameters from 1µm to 4µm. Mn was detected at this sampling point, possibly from an anthropogenic source [8].

Table IV: Elements present in the samples from point B out. (Counts - Area under the XRF peaks)

cut diameter (µm)	**Elements (K_α lines)**								
	Si	**S**	**Cl**	**K**	**Ca**	**Ti**	**Mn**	**Fe**	**Zn**
16	ND	ND	ND	ND	ND	ND	ND	ND	ND
8.0	ND	ND	ND	ND	252	ND	ND	450	ND
4.0	179	56	206	816	4913	558	ND	11144	577
2.0	139	49	144	890	4158	674	211	13187	998
1.0	67	106	ND	417	1459	251	107	5421	1402
0.5	ND	195	ND	161	203	ND	ND	869	655
0.25	ND	ND	ND	ND	63	ND	ND	89	ND
0.12	ND	335	ND	ND	90	ND	ND	521	165

ND : non detected

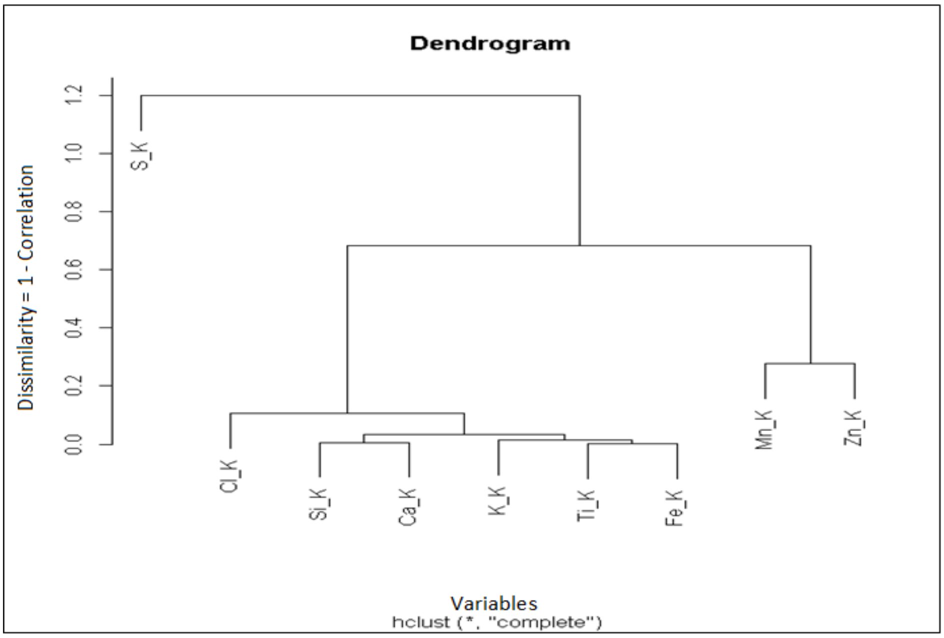

Figure 7: *Dendrogram of the elements at point B out*

The dendrogram obtained with the elements at this sampling point (Figure 7) shows the highlight of the S element, which may be linked to the origin of intense vehicular traffic, fossil fuel burning in the vicinity and pollution associated with industrial processes in the region [12]. It is still possible to observe the grouping between Mn and Zn, which are probably due to the suspension of particulates resulting from vehicle traffic [10], in addition to industrial processes.

3.3. Sampling Point C

In table V, at the sampling point C in, the elements Si, S, Cl, K, Ca, Ti, Fe and Zn were detected with the greatest contribution in the diameters from 2 **μ**m to 4 **μ**m. Figure 8 shows the dendrogram of the results obtained at this sampling point. It can be seen that the element S is totally separated from the other elements, forming a group by itself. The presence of S separately may be associated with some point source, internal, unidentified, in addition to the industrial source. The S element is most likely due to the proximity to a polymer industry and REDUC, as there is no intense vehicle traffic at this sampling point.

Table V: Elements present in the samples from point C in. (Counts - Area under the XRF peaks)

cut diameter (μm)	**Elements (K_α lines)**							
	Si	**S**	**Cl**	**K**	**Ca**	**Ti**	**Fe**	**Zn**
16	ND	ND	ND	ND	ND	ND	ND	ND
8.0	ND	ND	ND	ND	46	ND	ND	ND
4.0	ND	72	97	135	499	ND	599	145
2.0	34	81	77	195	549	86	1208	331
1.0	ND	263	ND	104	93	ND	276	190
0.5	ND	0	ND	ND	ND	ND	ND	ND
0.25	ND	49	ND	ND	ND	ND	ND	ND
0.12	ND	108	ND	ND	ND	ND	ND	ND

ND : non detected

The other elements are more closely correlated and may be due to natural sources. The Cl, for example, may be due to the proximity to Guanabara Bay; Ca, K and Fe, on the other hand, may be related to soil resuspension [8].

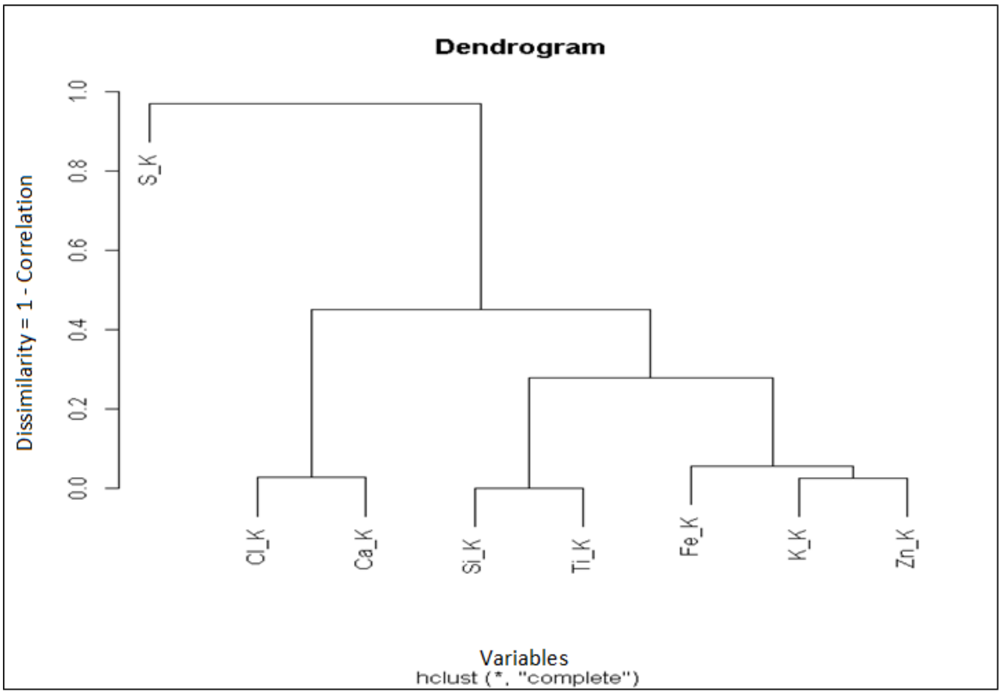

Figure 8: *Dendrogram of the elements at point C in*

Finally, in table VI, sampling point C out, the elements S, Cl, K, Ca, Fe and Zn were detected, highlighting the high contribution of Zn in the diameter of 0.12 **μ**m. This aerodynamic diameter is important because of its range in breathing, which can reach the deepest regions of the human respiratory system to the pulmonary alveoli and reach the circulatory system.

In figure 9, at sampling point C out, the dendrogram shows the Zn element as highlighted, alone and without correlation with the other elements detected. In this case, most likely, the presence of this element may be associated with particulates from the wear of tires and vehicle parts, since at this sampling point, there is a car garage with great movement. In addition, at this point there were cuts of galvanized metal structures, that is, coated with Zn, this probably also contributed.

Unlike the other points, Si and Ti were not detected, and it is possible to say that these two elements may be related to the type of floor and the pigmentation of the ceramic, in addition to wall paints, as this was the only point where the floor it was concrete (no ceramics) and had no walls nearby. According to the literature, ceramics have Si in their composition and paints can have Si and Ti [9].

Table VI: Elements present in the samples from point C out. (Counts - Area under the XRF peaks)

cut diameter (µm)	Elements (K_α lines)					
	S	**Cl**	**K**	**Ca**	**Fe**	**Zn**
16	ND	ND	ND	46	93	ND
8.0	ND	ND	ND	76	216	ND
4.0	65	309	77	406	697	352
2.0	92	254	157	407	1155	1631
1.0	47	ND	ND	81	135	787
0.5	41	ND	ND	36	ND	ND
0.25	ND	ND	ND	55	ND	340
0.12	27	ND	ND	ND	137	1261

ND : non detected

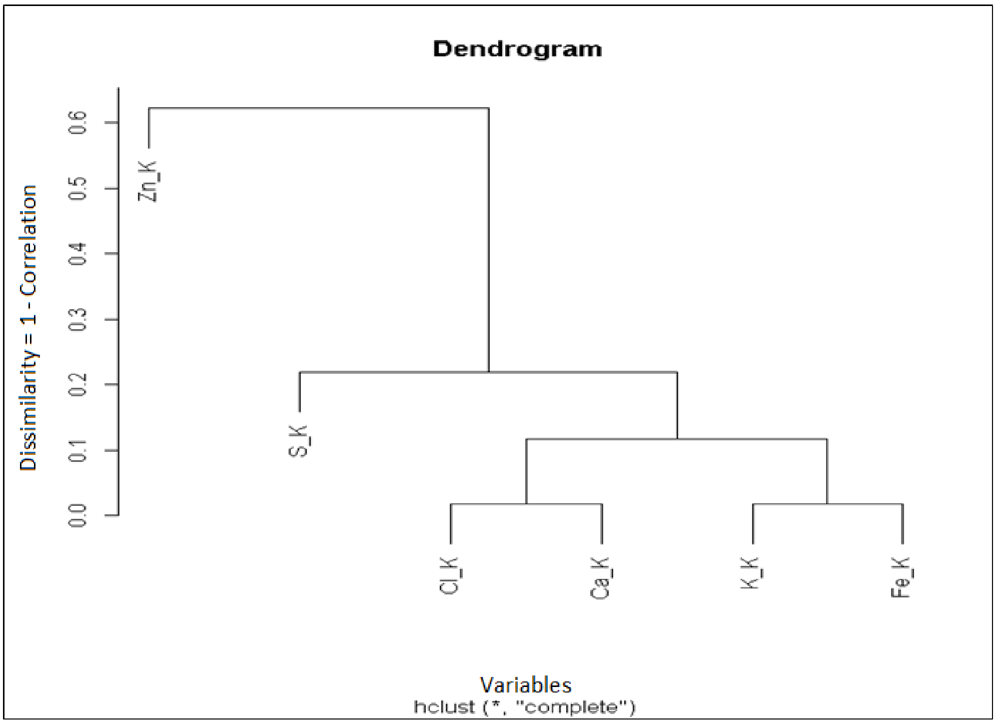

Figure 9: *Dendrogram of the C out point elements*

4. CONCLUSION

The X-ray fluorescence technique proved to be efficient in the detection of several chemical elements present in suspended particulates at collection points near REDUC, Campos Elísios. It was possible to detect the following chemical elements in the membranes analyzed by XRF: Ca, Cl, S, Fe, Mn, Ni, K, Si, Ti and Zn. Correlations were observed between some elements making it possible to identify the possible sources of these elements in the particulate matter. With the use of the impactor, it was possible to identify the size of the aerodynamic diameter of the particulates in suspension, which allows us to estimate how far they can reach within our respiratory system when inhaled.

From the data obtained, it was possible to verify the presence of some chemical elements characteristic of natural sources and anthropogenic sources, such as vehicular traffic, wear of metallic constituents and industrial processes. We believe that this study is relevant in the environmental area as it: a) expands the applications of the X-ray fluorescence technique, as it was used to analyze possible air pollution through particulate samples; b) contributes to the literature on the study of air quality in the region; c) motivates future academic research that is more detailed and with greater sampling in regions where there are large urban and industrial concentrations.

ACKNOWLEDGMENT

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001, Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) and Financiadora de Estudos Projetos (FINEP).

REFERENCES

[1] APRILE, G. G. et al. Comparison of the suitability of two lichen species and one higher plant for monitoring airborne heavy metals. **Environ Monit Assess**, v. 162, p. 291–299, 2010.

[2] KAMPA, M.; CASTANAS, E. Human health effects of air pollution. **Environmental Pollution**, 151(2): 362-367, 2008.

[3] BRITO, G. F. S.; SODRÉ, F. F.; ALMEIDA, F. V. O Impacto do Material Particulado na Qualidade do Ar. **Revista Virtual de Química**, v. 10 (5), p. 1335-1354, 2018.

[4] ALVES, C. Aerossóis atmosféricos: perspectiva histórica, fonts, processos químicos de formação e composição orgânica. **Química Nova**, V. 28 (5), p. 859-870, 2005.

[5] ARBEX, M.A.; SANTOS, U.P.; MARTINS, L.C.; SALDIVA, P.H.N.; PEREIRA, L.A.A.; BRAGA, A.L.F. Air pollution and the respiratory system. **J. Bras. Pneumol.** v. 38, p. 643–655, 2012.

[6] SALVI, S. Health Effects of Ambient Air Pollution in Children. **Paediatric Respiratory Reviews**, V. 8 (4), p. 275-280, 2007.

[7] PIRES, D. O. Inventário de emissões atmosféricas de fontes estacionárias e sua contribuição para a poluição do ar na região metropolitana do Rio de Janeiro. 2005. 194 f. Dissertação (Mestrado em Engenharia de planejamento energético) – Universidade Federal do Rio de Janeiro (UFRJ). Rio de Janeiro, 2005.

[8] CAMARINHA, G. C. Determinação Quantitativa de Fontes de Material Particulado Inalável na Atmosfera da Região Metropolitana do Rio de Janeiro. 2010. 175 f. Dissertação (Mestrado em Ciências) – Escola de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, 2010.

[9] FERREIRA, K. R. S.; SABEDOT, S.; SAMPAIO, C. H. Avaliação da presença de monazita em concentrado de ilmenita produzido na mina do Guaju (PB). **Rem: Rev. Esc. Minas**, Ouro Preto, v. 60, n. 4, p. 669-673, Dec. 2007 .

[10] SANTOS, R. S. Análise multielementar em folhas de Nerium oleander L. usando fluorescência de raios X por dispersão em energia. 2014. 141 f.. Dissertação (Mestrado em Física) – Instituto de Física, Universidade do Estado do Rio de Janeiro, Rio de Janeiro, 2014.

[11] MUKHERJEE, D. P.; KUMAR DAS, S. Influence of TiO_2 content on the crystallization and microstructure of machinable glass-ceramic. **Journal of Asian Ceramic Societies**. v. 4 (1), p. 55-60, 2016.

[12] INEA (Instituto Estadual do Ambiente). Relatório Anual de Qualidade do Ar do Estado do Rio de Janeiro – Ano base 2010 e 2011. 2013.