A method for accurate measurement of chemical elements concentrations present in total suspended particulates and PM_{10} in the atmosphere

Tania Renata Prochnow, Bernardo Liberman, Renato Pakter, Edson Chiaramonte, Jonas da Costa Carvalho, Davidson Martins Moreira, Emerson Alberto Prochnow e Masurquede Coimbra

RESUMO

Apresenta-se um método analítico para a identificação e a quantificação de elementos químicos presentes nas Partículas Totais Suspensas (TSP) na atmosfera e nos particulados PM_{10}. Este método foi aplicado para a quantificação de 16 metais em suspensão na atmosfera da região de Canoas, RS. Os resultados foram comparados com as análises de metais presentes na atmosfera do Centro Agrícola da ULBRA, na região de Montenegro (uma área agrícola na qual a direção predominante do ventos possibilita que ela seja considerada como um ponto com mínima poluição atmosférica) . Usou- se, também, a técnica da microscopia eletrônica para a comparação dos resultados e para a identificação da origem de várias partículas poluentes.

ABSTRACT

In this paper we present an analytic method for the identification and the quantification of chemical elements in the atmosphere present in TSP and PM_{10}. To the present moment, the method is applicable to a total of 16 metals. The method was used to analyze TSP and PM_{10} samples collected in the city of Canoas, in the greater Porto Alegre, Brazil. In order to obtain relative measures of PM_{10} concentrations, the method was also used to analyze samples from a *neutral* location. The results were checked against electronic microscopy findings, having an excellent agreement. Geological analysis of the electronic microscopy results was used to infer the pollutants source.

1. INTRODUCTION

Of the Total Suspended Particulates (TSP) in the atmosphere, particulates with average aerodynamic diameters of 10 microns or less, named PM_{10} , are of particular importance because they remain in the air for long periods of time and are inhaled into the deep lung. In sensitive individuals, exposure to PM_{10} is associated with effects on breathing and respiratory systems (aggravation of existing respiratory symptoms, like asthma), damage to lung tissue, cancer and premature death (EPA,1997; DONALDSON,1999; JANSSEN et all.,1997). Recent studies suggest an association between the PM_{10} emitted from the exhaust of vehicles and numerous health effects (BRUNEKREEF et all.,1997;PONKA,1998). Particulate matter can also cause damage to materials and represents a major cause of decrease of the visibility in many regions (PFEFFER,1994; BOUBEL et all.,1994).

For these reasons, in 1987, the Environmental Protection Agency (EPA), USA, (EPA, 1998; 2000; 1993) replaced TSP air quality standard with a PM_{10} standard. EPA′s national air quality standard for PM_{10} is 50 $\mu g/m^3$ (measured as an annual mean) and 150 $\mu g/m^3$ (measured as a daily concentration).

To accomplish an investigation of the damages of the atmospheric pollution, it is necessary to accurately quantify the concentrations of pollutants. In this paper we present an accurate analytic method for the identification and quantification of chemical elements present in TSP and PM_{10}. At the present moment, the method is applicable to a total of 16 elements.

This method was used to analyze TSP and PM_{10} samples collected near the highway BR 116, which is a major road which pass through the region of Canoas , south of Brazil.

The particular site of Canoas, was chosen because its high concentration of industries, high population density (2,900 habitants per km^2) and proximity to BR 116. In this region there are more than 1,000 industries. Among them, it is found an oil refinery, factories of cement, glass and crystal engines, vegetable oil, inks, leather, asphalt, and metallurgies. The highway BR 116 crosses Canoas and has a daily circulation of more than 120,000 vehicles, being 40% of trucks and buses.

However, this area lacks of data about the particulate concentration in the atmosphere. Measurements of the pollutants, mainly emitted from vehicles in the highway BR 116, is a basic necessity for the local population and the local environment control bureau.

2. METHODS

2.1 Sampling methods

Measurements of the atmospheric pollutants were conducted with the use of High Volume Sampler appropriate for TSP (named HI- VOL) and PM_{10}. To collect the particles suspended in the atmosphere, the sampler operates with a flow rate of 1.1- 1.7 m^3/ min for a period of 24 hours. The flow passes through a filter of quartz where the particles are collected. The special values of the flow rate and the entrance geometry favours the collection of particles up to 25 – 50 µm in the aerodynamic diameter. The ratio of the mass of particulate matter collected in 24 hours and the total volume sampled gives the concentration of TSP. To collect the PM_{10} particulate, the canopy of the high volume sampler is replaced by a PM_{10} inlet which prevents particles with aerodynamic diameters greater than 10 µm from reaching the filter. This should be accomplished with a flow rate of 1,13 m^3/ min (PROCHNOW et all., 2000; MARCAZZAN et all.,2001; CHAN et all., 2001) .

2.2 Chemical analysis

Four different solutions were tested to determine the digestion method that supplies the best results for the analyses of the elements that constitute the collected material. A fifth solution was used only for the lead analysis. The first three solutions (M1, M2, M3) were formulated with different concentrations of nitre-chloridric mixture. For the fourth solution (M4) a nitre-sulphuric mixture was used and, for the fifth (M5), it was added chloridric acid. For the selection of the best method of digestion, the filters were divided in four parts and each one submitted to different methods of digestion.

The digestions were carried through a microwave closed system. Each sample was placed into a block with 20 ml of digestion solution and submitted to all stages of digestion for microwaves with controlled temperature and pressure. After cooling, the digested material was filtered with analytical paper Whatmann and completed with Milli- Q water up to 250 ml.

The concentration of the elements were obtained with the use of an atomic absorption spectrophotometer equipped with flame, graphite oven and hydride generator**.** The calibration of this spectrophotometer is a critical point to get accurate values for the concentration of the elements. All variables involved, such as the intensity of the current, wavelength, mixture of gases, flame**,** interferents, sensitivity of the method, and curves of calibration, have been optimized.

After the optimization of the equipment conditions it was made, for each analyzed element, the determination of the degree of response of the equipment, the backup degree and the recovery degree(GR). The recovery degree was obtained between 90% and 110%, what means that the device has good response.

To guarantee reproducibility of the results, the system was always calibrated before and after each set of analysis.

Due to the agility of the technique, low cost and good reproducibility, the analysis for the alkaline elements was made with the use of flame photometer.

The analysis of the elements was done after all the procedures of calibration and optimization described above. Until the present moment, the developed methodology was applied to 16 elements: aluminum, cadmium, calcium, lead, copper, chromium, iron, lithium, magnesium, manganese, mercury, nickel, potassium, sodium, vanadium, zinc.

Analysis of the concentrations of the elements present in the white filters was also carried out. Analysis of the elements in the reagents was made to prevent the presence of possible contaminants in the digestion process

2.3 Electronic microscopy.

The analytical methods allow to determine the amounts of each element that constitute the atmospheric dust, but do not allow the study of the origin of the collected material. The investigation of the sources of the elements in the collected atmospheric pollutants was done with the use of the Electron Microscope- Scanning Electron Microscope (SEM), type XL 20. Sputtering was made with gold-palladium by means of a Baltec MED-020. The use of Electron Microscopy process gives the weight percentage of each element present in the analyzed dust.

3. RESULTS

The analysis made with the 16 elements shows that digestive solution M1 offers the best results for most of the analyzed elements.

However, the different sensitivity of every method for each element shows that it is necessary to choose an appropriate digestion method for the analysis of a specific element.

The determination of each element was performed three times to test reproducibility and to determine root means squared errors.

Table1, shows the results obtained in the analysis of vanadium in different filters and using the different methods of digestion. The best analytical response for vanadium was obtained with method M1. Comparative analyses using a standard sample were also performed, confirming the advantage of method M1.

Tab. 1. Vanadium analysis

Filter	Method	mg /kg	μg /m^3	% diff. rel. to M1
A3 - 5	M 1	104,4505	0,008571	
	M 3	71,2117	0,005843	- 31,82
A1 - 7	M 1	98,5378	0,007861	
	M 4	78,2411	0,006242	- 20,59
A2 - 9	M 1	98,4966	0,008015	
	M 2	88,1451	0,007173	- 10,50
A3 - 13	M 1	262,0707	0,016534	
	M 3	166,7656	0,010521	- 36,36
A1 - 14	M 1	80,0533	0,016089	
	M 4	49,0506	0,009858	- 38,72
A2 - 15	M 1	213,4646	0,008051	
	M 2	83,8744	0,003163	- 60,70
A2 - 16	M 1	45,5729	0,001420	
	M 3	22,9207	0,000714	- 49,70
A1 - 17	M 1	166,2817	0,009150	
	M 4	119,5255	0,006577	- 28,11
A3 - 18	M 1	165,4000	0,006986	
	M 2	142,3902	0,006014	- 13,91
A1 - 20	M 1	624,4218	0,013862	
	M 3	361,1512	0,008017	- 42,16
A2 - 21	M 1	171,2583	0,004714	
	M 4	136,2275	0,003750	- 20,45

Figure 1 presents the results obtained for different digestion methods applied for different elements.

Table 2 presents the masses collected during 24 hours, at the same place, for TSP and PM10.

Tab. 2. Concentrations of the elements present in atmospheric dust collected simultaneously with equipment for PTS and PM10.

Equipment	**PM10**		**PTS**	
Collected dust (g)	**0,1267**		**0,2119**	
Concentration in air ($\mu g/m^3$)	**82,40**		**126,76**	
Element	**g/kg**	**$\mu g/m^3$**	**g/kg**	**$\mu g/m^3$**
Al	9,116	0,751	1,037	1,236
Cd	0,018	0,001	0,020	0,002
Ca	13,764	1,134	15,549	1,852
Pb	2,249	0,185	1,807	0,215
Cu	0,460	0,038	1,184	0,141
Cr	0,323	0,026	0,250	0,029
Fe	31,152	2,567	31,878	3,798
Li	0,157	0,015	0,129	0,015
Mg	5,761	0,474	6,031	0,723
Mn	1,262	0,104	1,264	0,150
Hg	0,0035	0,0003	0,0022	0,0003
Ni	0,505	0,041	0,325	0,038
K	7,892	0,650	7,036	0,838
Na	14,530	1,197	13,803	1,644
V	0,601	0,011	0,624	0,013
Zn	19,968	1,645	17,286	2,059

In this table, it is observed that many of the analyzed metals are present in the inhalable particulates, as is the case of aluminum, lead, chromium and nickel. Others are present in more significant concentrations in TSP particles, especially the copper.

The elements found in larger concentration in these samples were iron, zinc, sodium, calcium and aluminum. The other elements, especially the most toxicants as mercury and cadmium, show very small concentrations.

Figure 2 presents, the comparative concentrations between the different elements analyzed in the two equipments.

Approximately 9,7 % of the component of the analyzed dust present in the total particulate had been determined quantitatively. For the inhalable dust this determination was approximately 10,8 %.

The electronic microscopy analysis of the samples shows a great percentage of carbon and silicon concentrations which indicate that these are the main components in the dust. This method, however, is not adjusted to the analysis of the dust because its results are expressed in weight percentages. Therefore, the lightest components can not be determined, as it is shows in figures 4, 5 and 6.

Also in the white filter, figure 3, pollutants elements are absent. However, the atomic absorption analysis of this filter presents traces of various elements, such sodium, iron, aluminum, zinc.

Electronic microscopy technique is extremely valuable in the investigation of the origin of the components of the atmospheric dust. The visualization of the individual form of each particle deposited on the filter allows the study of its origin. Figure 4 shows the presence of biological material (pollen). Also, it was possible to observe the presence of fibers and fungus.

In figure 5 it is possible to observe amorphous material resulting from industrial process or from combustion reactions. Figure 6 shows a crystalline structure resulting from the disaggregation of natural dust. In this figure, it is also possible to visualize the effect of the condensation of volatile organic compounds on solid particles.

4. CONCLUSIONS

The application of different methods of digestion allows to conduct the analyses to get the best results for specific element present in the pollutant atmosphere related with the activity of some region.

The analytic methodologies presented in this paper made possible the accurate quantification of a great number of elements present in the atmospheric dust.

These methodologies together with the techniques for dust collection using high volume samplers allow a average characterization of the dust for some region.

The use of electronic microscopy of sweepings allows the investigation of the origin of the particles present in the atmospheric dust.

Acknowledgment

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5. REFERENCES

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Figure 1: Results obtained for different digestion methods

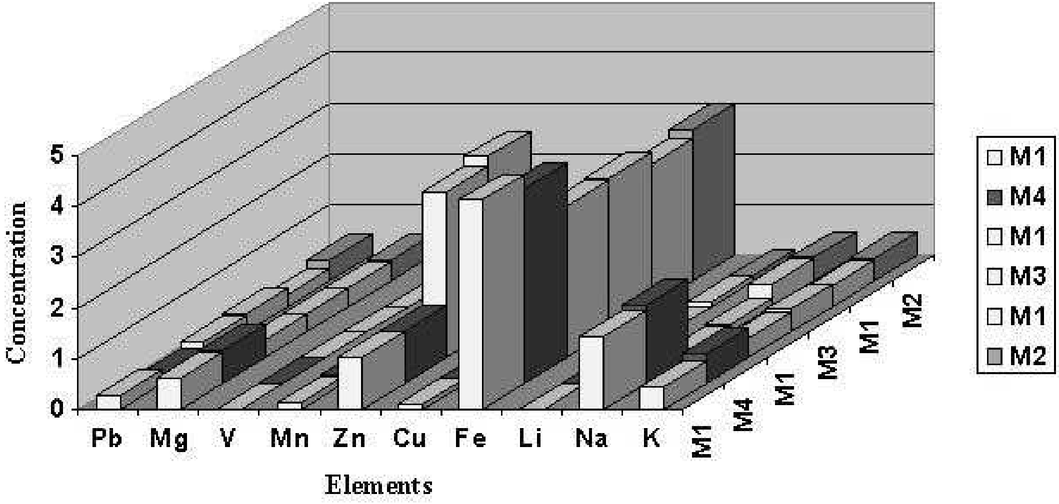
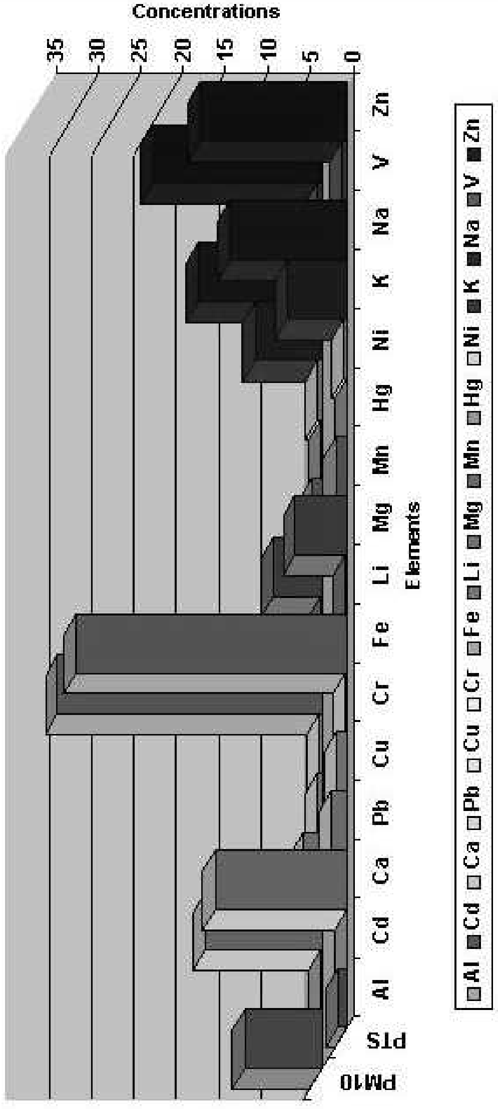
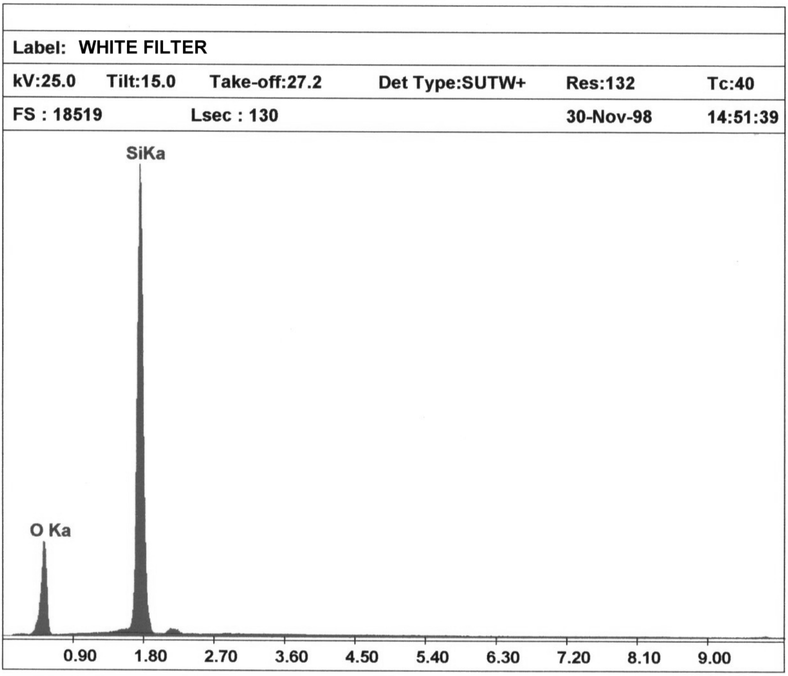


Figure 2:Element mass in dust (g/kg)





Label: WHITE FILTER

kV:25.0 Tilt:15.0 Take-off:27.2 Det Type:SUTW+ Res:132 Tc:40

FS : 18519 Lsec : 130 30-Nov-98 14:51:39

EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %
O K	45.67
SiK	54.33
Total	100.00

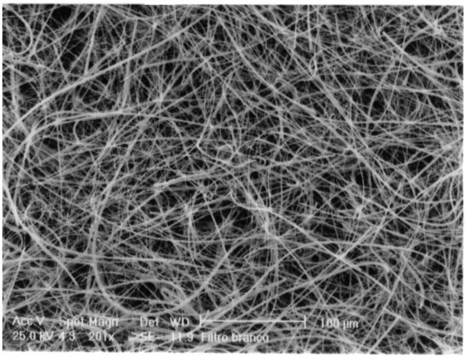
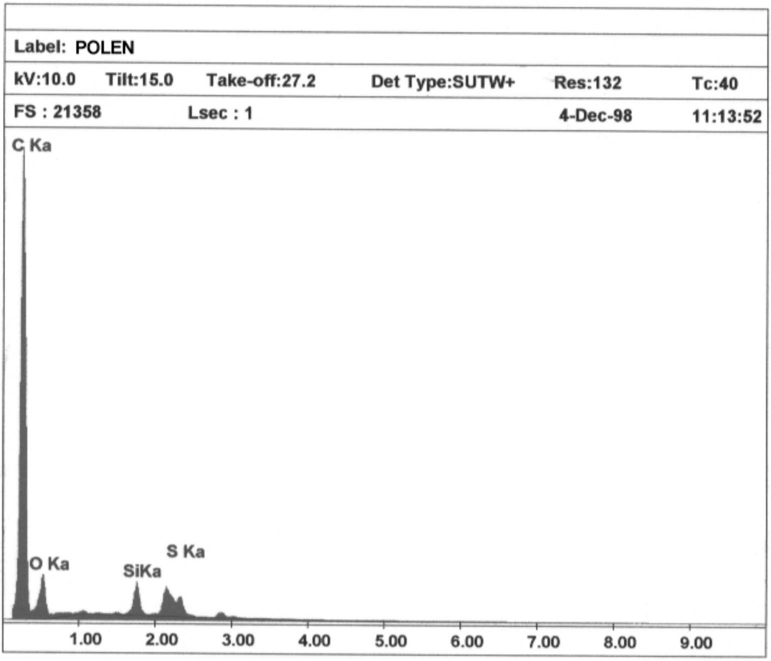


Fig. 3. Electronic microscopy analysis of the white filter.



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %
C K	82.67
O K	10.29
SiK	3.53
S K	3.52
Total	100.00

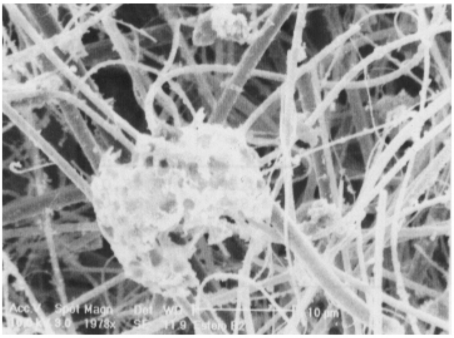
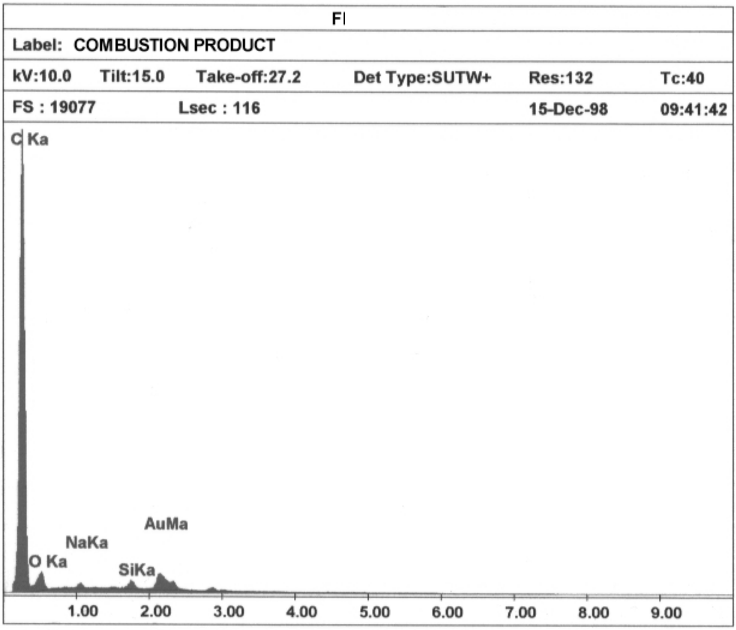


Fig. 4. Electronic microscopy analysis of the atmospheric dust – Pollen.



Fl

Label: COMBUSTION PRODUCT

kV:10.0 Tilt:15.0 Take-off:27.2 Det Type:SUTW+ Res:132 Tc:40

FS : 19077 Lsec : 116 15-Dec-98 09:41:42

EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %
C K	82.79
O K	5.22
NaK	0.67
SiK	1.20
AuM	10.12
Total	100.00

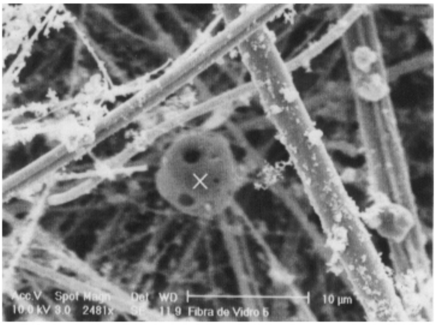
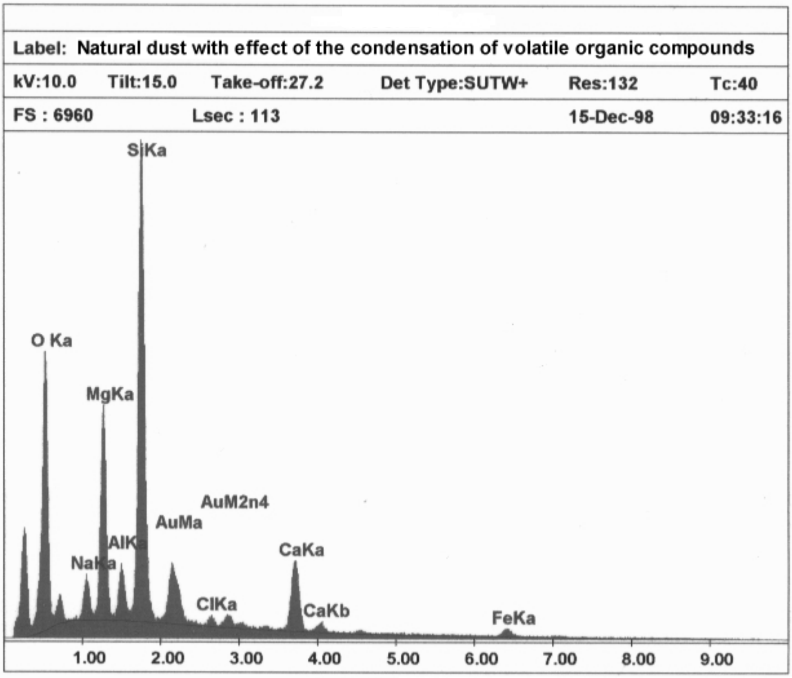


Fig. 5. Electronic microscopy analysis of the atmospheric dust – Combustion product.



Label: Natural dust with effect of the condensation of volatile organic compounds

kV:10.0 Tilt:15.0 Take-off:27.2 Det Type:SUTW+ Res:132 Tc:40

FS : 6960 Lsec : 113 15-Dec-98 09:33:16

EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %
O K	20.95
NaK	2.24
MgK	9.61
AlK	2.63
SiK	26.30
AuM	14.32
ClK	0.92
CaK	12.30
FeK	10.72
Total	100.00

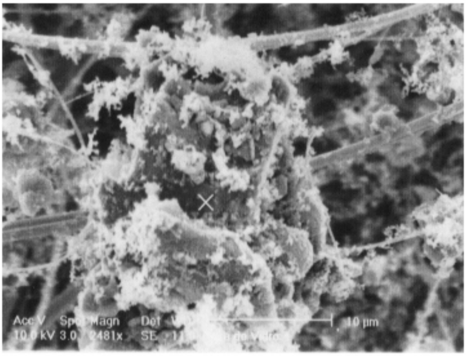


Fig. 6. Electronic microscopy analysis of the natural dust with +effect of the condensation of volatile organic compounds.

TANIA RENATA PROCHNOW
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Lutheran University of Brazil - ULBRA
Canoas, RS - Brazil