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Particulate matter from different fuels

Nancy Esther Quaranta
Universidad Technológica Nacional, Facultad Regional San Nicolás, Cólon 332.2900, San Nicolás, Argentina
Tel: 54-461-20830, Fax: 54-461-20820, E-mail: nancyutn@cablenet.com.ar

Abstract

The present study is developed into a bilateral project between the power company, Central Térmica San Nicolás (CTSN), and our work group, Environmental Studies Group which developes research activities in the San Nicolás Regional Faculty of the National Technological University. The objective of this work is the evaluation of the city air quality in relation to one of the characteristic air contaminants of this kind of factory: the particulate matter (PM). Another purpose of this study is to correlate the results (PM concentration, morphology, and chemical composition) with the kind of the used fuel. During the studied period the power company used different kinds of fuel like national and South African coal, fuel oil and natural gas. The analysis of this specific contaminant involves daily sampling, samples preservation and evaluation according to international standard method (high volumen gravimetric method). The particulate matter is characterized by optical and electronic microscopies, EDAX and X-ray diffraction. The results show that the PM pollution level keeps under the established level for air quality, even in the more unfavorable areas taking into account the meteorological data and the factory as emission source. The particulate matter characteristics depend on the kind of fuel burnt. It determines the PM chemical composition, morphology and particle size distribution.

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Introduction

During the last 40 years the environmental problem has stopped being a fashion and has turned out to be an actual concern that is shown in inminent need of strategic changes. Industry, the main author of our development, is also the fundamental support for those required changes.

The main sources of pollution in the urban areas are: transports, power production and industrial processes in general. Industrial activities generate specific contaminants for each process, as regards their characteristics and effects.

The primary contaminants emitted to the atmosphere during the combustion processes are carbon oxides, nitrogen oxides, sulphur dioxide and particulate matter in general, as well as other compounds in concentrations that depend on the process.

The particulate matter is the only atmospheric contaminant that hasn't got a definite composition and has as principal components a fraction soluble in water that consists of sulfates, nitrates, chlorides, amonium salts, etc., and a fraction that is not soluble which contains powder and minerals coming from the ground, coal absorbed gases, lead, hydrocarbons, etc.

The atmospheric particles produce serious damages to the human organism, they penetrate by respiratory system and their breathing grade depends on the particle sizes. It is not clear if the effects on the health are mainly produced by the particle physical characteristics, or if they are the result of the chemical composition of the particles.

The natural sources that can be mentioned are: soil erosion, volcanic eruptions, forest fires, pollen and spores, etc. The sources of anthropogenic origin are combustion processes, industry and vehicles.

The degree of pollution in a region does not depend only on the sources but also on the dispersion of the pollutants in the air. This is directly related to the meteorologic conditions of the area, specially wind, rain and temperature of the surrounding atmosphere.

It is here where the mathematical models of contaminant difussion take a tremendous importance. The main aim of these standards is to predict the evolution of the contaminants so as to be able to prevent the effects they cause on the systems. The environmental standards more developed at present are the ones that predict the behaviour of the gas and particulated pollutants in the atmosphere.

The present study is developed into a bilateral project between the power company, Central Térmica San Nicolás (CTSN), and our Institution (FRSN).

The aim of this work is to evaluate the quality of the air in the city in relation to the particulate matter, taking CTSN as a source, and trying to correlate PM concentration, morphology and chemical composition to the kind of fuel used.

Experimental

Three monitor stations were used, whose locations were determined by means of a diffusion model [1], taking into account the meteorologic conditions, the kinetic conditions of evacuation of gases and the height of emission. The meteorologic station is located in the FRSN.

Two of the sampling stations are located in the predominant directions of the frequency of winds, that is, down wind the CTSN, whereas the third is barely influenced by this source due to its location. The determined results for this sampling station can be considered estimative of bottom level of pollution of the area.

This basic level of pollutants can be also determined by means of the analysis of the results obtained during periods of minimum production of the factory, or, better still, when the factory stops working. In this research in particular, which covers an evaluation period of a year, it is considered for this analysis two months in which the plant production was 10% of the usual one.

The aim of this work is the specific evaluation or Particulate Matter (PM), and its relation to the kind of fuel used. During the period under study, the plant used different fuels: solid fuels coming from Rio Turbio, Argentina, and from South Africa, liquid fuels, specially fuel oil, and natural gas. The obtained results were analysed trying to correlate the characteristics of the particulate matter with the kind of fuel used.

The strategy for the picking up, handling, conservation and analysis of the samples are in accordance with the standard criteria of international institutions [2,3].

The samples were picked up daily at the three sampling stations. The samples were taken from a height greater than five meters to diminish the influence of the traffic and get atmospheric powder.

The evaluation of total suspended solids (PM) was done through the method of high volume (gravimetric), keeping the particles on membranes or filters. It was used paper-filters, respecting faithfully the drying criteria.

For the picking up of PM a high volume equipment was used, with time or volume way of operating. This unit is based on a microprocessor designed to eliminate the use of mechanical rotation and time mechanic measurers, which simplifies the sampling process and adds great accuracy to the data. For the gravimetric determinations an analytic balance with 0.1 sensibility was used.

The characterization of the particulate matter was done by optical microscopy, scanning electronic microscopy (SEM), X-ray electronic diffraction (EDAX), and X-ray diffraction.

The EDAX analyses were done on the particulate matter samples extracted from the filters, in order to avoid possible mistakes due to the Si and Ca contents of them.

The optical observance took place in a Zeiss microscope, with an annexed Phillips video camara, which allows the images to be digitalized. The SEM and EDAX analyses were performed with a Phillips 505 equipment. The analyses of the X-rays of the powdered samples were obtained for values 2θ between 10° and 70° with a Phillips PW 1390 equipment, with $CuK\alpha$ radiation and Ni filter. The operating conditions were 40 kV, 20 mA and 1°/min speed. The obtained diffraction patterns were analysed according to the ASTM standards [4].

Results and Discussion

The monthly average of total suspended solids in the air (PM) calculated as arithmetic media of daily concentrations of 24 hour samples, are inferior to the values established as 24 hour average allowable concentration in the Standards for air quality in the National Legislation (PM10: 150 $\mu g/m^3$), as well as they are inferior to the 24 hour average allowable concentration criteria of WHO and EPA [2,3].

During the period under investigation, the days when higher concentrations of PM were determined coincided with windy and dry weather, so it is infered that these levels go together with an increase of botton level rather than an increase in the specific sources. San Nicolás is a rather small city, that is the reason why the area could be considered as semi-urban one.

The bottom level determined during the months of minimum production of CTSN was 30 $\mu g/m^3$ on rainy days, 70 $\mu g/m^3$ on dry and not windy days, and 90 $\mu g/m^3$ on dry and hard windy days. These values coincide with the ones usually obtained in the sampling station located in an up-wind area from the plant.

In the studied period the results of the particulate matter were related to the different kinds of fuels used, taking into account the basic levels and the meteorologic conditions prevailing in each period according to the different fuels.

The concentration of particulate matter for the different kinds of fuels turned out to be slightly superior in the case of PM coming from solid fuel. Under similar climate conditions (temperature, wind and humidity) values 10% above were obtained.

Some important variations in concentration were observed, which coincided with the meteorologic changes and not with the kind of fuel used.

The EDAX analysis and the microscopic observations (SEM) show important differences as regards the PM chemical composition and the distribution of the particle size, depending on the fuel used.

In Table 1, the chemical composition determined by EDAX is observed, for the PM picked up during the periods when the different fuels are used. Different letters were used to name the samples, indicating the kind of fuel used during the period when they were taken (s:solid, l:liquid and g:gas). The sample named PMb refers to particulate matter taken in the period of minimum production of the plant (botton level).

Table 1: EDAX analysis of the particulate matter.

Element	***PMs (%)***	***PMl (%)***	***PMg (%)***	***PMb (%)***
Fe	20.7	14.3	16.3	8.6
Ca	13.9	18.1	17.0	5.5
Mg	2.0	----	----	----
Si	37.9	38.3	38.0	61.5
Zn	1.3	----	----	----
Al	18.4	29.3	28.7	24.4
Na	2.8	----	----	----
K	3.0	----	----	----

Other elements found in very small concentrations are: P, Cl, Ti, Ni, V, Cu and Pb.

The analysis of the results leads to establish a relationship between the kind of fuel and the chemical composition of the produced particulated material. When the fuel is solid, the obtained PM contains elements such as Mg, Zn, Na and K, which do not appear or appear in very small concentrations, in the case of liquid or gaseous fuels. In these cases, the same elements detected in the analysis of the PMb sample are observed, although they appear in different proportions. The materials coming from liquid and gaseous fuels are more richer in Ca and Fe than MPb.

Figure 1 is a SEM photograph where the morphologic characteristics of the particles sticked to the fibres of the collector filter can be observed.

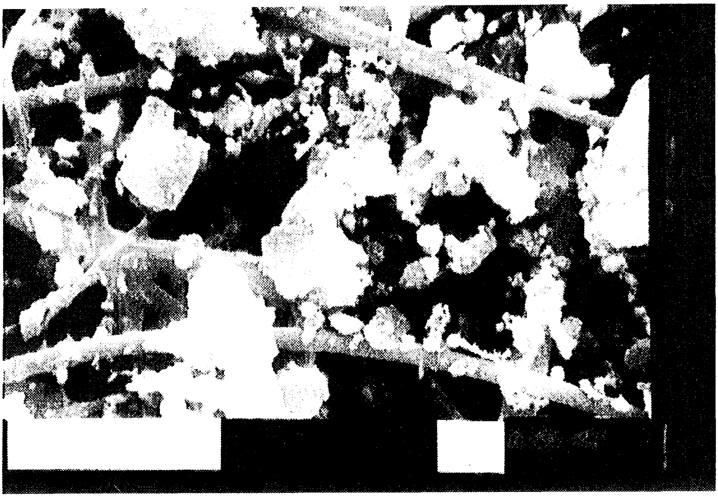

Figure 1: PMs SEM microphotograph. Bar: 10μm.

The analysis of the particle size distribution done by SEM shows considerable differences among the samples PMs, PMl and PMg. Numerous samples for each different kind of particulate matter were used, as well as counting fields at different augmentation for each sample. The obtained average values correspond to the counting of 50 fields for each augmentation used (100x, 500x, 1000x, 2000x and 5000x). In Table 2 the obtained results, expressed in percentage of particles corresponding to each analysed size are observed.

It is clearly seen that when the fuel used is solid, the particulate matter presents a higher percentage of big particles (>4μ). In the case of liquid and gaseous fuels, the particle size distribution was similar between them, with a high percentage of small particles. In order to establish a comparison, the distribution obtained for the samples PMb is included in the table.

Taking into account the results of EDAX and the particle size distributions it is possible to say that when the fuel is liquid or gaseous, a particulate matter formed by smaller particles rich in Ca and Fe is obtained, and when it is solid, the particles are bigger in size and they have important concentrations of Fe and Ca, as well as Mg, Na and K.

Table 2: Particle size distribution in particulate matter samples.

Particle Size (μ)	***PMs (%)***	***PMl (%)***	***PMg (%)***	***PMb (%)***
< 0.5	39	67	68	58
1-3	26	22	24	24
4-9	19	7	5	10
> 10	16	4	3	8

The X-ray analyses done on the samples gave as a result very complex diffractograms due to the presence of a great variety of mineralogic phases. The probable phases that have been determined are the following: calcium silico-aluminate, ferric oxide, sphalerite, chalcopyrite, silicates and bornite.

Figure 2: Optical photograph of coal particle. Aumengtation 2000x.

The morphologic study of the PM, done through optical microscopy, shows iron oxide particles, carbon material, glittering SiO_2 particles, and the presence of microspheres, typical of combustion processes at high temperatures. These formations are easily distinguished through this technique, due to the different colours they have and their morphologic differences. The presence of carbon particles and microspheres is greater in the case of samples coming from solid fuel. Figures 2 and 3 shows this kind of particles.

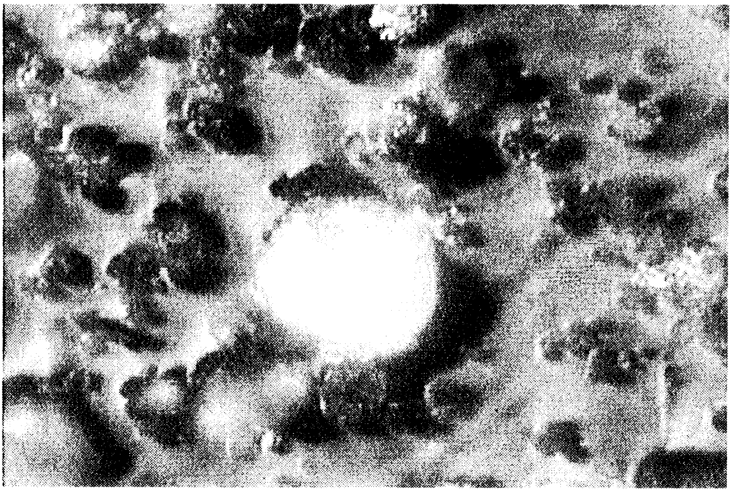

Figure 3: Optical photograph of a microsphere. Aumengtation 2000x.

The SEM and EDAX analyses, which were performed on individual particles, allow to determine compositions and morphologies which are common to the ones found in nature, and other kind of particles of anthropogenic origin, with very particular shapes and complex compositions. The samples obtained during the period when solid fuel was used, present the pecularity of the presence of alumina particles, Ca chloride and a great quantity of silicoaluminous and carbon material. Figures 4 to 6 show some of these peculiar formations.

In the case of PM samples derived from the use of liquid and gaseous fuels, an important quantity of spheric particles of Cu and Fe are found. It is noticeable the presence of silicates and silicoaluminates. In the Figures 7 to 9 it can be observed the remarkable differences in the morphology of these particles.

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Figure 4: PMs SEM photograph: alumina particle

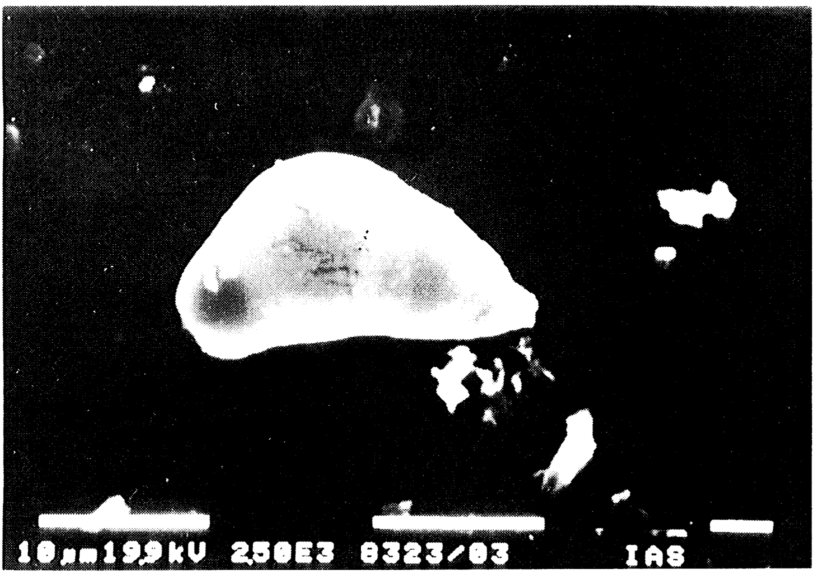

Figure 5: PMs SEM photograph: calcium chloride particle.

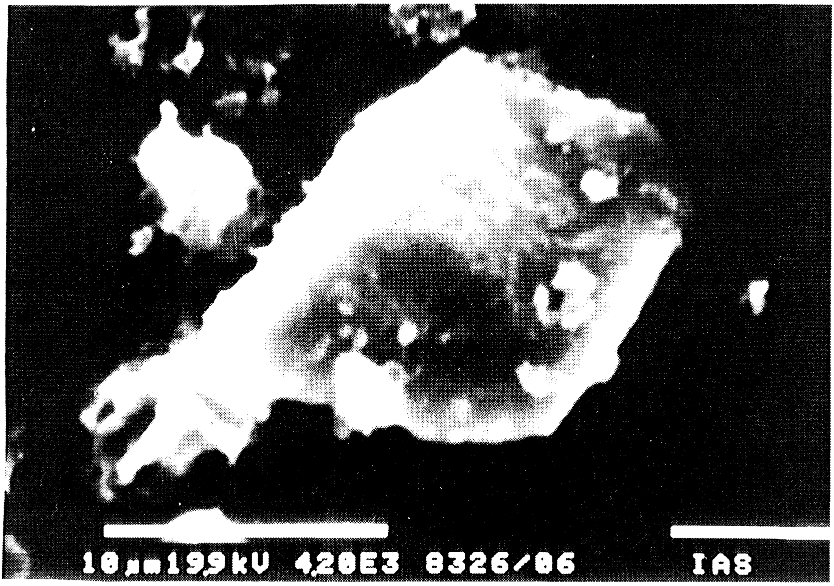

Figure 6: PMs SEM photograph: calcium silicoaluminate particle.

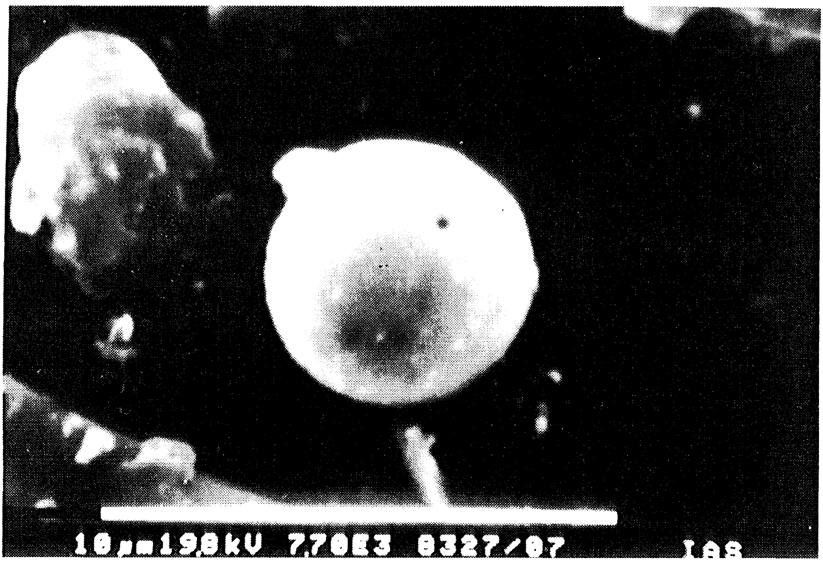

Figure 7: PMl SEM photograph: Cu particle.

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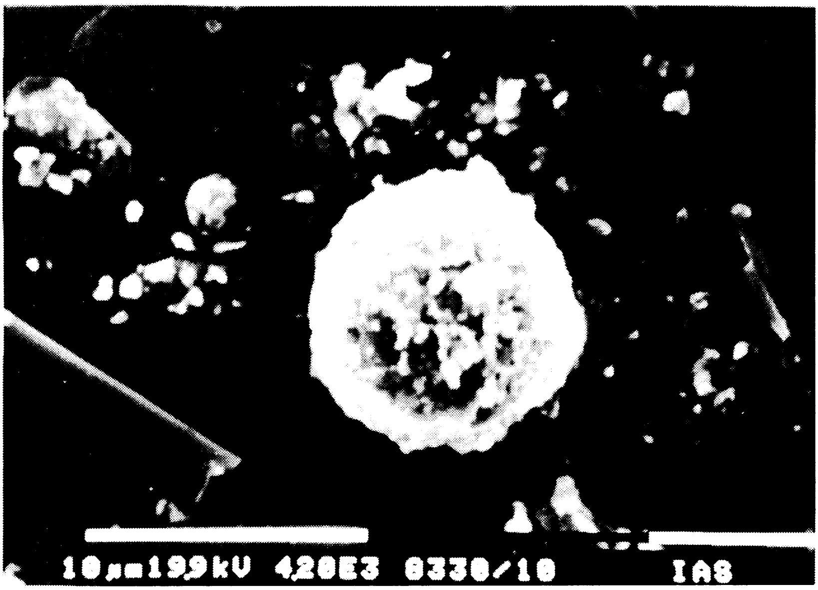

Figure 8: PMg SEM photograph: Fe particle.

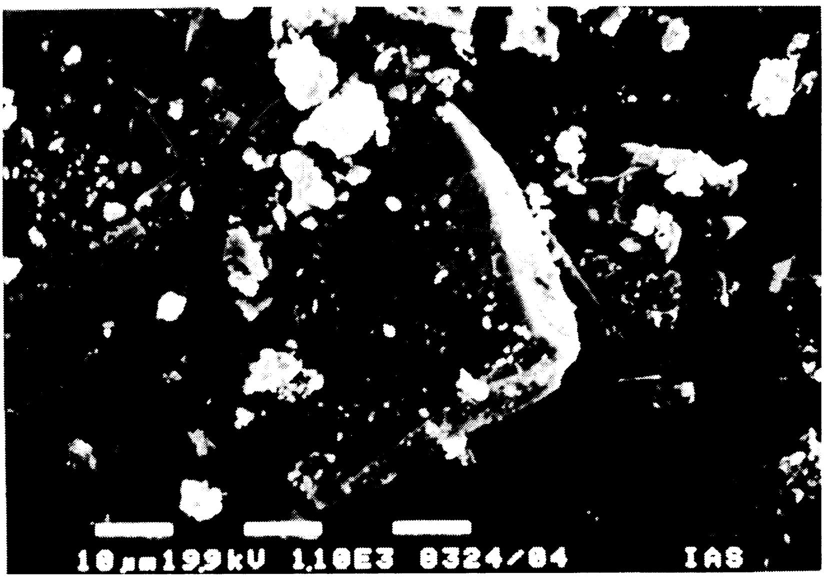

Figure 9: PMl SEM photograph: calcium silicate particle.

Conclusions

The present study contributes to the knowledge of the one of the air contaminants characteristic of combustion processes: the particulate matter.

The levels of this pollutant evaluated in the areas considered as the most unfavourable, taking as a source the power plant Central Térmica San Nicolás, are kept under the levels established for the air quality.

The concentration of particulate matter is slightly modified by the kind of fuel used.

The kind of fuel used has an important influence in the chemical composition, particle size distribution and morphology of the particulate matter produced.

A particulate matter formed by smaller particles rich in Ca and Fe is obtained when the fuel is liquid or gaseous. When it is solid, the particles are bigger in size and they have important concentrations of Fe and Ca, as well as Mg, Na and K.

References

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[4] Joint Committee on Powder Diffraction Standards. ASTM Powder Diffraction File. 1993.

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