

## EMISSION AND ATMOSPHERIC IMPACT OF A CUBAN REFINERY

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## ABSTRACT

In the processes of an oil refinery, considerable emissions of atmospheric pollutants are generated that produces hazard to man's health and the environment. In this study, the obtained results of the characterization of the gaseous emissions by chimneys of the furnaces and boilers of the refinery are presented. The sampling and analysis of SO<sub>2</sub>, NO<sub>x</sub>, CO, total suspended particles, and flow measurements were carried out. The aromatic hydrocarbons were determined by UV Spectroscopy. The model of dispersion of pollutants emitted by chimneys was executed using the software for the calculation of the gas concentration from continuous industrial sources following the methodology approved in the Cuban standards, according to the Berliand Model. We conclude that the combustion processes of the Refinery reflect a fault, given the particles emissions. The emissions of the furnaces and boilers exert negative impact or pressure on the atmospheric environment in the area.

**Keywords:** refinery, impact, heaters, boilers

## NOMENCLATURE

A	atmospheric thermal stratification constant
C <sub>20 min</sub>	instantaneous concentration, mg/m <sup>3</sup>
C <sub>24 h</sub>	daily average concentration, mg/m <sup>3</sup>
CO	carbon monoxide
D	stack diameter, m
Dist	distance, m
E	gases emission, g/s
GF	glass fiber
H	stack height, m
HCA	aromatic hydrocarbons
NO <sub>x</sub>	nitrogen oxides
RC	concentration ratio
SO <sub>2</sub>	sulfur dioxide
T	stack gases temperature, °C
TSP	total suspended particles
v	stack gases velocity, m/s
VOC	volatile organic compounds

## Greek symbols

α	confidence level
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## INTRODUCTION

The correct evaluation of the atmospheric environment to know the levels of pollutants in the oil activity is one of the fundamental demands for the taking of measures that guarantee to maintain the appropriate levels with relationship to the

quality of the environment (Slater, 1996).

The nitrogen oxides (NO<sub>x</sub>) are chemical compounds, in their largest part derived from combustion processes, product of the contained nitrogen in the air that is required for the combustion. There also exist natural sources, mainly for the bacterial activity in the soil.

The so called acid rain is a different form of air pollution originated by wet deposition of sulfur and nitrogen oxides that has been studied a lot in recent years (UNEP, 1992; López, 1995).

The total suspended particles (TSP) that originate from the incomplete combustion of carbon (soot) increase the existent breathing and cardiovascular illnesses, they alter the organic defense systems, damage lung tissues and can cause cancer and premature death (Porteous, 1996). People with flu, asthma or lung or cardiovascular illnesses are the most vulnerable, along with the children and the elderly.

The volatile organic compounds (VOC) can cause great number of noxious goods for the health, being cancer one of the worries, since it is not established a clear threshold of exposure. The cancer, is assumed to take place when a simple cell, due to changes in its DNA, spreads by multiplying without control and at great speed. It has been demonstrated that very small concentrations of VOC can attack the DNA. The affected cell can increase its speed of duplication in a non controlled way until reaching a high concentration of cells that is recognized as a cancer (Wagner, 1996).

The carbon monoxide (CO) is the most abundant and broadly distributed atmospheric pollutant of those that are in the inferior layer. It is present in the flue gases of vehicles and in effluents for incomplete combustion.

The short and long term monitoring of emissions is of great importance to determine if the oil activity in a certain area is causing contamination. The effective programs of monitoring can identify the problems before they become a threat to the environment (Kiely, 1997).

One of the factors to keep in mind in the sampling of gases is the heterogeneity of the discharge in the duct, which is manifested in the distribution of speeds (Yoest and Fitzgerald, 1996).

For the sampling of gases three main methods have been broadly utilized: scrubbing, condensation to low temperature and adsorption (Cheremisinoff and Morresi, 1978; Calvert and Englund, 1984; Yoest and Fitzgerald, 1996; Brieda et al., 1986; Rudolph et al., 1997).

The recently developed equipments for the sampling and automatic determination of concentrations of gases in stationary sources (ISO 10396, 1993; Jahnke, 1993) include some of these basic methods, although their recommended locations are in places with easy access and they are affected by high concentrations of particles (Novello, 1995; White, 1995).

The sampling of particles under isokinetic conditions has to guarantee representative samples of each emission, avoiding inertial forces that become more significant for the particles bigger than three microns. The well-known methodologies are applied using a system that inserts a filter paper to pick up the particles. Filters of glass fiber type GF/A and filters FPP-15 are used. The samples take in the same points of measurement of speed, picking up samples integrated in the time, applying the concept of accommodation of temporary and spatial variations before referred.

For the calculation of the dispersion of pollutants in the atmosphere three fundamental theoretical systems exist, with multiple numeric solutions, for their practical use in the establishment of the environmental impact of emissions of stationary sources.

Starting from the basic formulas of Berliand, different methodologies of calculation of dispersion of pollutants were developed, finding wide acceptance and application in Eastern Europe

and Cuba, where it has been adopted as standard methodology (NC 39, 1999) using a value of 200 for the constant of atmospheric thermal stratification (A) according to that proposed for our environmental conditions (López, 1984).

## EXPERIMENTS

The gaseous emissions of stationary sources of the boilers and ovens of a Cuban refinery of petroleum were characterized, by flow measurement and sampling program according to established methodologies (Yoest and Fitzgerald, 1996; ARPEL, 1998; ARPEL, 1997).

The sampling of SO<sub>2</sub>, NO<sub>x</sub>, CO, CO<sub>2</sub> and O<sub>2</sub>, were executed with a Combustion Analyzer, MSI model from Draeger. The sampling of total suspended particles in chimneys was carried out isokinetically by its collection in a filter for its analysis for the gravimetric method (ISO 9096, 1992). Measurements of flow by means of a Pitot type S tube were also carried out.

The sampling to determine aromatic hydrocarbons was carried out on activated carbon with later elution with n-hexane for its analysis for Ultraviolet spectroscopy in a spectrophotometer Cintra 40 of the GBC, using n-hexane bi distilled like reference. The concentration was calculated by means of a calibration curve prepared with an international standard. The absorbances were obtained to 255 nm with quartz cuvette of 1 cm of light path, slit of 1.5 nm and time of integration of 1 second. The spectra were obtained in the same equipment in the range of 200 - 400 nm, interval of data of 0.853 nm, slit of 1.5 nm and speed of registration of 1000 nm/s.

The model of dispersion of pollutants emitted by chimneys was executed using the program for the calculation of the concentration starting from continuous industrial sources (Álvarez, 1994) following the methodology approved in the Cuban norm (NC 39: 1999) according to the pattern of Berliand. The value of the constant of atmospheric thermal stratification A that it defines the most adverse natural conditions of diffusion took similar to 200, according to that proposed for our country for flat areas or with topography of little complexity and height, which has been accepted in the Cuban norm of reference. The meteorological data were taken from the Climatic Summary of Cuba (1991), published by INSMET.

The model of the dispersion was carried out

for the SO<sub>2</sub> that is the fundamental pollutant emitted by the valued sources. The data of the emissions of ovens and boilers (Tab. 1) for the dispersion calculations were obtained in the own emission sources, giving higher validity to the survey.

Table 1. Data of emissions for calculations of dispersion of pollutants.

Chimneys		v (m/s)	D (m)	H (m)	T <sub>g</sub> (°C)	E (g/s)	ΔT (°C)
Ovens	F 101	1.20	3.00	55	590	42.6	547
	F 102						
	F 103						
Boilers	1	3	1.20	8.36	363	7.2	320
	2	3	1.20	8.36	363	7.2	320
	3	3	1.20	8.36	363	7.2	320

In the cartography it was considered the annual average frequency of occurrence of the mean values of speed for each one of the 16 directions of the wind (Álvarez, 1994), taking the meteorological data that appears in the Climatic Summary of Cuba (1991).

For the development of this work the digital sheets of Cuba were used (sheet 1: 250 000), made for the Geographical Information System INFOPET (1999) of the Petroleum research Center (CEINPET). The geodesic data were converted to the Lambert North Coordinated System.

The data of the relative concentration of the SO<sub>2</sub> were interpolated using the system Surfer 7 for Windows starting from the results of the program of calculation of the dispersion, using as interpolation method a liner krigging, adding it to the cartographic representation of the area.

In the statistical prosecution of data the program STATISTICA was used to determine behavior averages and correlations of interest.

**RESULTS AND DISCUSSION**

As it is observed in Tab. 2, the level of concentration of sulfur dioxide in the ovens and the boilers are about three times higher than the limits that should not be exceeded of pollutants emitted by chimneys for these processes (World Bank Group, 1997), as a result of the use of crude oil with high sulfur content (ARPEL, 1992). In the ovens, the levels of NO<sub>x</sub>, as the suspended particles are inside that regulated. The Aromatic Hydrocarbons are not regulated in these norms, although the opposing levels are considered high, keeping in mind their adverse effects to human health. In the boilers the concentrations

of PST are superior to the limits before referred, and it also reflects a faulty combustion (ARPEL, 1999). The NO<sub>x</sub> content is within the regulation.

It can be seen in Tab. 3 that the emitted load of SO<sub>2</sub> for the ovens and boilers are significant.

Table 2. Characterization of emissions originated in chimneys of Refinery<sup>a</sup>.

Chimneys <sup>a</sup>	SO <sub>2</sub> (mg/m <sup>3</sup> )	NO <sub>x</sub> (mg/m <sup>3</sup> )	CO (ppm)	HCA (mg/m <sup>3</sup> )	PST (mg/m <sup>3</sup> )
Ovens F101, F102, F103	5982	110	55	3.8	12
Boiler 1	6337	119	64	2.5	144
Boiler 2	6337	119	64	2.5	144
Boiler 3	6337	119	64	2.5	144
Standard	< 2000 <sup>b</sup>	460 <sup>b</sup>	-	-	100 <sup>b</sup>

<sup>a</sup> Average Values of pollutants.

<sup>b</sup> Limits that should not be exceeded of pollutants emitted by chimneys of boilers, ovens, incinerators and equipments of electric generation (World Bank Group, 1997).

Table 3. Average polluting load that contribute the valued chimneys, kg/h.

Chimneys	Flow (Nm <sup>3</sup> /h)	SO <sub>2</sub>	NO <sub>x</sub>	PST
Ovens F101, F102, F 103	25434	152	2.8	3.7
Boiler 1	4069	25.8	0.48	0.58
Boiler 2	4069	25.8	0.48	0.58
Boiler 3	4069	25.8	0.48	0.58

**Modeling the Dispersion**

As it is observed in Tab. 4, for the boilers the instantaneous maximum concentration of SO<sub>2</sub> finds it at a distance of 210 meters of the source, which means that for concentrations of 20 minutes that area it is contaminated by this pollutant, since the relationship C/CMA is superior to one (NC 39, 1999).

Table 4. Boilers. RC 20 minutes, direction: S-N. Probability of Occurrence: 20%.

Dist (m)	C <sub>20 min</sub>	RC <sub>20 min</sub>	C <sub>24h</sub>	RC <sub>24h</sub>
0	0	0	0	0
50	0.23971	0.47942	0.06009	1.20173
100	0.65386	1.30772	0.1639	3.27797
150	0.94621	1.89242	0.23718	4.7436
200	1.0355	2.071	0.25956	5.19122
210	1.03697	2.07394	0.25993	5.1986
250	0.99786	1.99571	0.25013	5.00251

In Fig. 1 it is corroborated what had been previously mentioned. Similarly, the daily average concentration (24 hours) is a lot superior to that established in the Cuban norm for the ambient air ( $0.05 \text{ mg/m}^3$ ), reflected in the high ratio of concentration obtained ( $RC_{24h} = 5.2$ ).

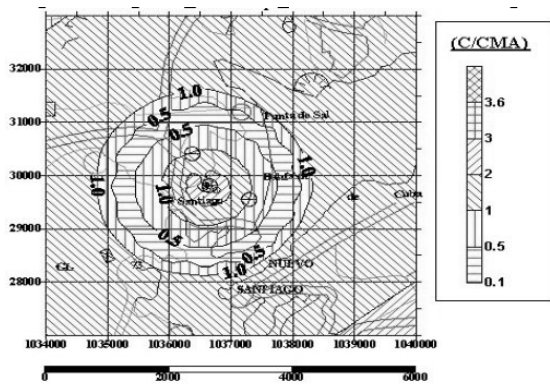


Figure 1. Values of concentration ratio regarding the acceptable one in the boilers.

In Tab. 5 it can be seen that, for the ovens, the instantaneous maximum concentration of  $\text{SO}_2$  occurs at a distance of 1200 meters of the source, thus for concentrations of 20 minutes and of 24 hours that area is not polluted, since the relationship  $C/CMA < 1$  in both cases, because the height of the chimney, favors the dispersion of the studied pollutant.

In Fig. 2 it is corroborated what was seen before for the emissions of the ovens of the refinery.

In Fig. 3 the impact is shown to take place on the whole area by the boilers and the ovens, and a quite extensive area is observed to be contaminated by  $\text{SO}_2$ , since the  $C / CMA > 1$ .

Table 5. Ovens. RC 20 minutes, direction: S-N. Probability of occurrence: 20%.

Dist (m)	$C_{20 \text{ min}}$	$RC_{20 \text{ min}}$	$C_{24h}$	$RC_{24h}$
0	0	0	0	0
100	0.00395	0.00789	0.00099	0.01979
500	0.05917	0.11834	0.01483	0.29662
1000	0.10649	0.21297	0.02669	0.53385
1200	0.10856	0.21711	0.02721	0.54422
1500	0.10236	0.20473	0.02566	0.51317
2000	0.09069	0.18137	0.02273	0.45463
2500	0.07909	0.15818	0.01982	0.39649

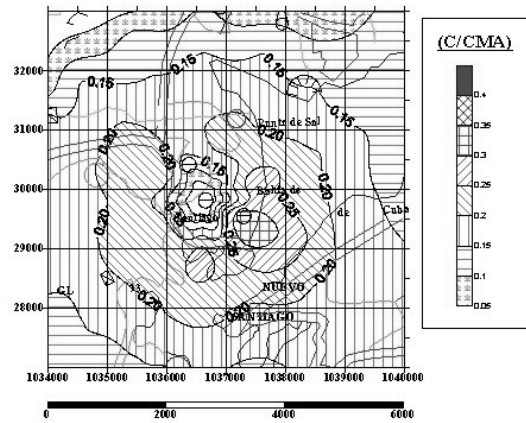


Figure 2. Values of concentration ratio regarding the acceptable one in the ovens.

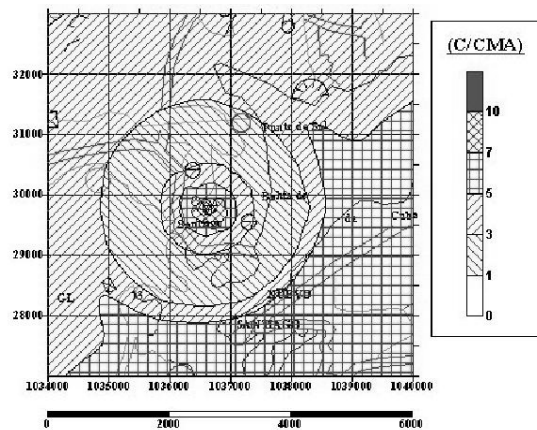


Figure 3. Values of RC 20 minutes regarding the acceptable one, ovens + boilers.

**Statistical analysis**

The multivariate statistical analysis using the method of union of the centroide of group of couples weighed by the Euclidean distances shows in the tree diagram (Fig. 4), two very defined groups of variables, one of those reflects the relationship of the CO with  $\text{NO}_x$  and TSP, associated to the conditions of operation of ovens and boilers, and the other one relates to the CO with the aromatic hydrocarbons.

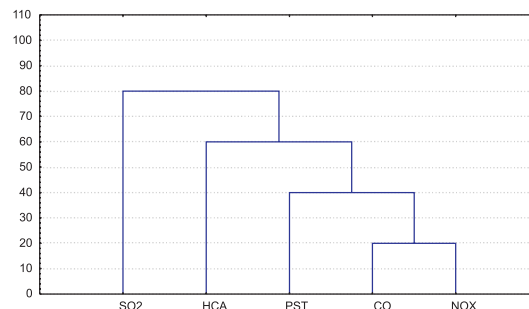


Figure 4. Diagram of tree of the variables.

From the regression analysis step by step, highly significant correlation coefficients were obtained for  $\alpha = 0.05$  of the levels of concentration of the NO<sub>x</sub> and the aromatic hydrocarbons with the CO (Tab. 6).

Table 6. Obtained correlation coefficients.

	NO <sub>x</sub>	HCA	TSP
CO	0.999	0.961	0.810

## CONCLUSIONS

The combustion processes in the ovens and boilers of the Refinery reflect a faulty combustion, given the found emissions of particles. The combined emissions of the ovens and boilers exercise negative impact or pressure on the atmospheric ambient in the area.

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