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INVESTIGATION OF ATMOSPHERIC PARTICLES SOURCES IN URBAN AND INDUSTRIALIZED AREA AT DUNKERQUE, FRANCE

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ABSTRACT

A physico-chemical characterization of different atmospheric particles samples collected at Dunkerque (France) under the influence of the city centre or a heavy industrialized area has been undertaken. Analytical techniques SEM-EDX, GC-MS, XRD and EPR have been used in combination to reveal specific features following the particulate matter origin. The SEM-EDX study shows the influence of different industrial sources with the detection of Fe-rich spherules, Mn-rich and C-rich particles. The latter were associated to particle-phase PAHs. Specific information on some chemical forms of Fe and Mn present in particles were obtained by XRD and EPR techniques and correlated to the particles origin.

Key Words : Industrial emissions, Suspended Particulate Matter, chemical form, tracer

1. INTRODUCTION

A majority of atmospheric particulate matter in urban and industrial areas is a result of human activities. Many potential anthropogenic emission sources can generally be listed : vehicle and chimney exhausts, waste incineration and various industrial processes. Sometimes it can be difficult to identify the origin of particles as some elements as Fe, Ca, Al, Si, Ti,... can be found in different particulate emissions and can also be encountered in natural particles (Ebert et al., 2000). For this reason, the knowledge of the elemental chemical composition is not always sufficient to indicate the particles origin. To be able to link physicochemical characteristics of particles to their origin, an approach consists to apply in combination different analytical techniques for their specific contribution, and permitting finally to get complementary information.
The purpose of this work is to compare different atmospheric particles samples collected under the influence of a city centre and others under the influence of different industrial activities. Different techniques have been applied to evidence physico-chemical parameters that could be used to differentiate between the urban and the

different industrial particles. The morphology of particles and their individual composition have been studied by SEM-EDX. The organic fraction of particles has been analysed by GC-MS. Complementary investigation of the inorganic fraction has been undertaken with the use of XRD and EPR techniques, to specify the structure and the chemical environment of some metal elements.

2. MATERIALS AND METHODS

2.1. Study Area and Sampling methodology

Sampling was performed at Dunkerque situated on the southern coast of the North Sea (51°04'N ; 2°38'E). This city counting 210 000 inhabitants has been subject to a high implantation of industries in the field of metallurgy, petrol refinery and chemistry during the last 30 years. In 2003, it was estimated that the area of Dunkerque was responsible of 65% of the total industrial emissions of particles in the Nord-Pas-de-Calais county, one of the most industrialized county in France. In the present study, we focused on especially some particulate emissaries present in this area : steel plant (steel works, coke plant, blast furnace, iron ore handling and tanker unloading), ferromanganese metallurgy plant, and particles induced by transport and human activities in the city have also been studied to make a comparison. Five samples have been collected at a distance between 300 meters and 500 meters downstream from the following sources: A: urban emissions, B: coke plant, C: iron and steel plant, D: tanker unloading and blast furnace, E: ferromanganese metallurgy plant.

Atmospheric particles have been collected using high volume samplers (100 m^3/h) onto cellulose filters (Whatman® 41) and glass fibre filters (Whatman® GF/F). In parallel, sampling was also done on polycarbonate filters at a flow rate of 5 m^3/h filter in order to perform SEM-EDX study. To reduce analytical blank, cellulose filters and glass fibre filters have been cleaned prior to the sampling using an acid washing solution and a heating treatment at 450°C respectively.

2.2. Analytical techniques.

SEM images and automated single particle analysis were performed on a LEO 438 VP microscope equipped with an Energy Dispersive X-ray spectrometer (Oxford instruments, UK) (SEM-EDX). For each sample, 1000 particles were analysed. Carbon, nitrogen and oxygen were not taken into account in this analysis. Each data set was then submitted to hierarchical cluster analysis (HCA) using IDAS, a windows based software for cluster analysis (Bondarenko et al., 1996), then similar particles are grouped according to their composition giving the different types of particles in the sample.

Polycyclic aromatic hydrocarbons (PAHs) present as particle-phase PAHs were Soxhlet extracted with dichloromethane for 18 h. The extract was then concentrated to 0.2 ml under pure N_2 gas. PAHs were subsequently analyzed by chromatographic method coupled to mass spectrometry (GC-MS Varian saturn 4D).

X-ray diffraction (XRD) analyses were performed on a Bruker D8Advance X-ray diffractometer using CuKα radiation generated at 40 kV and 40 mA. The 2Θ range was varied from 10 to 70° in steps of 0.02°. Measurements were directly performed on glass fibre filters with an integration time of 25 seconds. The EPR spectra were

recorded at room temperature (T_A = 293 K) and at liquid nitrogen temperature (T_{LN} = 77 K) on a EMX Bruker spectrometer, using a cavity operating with a frequency of ~9.5 GHz (X-band). EPR parameters considered were : (a) *g factor* value, (b) *peak-to-peak signal width* ΔHpp, (c) *normalised double integration value of a signal recorded* at room temperature $Ns(T_A)$ and at liquid nitrogen $Ns(T_{LN})$. Moreover the *$Ns(T_{LN})$ / $Ns(T_A)$ ratio* was determined to get informations about interactions between species and their magnetic properties (Ledoux et al., 2005).

3. RESULTS

3.1 SEM-EDX

Individual particle analysis of A sample collected close to the city centre (Table 1) shows that this sample is composed with a wide variety of particles with low size (<10 μm) being dominated by gypsum (32.7%), Fe-rich (19.9%) and aluminosilicates (13.6%). SEM images of such particles indicate that gypsum (Fig. 1.f) have an angular shape whereas aluminosilicates (Fig. 1.d) and Fe-rich particles (Fig. 1.c) do not have any specific geometry. Carbon particles are not considered in the automated individual particle analysis, nevertheless, many soot particles (Fig 1.h) are observed on this sample. Soot can be typically related to the

Table 1. Types of particles identified using individual particle analysis* (SEM-EDX) and Hierarchical Cluster Analysis.

Particle type	A	B	C	D	E
Aluminosilicates	13.6	6.1	19.1	4.1	5.6
Ca-rich**	2.1	6.6	1.6	4.9	14.5
Ca-S (Gypsum)	32.7	2.3	3.7	1.3	13.8
Other Ca compounds (Ca-Cl ; Ca-S-Si ; Ca-Fe-Si ; Ca-S-K)	5.7		9.5	9.5	1.9
S-rich	1.4		0.6		
Si-rich	4.3	4.1	3.5	1.8	3.2
Other Si Compounds (Si-Al-S ; Si-Al-Mn ; Si-Al-Fe)	5.6	6.2	2.0		5.3
Cl rich	1.9	0.4	6.4		
Na-rich	1.8		11.7		
Other Na Compounds (Na-S-Ca)	3.6		2.2		
Fe-rich	19.9	68.2	33.0	71.6	8.1
Other Fe Compounds (Fe-Ca ; Fe-Ca-Si ; Fe-Ca-S ; Fe-S-K)	7.3	4.9	4.0	6.8	8.5
Mn-rich		1.1			21.8
Other Mn Compounds (Mn-Fe ; Mn-Al-Fe ; Mn-Ca ; Mn-Zn ; Mn-Cl)			1.3		17.1
Pb-rich			1.3		0.3

* carbon, nitrogen and oxygen not considered in the individual particle analysis

** rich compounds composed with more than 75 wt% of the element, other compounds containing a major concentration of the considered element

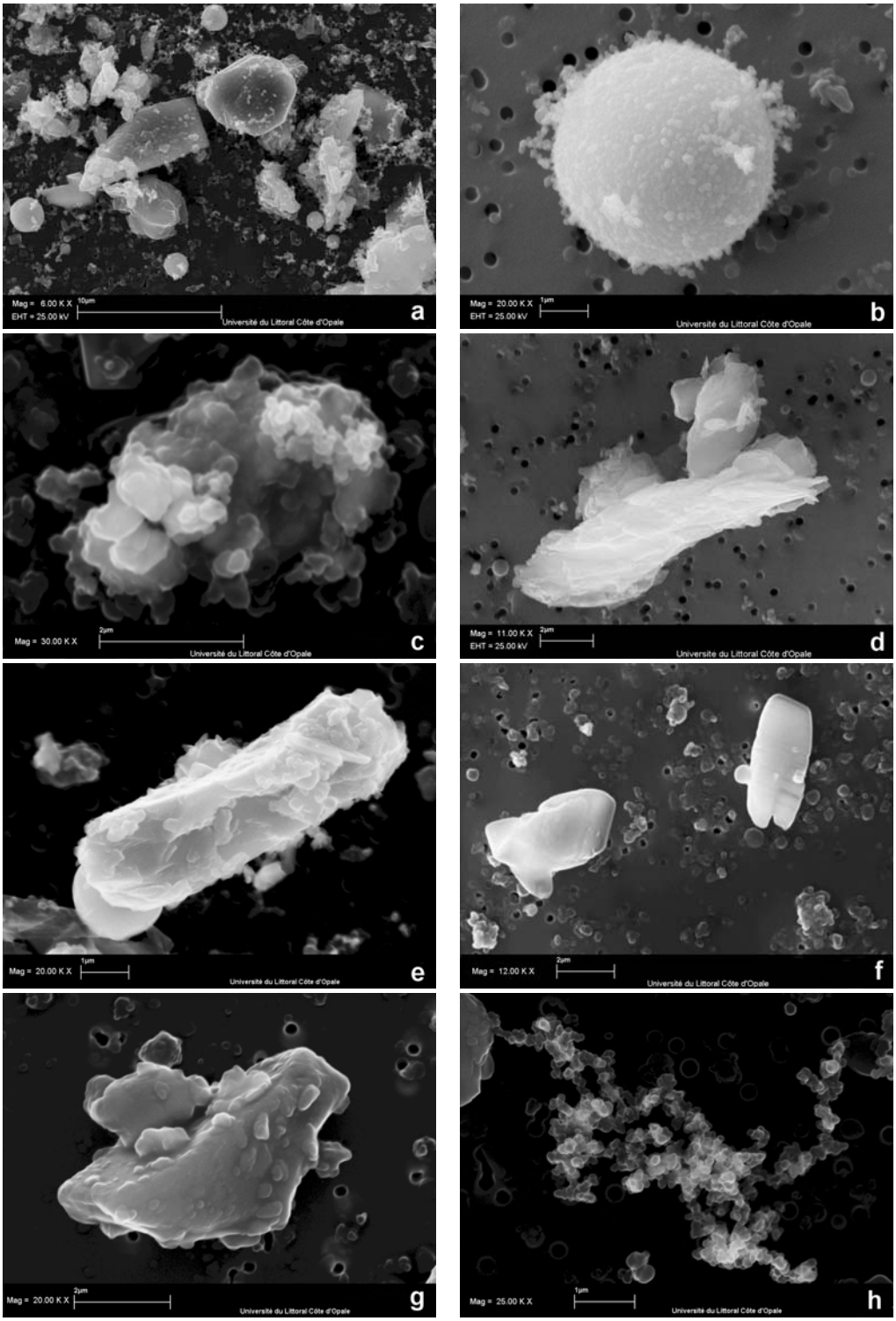

Figure 1. Secondary Electron images of some particles collected in the atmosphere of Dunkerque downwind of different sources : a) Fe ores with angular shape and spherical Fe oxide ; b) Spherical iron oxide ; c) non spherical Fe oxide ; d) Aluminosilicates ; e) Mn-rich ; f) Gypsum ; g) Carbon-rich particle ; h) soot

traffic (Ortner, 1999) with the presence of extremely busy roads inside and southwest of the city. These data for A sample were assumed to be representative of particles found in the city air, even if variations in the chemical composition of particles are typically expected (Ebert et al., 2000). In B sample collected downwind of the coke plant, other C-rich particles (Fig 1.g) appearing with irregular shape and smooth surface were identified (almost 80% of particles). Such particles can be assumed as the most representative of the coke plant activity (coke and coal particles). This influence is also recognized with the detection of Fe-containing particles, due to the presence of iron in the coal raw material. Individual particle analysis shows that C sample is mainly composed with Fe-rich particles (33.0%) and aluminosilicates (19.1%). Fe rich appears in this case as perfect spherical particles (< 5 μm) themselves composed with smaller spherical particles (Fig. 1.b). Xhoffer et al. (1991) reported that such Fe-rich spherules can be classified as purely anthropogenic. These particles are formed during high temperature processes as the coal combustion (Esbert et al., 2001) but can be most likely derived from industrial processes encountered in steel factories (Moreno et al., 2004). D sample collected under the simultaneous influence of Fe ore tanker unloading and blast furnace emissions is also dominated by Fe-rich particles. The proportion of such particles (71.6%) is very high compared to the other samples and it is important to notice that these Fe-rich particles have two different morphologies (Fig. 1.a). First ones are spherical with a smoother surface than steel factory particles and, are characteristic of the blast furnace emissions insofar as the process requires high temperatures. Second ones are mainly angular and are attributed to Fe ore particles. Mn-rich particles are only detected in E sample collected under the influence of the ferromanganese metallurgy plant (Table 1). Mn bearing compounds represent 38.9% of the particles which however do not possess any specific morphology (Fig 1.e). In parallel, only a weak proportion of Fe-rich particles is detected in this case.

3.2. Organic compounds

Due to the differences revealed by SEM on the type of carbon-rich particles found downwind of the city and the coke plant, investigation in PAHs compounds was then undertaken. The range of PAHs concentrations were generally higher under the

Table 2. Concentration ranges (ng/Nm^3) of individual PAH in particles collected under the influence of the city or industrial sources.

Compounds	Acronyms	Coke plant	City
Phenanthrene	PA	23-62	1-4
Anthracene	Ant	15-44	1-2
Fluoranthene	FL	20-67	1-12
Pyrene	Pyr	16-58	1-10
Benzo(a)anthracene	BaA	3-59	2-16
Chrysene	CHR	16-80	1-3
Benzo(b+k)fluoranthene	B(b+k)F	18-60	1-11
Benzo(a)pyrene	BaP	24-84	1-11
Indeno(123dc)pyrene	IND	16-42	1-2
Benzo(ghi)perylene	BghiP	10-26	1-2

influence of the coke plant unit (Table 2). More precisely, the proportion of PA and Ant tends to be higher in samples from the coke plant than the city ones, in agreement with observations of Khalili et al. (1995). On the contrary, constant tendencies appeared for Fl and Pyr. Hence, concentrations ratios could be proposed to differentiate the PAHs origin : (PA + Ant)/ FL ratio is at least twice higher for the coke plant influence than the city one.

3.3 XRD

Figure 2 shows the X-ray diffractograms relative to A, C, D and E samples. Only a few diffraction lines were observed on the diffractogram of particles collected under the influence of the city (A) with two low intensity lines at about 11° and 21° attributed to the presence of gypsum $CaSO_4.2H_2O$ (JCPDS 33-1311). No diffraction lines were detected for B sample but results obtained for other industrial influences are very different. For the samples collected under the influence of the steel factory (C) or the iron ores handling area and the blast furnace (D), iron oxides are detected. Hematite (α-Fe_2O_3) is mainly identified by the lines at 2θ = 33° and 35.5° (JCPDS 33-0664). Moreover, a split up of the line at 35.5° is observed and indicates the simultaneous presence of hematite and magnetite, Fe_3O_4 (JCPDS 19-0629). These two iron compounds have already been observed in atmospheric particles collected near iron and steel manufacturing facilities (Machemer, 2004). The presence of quartz SiO_2 (JCPDS 46-1045) and calcite $CaCO_3$ has also been noticed in C and D samples, in agreement with SEM-EDX data evidencing Si-rich and Ca-rich particles respectively. Well crystallized calcite particles are detected in E sample but despite its high proportion of Mn containing particles, no characteristic crystalline structure associating Mn was detected by XRD. The absence of iron oxides in E sample confirms that particles were not collected under the influence of the steel manufacturing facilities.

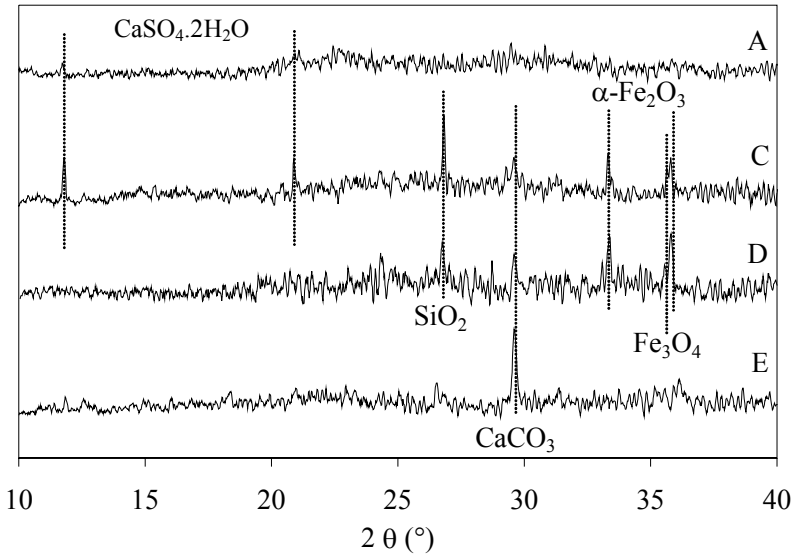

Figure 2. XRD patterns obtained for suspended particulate matter collected under the influence of the city (A) and different industrial sources (C-E).

3.4. Electron Paramagnetic Resonance

Figure 3 displays EPR spectra recorded at 293 K and 77K for the different particles samples. For winds under the influence of the town (A sample), the EPR spectra obtained are the superimposition of two elementary signals: a signal centrered at g = 2.003 with ΔHpp = 11 G relative to carbonaceous radicals (Yordanov et al., 1996) and a broad signal (T_A: g = 2.084 and ΔHpp = 564 G and T_{LN}: g= 2.161 and ΔHpp = 957 G). This latter signal was previously observed and attributed to Fe^{3+} ions in interaction, revealing the aggregation of the paramagnetic species (Ledoux et al., 2004). In the case of particles collected under the influence of the coke plant (B sample), the same EPR features were revealed with however a more intense signal of carbonaceous radicals. This observation could be related more specifically to radical stabilized in carbonaceous particles emitted from the coke plant. This observation is

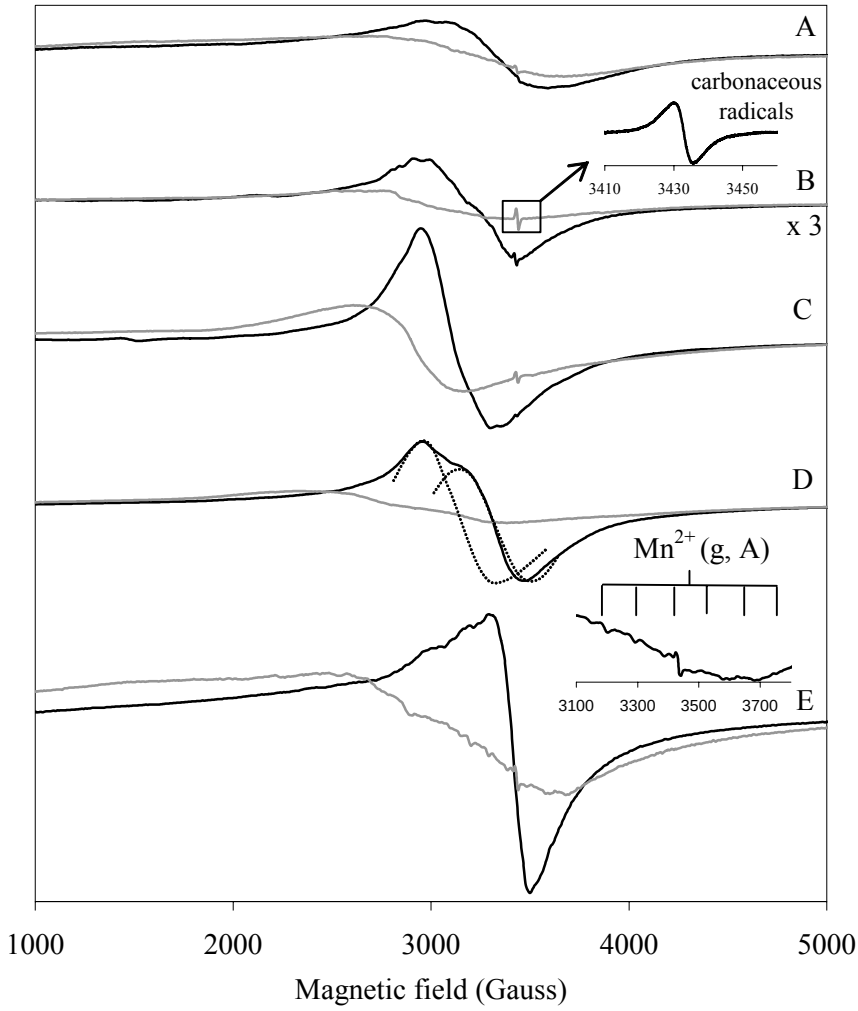

Figure 3. EPR spectra for particles from urban and industrial activities origins: spectra recorded at 293 K (black line) and 77K (grey line). Superimposition of signals (dashed line) giving the resulting experimental signal for D sample.

in agreement with the SEM and organic compounds analysis given above. As mentioned by SEM-EDX and XRD techniques, the influence of siderurgic activities has been detected in C and D samples. Particularly for winds from the steel factory, intense EPR signals were mainly obtained (T_A: g = 2.188 and ΔHpp = 390 G and T_{LN}: g = 2.380 and ΔHpp = 564 G). This signal, relative to species present in iron-rich particles, is characterized by a high g value in comparison with the EPR signal one relative to A sample. This difference can be explained considering the presence of both α-Fe_2O_3 (antiferromagnetic) and Fe_3O_4 (ferrimagnetic) phases in the Fe-rich spherules of C sample. Indeed, a shift of the EPR line toward low magnetic field is consistent with a ferrimagnetic ordered state of the species detected (Guskos et al. 2002). Consequently this EPR signal could be ascribed to Fe^{3+} species present in the iron oxide spheres resulting from the high temperature treatment encountered in the steel unit.

The EPR spectra of D sample correspond to the superimposition of two signals: the first one corresponds to the presence of Fe^{3+} species in iron oxide spheres as in the case of C sample and the second one is a new signal characterized at T_A by g = 2.110 and ΔHpp = 360 G. The intensity of this signal is drastically decreased at T_{LN} ($Ns(T_{LN})$ / $Ns(T_A)$ <0.5) evidencing that such species possess antiferromagnetic properties, similar to that encountered in α-Fe_2O_3. Taking into account XRD and SEM-EDX, we deduced that the iron-rich particles with angular shapes correspond to α-Fe_2O_3 particles leading to the observation of the second EPR signal in D sample. The EPR technique allows to us in this case (D sample) the discrimination of at least two influences of iron-rich particles.

The E sample (containing a high proportion of Mn rich particles) gives an intense signal at T_A (g = 2.049 ; ΔHpp = 360 G), markedly broadened at T_{LN} (g = 2.230 ; ΔHpp = 360 G) and $Ns(T_{LN})$ / $Ns(T_A)$ = 2.3. A g value around g = 2 and a high $Ns(T_{LN})$ / $Ns(T_A)$ ratio can both be considered to ascribe a such signal to the interaction between of few species mainly corresponding to Mn^{2+} ions with a low level of aggregation. In addition, we observed a specific signal of isolated Mn^{2+} ions (g = 2.002 and A = 96 G) proposed as a tracer of particulate emissions from manganese metallurgic plants (Ledoux et al. 2005).

4. DISCUSSION AND CONCLUSION

From these characterization data, it is possible to propose specific physico-chemical parameters related to the different emission sources. The Fe-rich particles possess different characteristics dependent on their origin. Under the influence of the city, most of Fe-rich particles do not have specific geometry. From XRD and EPR data, the latter are not crystallized and correspond to Fe^{3+} ions in interaction inside small aggregates (Ledoux et al. 2004). On the contrary, two kinds of Fe-rich particles were collected downwind of the steel manufacturing facilities. First, we detected iron ores particles with angular shape corresponding to hematite α-Fe_2O_3. Because this phase possess antiferromagnetic properties, such particles gives a specific EPR signal intensity evolution versus the recording temperature ($Ns(T_{LN})$ / $Ns(T_A)$<1). On the other hand, the Fe-rich spherules are the result of the condensation of iron released into the

atmosphere during high temperature processes. Taking into account the high temperature and the low oxygen partial pressure, when this condensation occurs, the particules formed are not completely oxidized. Indeed, we detect even after transport in the atmosphere both Fe_3O_4 and α-Fe_2O_3 for the Fe-rich spherules. The stability of Fe_3O_4 could be explained considering spherules as magnetite Fe_3O_4 particles with their surface partly oxidized in hematite (α-Fe_2O_3).

SiO_2, $CaCO_3$ and $CaSO_4$. $2H_2O$ are frequently encountered in suspended particulate matter, assigned to natural and anthropogenic particles. Inside the industrial area and notably the steel manucfacturing facilities, we have to notice that Si and Ca containing compounds are found in ores and fluxing agents respectively, so that these elements can be included in particles re-suspended in the atmosphere. In addition, $CaSO_4$. $2H_2O$ can also be secondary particles being formed in the atmosphere by the oxidation of SO_2 with Ca-rich particles.

Under the influence of the ferromanganese factory, no specific particles shape, neither specific crystallized phase were noticed. In this case, the origin was clearly confirmed by the individual particle analysis (almost 39% of Mn bearing particles) and by specific EPR signals (Mn^{2+} isolated species and Mn^{2+} small aggregates).
Finally, the combination of the different techniques applied in this work appeared as a successful approach to evidence physico-chemical parameters to differentiate the atmospheric particles origins.

5. ACKNOWLEDGMENTS

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