

# Mineralogy and Elemental Composition of Brake Pads of Common Use in Spain

/ FULVIO AMATO (1, 2\*), ORIOL FONT (1), NATALIA MORENO (1), ANDRÉS ALASTUEY (1), XAVIER QUEROL (1)

(1) Institute of Environmental Assessment and Water Research, Spanish Research Council (IDÆA-CSIC), C/Jordi Girona 18–26, 08034 Barcelona, Spain

(2) TNO Environment and Geosciences. Dept. of Climate, Air and Sustainability. P.O.Box 80015, 3508 TA Utrecht, The Netherlands

## INTRODUCTION

Erosion of vehicle brake linings is recognized as a significant source of atmospheric particulate matter (PM) in large cities (Amato et al., 2009; Wahlin et al., 2006; Thorpe et al., 2007). The few estimates over Europe were found to vary from negligible up to 4.0 (10%) of daily PM<sub>10</sub> mass. Although the contribution of brake particles is not dominant in terms of mass, their health concern might be the most relevant.

After the ban of asbestos fibers for brakes manufacturing in mid-90s, composition of brake linings has rapidly changed but there is still a number of possible toxics used (heavy metals, sulphides, PAHs etc.) and the information on materials employed by each manufacturer is missing. Generally, materials used for brake linings include metallic friction materials (Fe and Fe-Cu oxides), lubricants (graphite and Fe-Sb-Mo-Sn-Mn sulphides) and mineral fibers (barite, calcite, zircon and Al-silicates) used as fillers. However composition can change largely from one brand to another and from one country to another. Also, the composition and size of brake particles can change during braking due to the high temperature and friction stress. As example, at  $T > 850^\circ\text{C}$ ,  $\text{Sb}_2\text{S}_3$  (stibnite) is converted to  $\text{Sb}_2\text{O}_3$ , which is classified as possible carcinogenic in humans (IARC, 1999). A detailed inventory, at national level, of manufacturers and brake materials is urgently needed, in combination with field and laboratory tests.

This study aims to investigate the chemical and mineralogical composition of different brake pads, commonly used in Spain. This type of information is of high interest and urgent need for emission inventories, toxicological and epidemiological studies.

## METHODS

Four car brake pads (FERODO B, BENDIX, ROAD HOUSE and BOSCH) and one bike brake pad (FERODO A) were selected for mineralogical, textural and chemical characterisation.

A vertical section of brake pads was obtained by a diamond disk saw and subsequently a fraction of  $1\text{ cm}^3$  including the metallic support, was removed. The lateral and friction sections of this fraction were polished for subsequent textural, morphological and particle resolved composition analysis.

The metallic support was carefully separated from the friction area from the remaining fraction of the vertical section. Sections of metallic support were used for the determination of mineral composition. The friction area section was crushed and milled for subsequent mineralogical and chemical composition.

The mineralogy of brake pad samples was determined by X-ray powder diffraction (XRD). XRD patterns were collected using a Bruker D8 Advance diffractometer with monochromatic  $\text{Cu K}\alpha_{1,2}$  radiation ( $\lambda = 1.5405$ ) operated at 40 kV and 40 mA. The primary parallel X-ray beam was generated by a Göbbel mirror and the scattered beam was analyzed by a Sol-X detector with the following scanning parameters: from 4 at  $60^\circ$  of  $2\theta$ , a step size of  $0.05^\circ$ , and time per step of 3 s.

The texture, morphology and particle resolved composition of brake pads were investigated by a Quanta 200 Scanning Electron Microscope equipped with energy-dispersive X-ray analyser (SEM-EDX).

For chemical determination samples

were acid-digested in duplicate by using a two-step digestion method devised by Querol et al. (1995). The resulting solution was then analysed by Inductively-Coupled Plasma Atomic-Emission Spectrometry (ICP-AES) and by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) for 57 major and trace elements, respectively. The international reference material NBS1633b was also digested to determine the accuracy of the analytical and digestion methods.

The content of Hg was carried out by a LECO AMA 254 gold amalgam atomic absorption spectrometer.

## RESULTS

The mineralogy of the friction materials of the brake pads studied showed a large variety of mineral species manufacturing, giving rise to overlapping of peaks among XRD patterns resulting in a relatively complex XRD-spectrum of difficult interpretation. Furthermore, a markedly preferential orientation of a given lattice spacing of some mineral species (mainly graphite) is evidenced in XRD spectra of brake pads causing potential overestimation of the graphite content. The preferential orientation may be produced in the hot pressing step of brake pad manufacture. The above factors and the occurrence of highly acid insoluble species, makes determination and quantification of brake pads composition a non straightforward task.

In spite of the aforementioned it can be stated that metallic Fe and graphite (C), are the major and common crystalline components among the four car brakes pads studied. Corundum ( $\text{Al}_2\text{O}_3$ ) is also present in XRD detectable levels ( $>1\%$  wt) in all car brake pads trademarks. Other mineral species detected in specific samples are barite ( $\text{BaSO}_4$ ),

**palabras clave:** PM, No-combustión, Desgaste frenos, Mineralogía, Metales, Carbono

**key words:** PM, Non-exhaust, Brake wear, Mineralogy, Metals, Carbon

hematite ( $\text{Fe}_2\text{O}_3$ ), metallic Cu, tenorite ( $\text{CuO}$ ), zircon ( $\text{ZrSiO}_4$ ), calcite ( $\text{CaCO}_3$ ), periclase ( $\text{MgO}$ ), vermiculite, and sulphide species such as stibnite ( $\text{Sb}_2\text{S}_3$ ), pyrite ( $\text{FeS}_2$ ), chalcocopyrite ( $\text{CuFeS}_2$ ), covellite ( $\text{CuS}$ ), sphalerite ( $\text{ZnS}$ ), hauerite ( $\text{MnS}_2$ ), and molybdenite ( $\text{MoS}_2$ ). FERODO motorcycle brake pad shows a more simple composition than that of car brake pads, with metallic Fe, graphite, and barite as major components and traces of portlandite ( $\text{Ca}(\text{OH})_2$ ). It is worth mentioning the occurrence, in trace amounts, of Sb-oxide ( $\text{Sb}_2\text{O}_5$ ), Sb-sulphate, and zincite ( $\text{ZnO}$ ) in Ferodo B worn brake pads. These mineral phases arise from the oxidation of stibnite and sphalerite due to the high temperatures reached during brake operation.

Metallic Fe and hematite are the most common friction materials employed. Metallic copper and tenorite are also employed as friction materials in FERODO and BENDIX car pads, respectively. Major differences among different manufacturers are found in the type and proportion of lubricants (sulphide species), and mineral fillers employed. Besides graphite and sphalerite, which are employed in all car brake pads, molybdenite and stibnite are largely used in FERODO B, pyrite and hauerite in ROAD HOUSE, covellite, chalcocopyrite in Bosch, while only stibnite is used in BENDIX pads. It is worth mentioning the occurrence of sphalerite Hg-rich in ROAD HOUSE and that of Sb-oxide ( $\text{Sb}_2\text{O}_5$ ), Sb-sulphate, and zincite in FERODO B worn brake pads.

As regards mineral fillers, calcite is the major mineral filler in FERODO B brake pad with minor proportions of barite and zircon. ROAD HOUSE and BOSCH brake pads use calcite and barite, minor proportions of zircon and traces of periclase, while zircon and barite are the mineral fillers employed in BENDIX pads and only barite in FERODO car brake pad. Barite and trace proportions of portlandite are the mineral fillers employed for the manufacture of Ferodo motorcycle pads.

The SEM analysis revealed that friction material of brake pads is directly hooked to the metallic support, displaying similar textural patterns among brake pad trademarks selected. The brake pad manufacture process results in aggregates of coarse Carbon particles (generally 0.3-0.8 mm), relatively coarse (0.1-0.5 mm) particles

(commonly shaving-like particles) of metallic components (mainly metallic Fe and hematite, metallic Cu and tenorite in FERODO and BENDIX car brake pads, respectively), and aggregates of synthetic cylinders of Mg-K-Ca aluminosilicate species (vermiculite). These coarse particles are surrounded by a finer matrix (<0.1mm) of variable composition among brake pads trademarks since lubricants and mineral fillers are the major components of pads matrix. Needle C particles are clearly detected in specific samples, probably corresponding to aramid fibbers as reported elsewhere (Weiss et al, 2006), which are used for linking the matrix components.

As expected from the XRD and SEM analysis Iron (13.2-45.6%) and C (26-32%) are the elements with higher concentrations in car and motorcycle brake pads. As mentioned above the low C/Fe concentrations are not in agreement with the high graphite/Fe species XRD intensity ratio. Besides the high intensity of graphite lattice (002) the use of powder Fe may reduce the XRD intensity of Fe species, enhancing the C/Fe species XRD intensity ratio.

FERODO car brake pads shows the highest concentrations of Zn, Mo and Cu, the lowest of Al, Ca, Mg, K, and Ba, and relatively high of Sb, and S indicating the prevalence of lubricant sulphide species (sphalerite, molybdenite, and stibnite) over mineral fillers. BENDIX brake pads show the highest content of most of mineral fillers bearing elements (Al, Mg, K, Ba and Zr) and relatively high concentrations of Ca. Given that stibnite is the only sulphide employed as lubricant detected by XRD, this brake pad trademark also displays the highest concentrations of Sb, and similar S concentrations than that of Ferodo. The concentrations of Zn and Cu reach relatively high values due to the occurrence of zincite and tenorite.

ROAD HOUSE and BOSCH pads are characterised by the highest content of S (3.3 and 2.4%, respectively), Ca (4.3 and 2.1%, respectively), and high contents of other mineral filling elements, such as Ba and Al. The concentrations of Zn and Mn in ROAD HOUSE pads are considerably high due to the use of sphalerite and hauerite.

Regarding the concentrations of other elements of environmental concern, it has to be pay special attention to Hg.

This metal attained very high concentrations (around 2 mg/kg) in ROAD HOUSE and FERODO brake pads

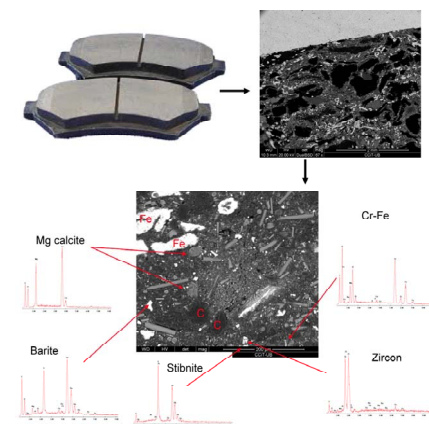


fig 1. A detail of SEM analysis of the BENDIX brake pad.

## REFERENCES

- Amato, F., Pandolfi, M., Viana, M., Querol, X., Alastuey, A., Moreno, T., (2009): Spatial and chemical patterns of PM10 in road dust deposited in urban environment. *Atmospheric Environment* **43** (9), 1650-1659.
- IARC (1989): Antimony trioxide and antimony trisulfid. in: "Some organic solvents, resin monomers and related compounds, pigments and occupational exposures in paint manufacture and painting" International Agency for Research on Cancer IARC, editor. IARC Monographs n the Evaluation of Carcinogenic Risks to Humans, **47**, 291-305.
- Querol, X., Fernández-Turiel JL., López-Soler, A. (1995): Trace element behaviour in a large power station. *Fuel*, **74**, 331-343
- Thorpe A. & Harrison R.M. (2008): Sources and properties of non-exhaust particulate matter from road traffic: A review. *Science of Total Environment*, **400** (1-3), 270-282
- Wählén P., Berkowicz R., Palmgren F. (2006): Characterization of traffic-generated particulate matter in Copenhagen. *Atmospheric Environment*, **40**, 2151-2159.
- Weiss, Z., Crelling J.C., Simha Martynkova, G. Valaskov, M., Filip, P. (2006): Identification of carbon forms and other phases in automotive brake composites using multiple analytical techniques. *Carbon*, **44**, 792-798.