



	<b>Experiment title:</b> Nickel and chromium speciation in PM10 particulate matter	<b>Experiment number:</b> 26-01-834
<b>Beamline:</b> BM26A	<b>Date of experiment:</b> from: 24/06/2009 to: 28/06/2009	<b>Date of report:</b> 14/12/2009
<b>Shifts:</b> 15	<b>Local contact(s):</b> Sergey Nikitenko	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> <b>Mr. Kristof Tirez; VITO, Boeretang 200, 2400 Mol, Belgium</b> <b>Dr. Geert Silversmit*; Ghent University, Analytical Chemistry, Krijgslaan 281 S12, B-9000 Ghent.</b> <b>Prof. Laszlo Vincze; Ghent University, Analytical Chemistry, Krijgslaan 281 S12, B-9000 Ghent.</b>		

## Report:

### *Scientific background and aim of the proposal*

The toxicity of nickel and chromium compounds in the environment varies significantly among the different chemical species. Nickel (sub)sulphide (NiS and Ni<sub>3</sub>S<sub>2</sub>) is considered the most carcinogenic nickel species, whereas the toxicity of water soluble Ni salts (e.g. NiSO<sub>4</sub>) is more controversial. Therefore, understanding the speciation of Ni in ambient air is of the utmost importance for the assessment of respiratory health risks associated with Ni exposure. In the case of chromium, the hexavalent oxidation state (Cr<sup>6+</sup>) is known as a toxic and carcinogenic species.

The aim of this proposal was to identify the Ni and Cr species in PM10 dust filters collected in workplace environment and in ambient air outside the production site. To achieve this goal linear combination analysis of Ni K and Cr K XANES spectra recorded on PM10 filters was proposed. The exact determination of the Ni and Cr composition in the PM10 dust is a necessity to obtain a good estimate of the toxicity of the exposure to Ni and Cr inside and outside the production site.

### *Experimental method*

For the collection of the PM10 dust, a fixed volume of air (2.3 m<sup>3</sup>/h) is pumped through an inlet during 24 hours and particles are collected on a Quartz filter and a diameter of 47 mm. The inlet separates the particles with diameter larger than 10 μm (PM10) so that only the small particles will be attached to the filter. Ni K XANES spectra of Ni foil and of reagent grade NiS, NiNO<sub>3</sub>, NiCO<sub>3</sub>.NiOH and Ni<sub>2</sub>SiO<sub>4</sub> were measured as base spectra for the linear combination analysis (see Figure 1, left). For the Cr analysis, reference spectra from Cr foil, Cr<sub>3</sub>C<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, FeCr<sub>2</sub>O<sub>4</sub>, Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Cr<sub>2</sub>C<sub>3</sub>, and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> were measured.

The linear combination analysis was performed with an in-house developed software routine written in IDL.

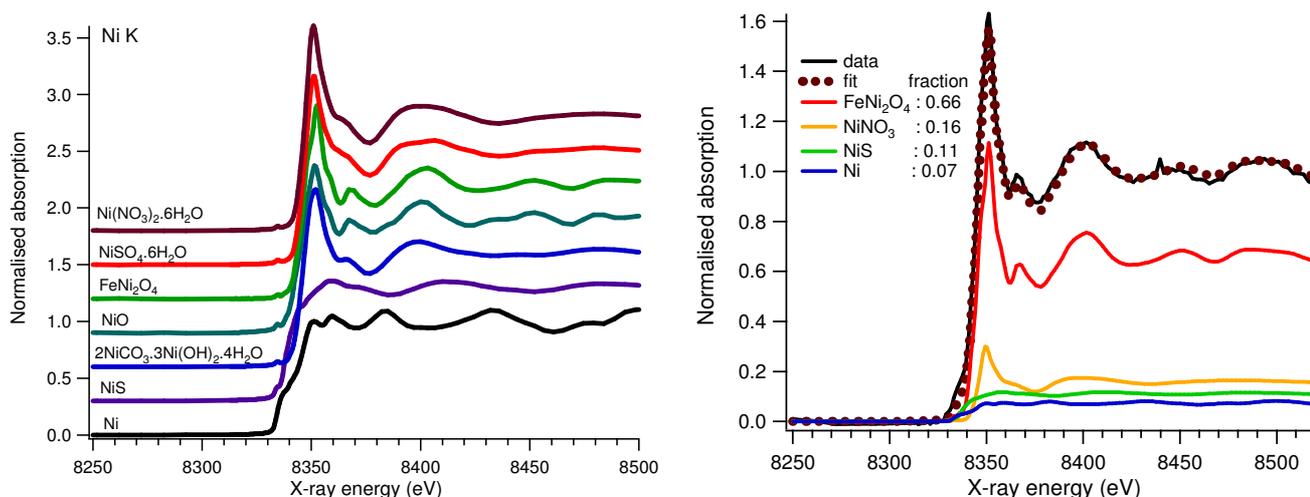
### *Results obtained*

#### *Ni K XANES analysis*

Ni K XANES spectra of PM10 air particulates were recorded on filters collected in work place environment and in the vicinity of the factory. Fortunately, the filters collected outside the factory site contain mainly the oxidic phase FeNi<sub>2</sub>O<sub>4</sub>. However, the filters collected in the workplace environment do contain a nickel

sulphide species (NiS) and metallic Ni. An example spectrum of a filter collected in the workplace environment with the linear combination fit is given in Figure 1, right.

In addition to the filter samples, also dust samples simply collected from the work place floor were analysed. These samples show large fractions of Ni sulphides (up to 17%) and Ni metal (up to 35%).

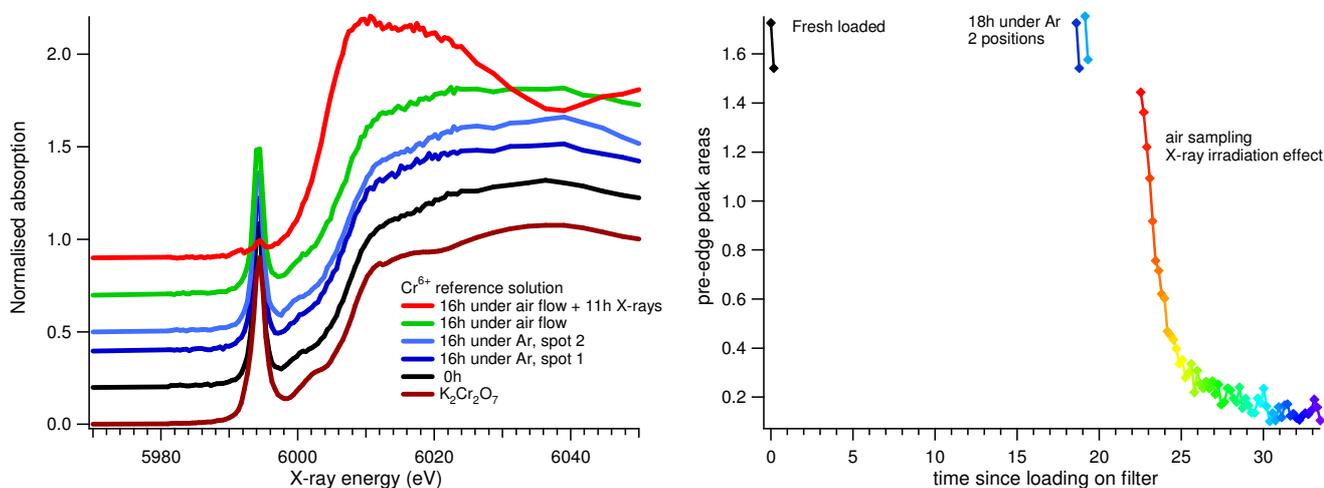


**Figure 1:** Normalised Ni K transmission XANES spectra for the Ni reference compounds (left) and the spectrum obtained on a PM10 filter collected in work place environment together with the linear combination fit (right).

### Cr K XANES analysis

The Cr K XANES spectra of the samples collected inside and outside the production site all show a clear  $\text{FeCr}_2\text{O}_4$  signature. So the  $\text{Cr}^{3+}$  oxidation state is present and not the very carcinogenic  $\text{Cr}^{6+}$ .

Concerning the analysis of  $\text{Cr}^{6+}$  compounds by air sampling, very few information is available in the literature with respect to the stability of this chromium species after exhaustion in the atmosphere. In order to assess this question, Cr K XANES spectra were recorded on a  $\text{Cr}^{6+}$  reference solution loaded on a filter. Spectra were taken after storage for at least 16 hours under inert atmosphere (Ar) and under air flow (simulating the PM10 particulate sampling conditions). Furthermore, in order to examine the effect of the illumination with the synchrotron beam on the  $\text{Cr}^{6+}$  stability, faster XANES spectra (measuring time of about 11 min) were recorded subsequently for 11 hours (see Figure 2, left). As  $\text{Cr}^{6+}$  compounds have a very intense pre-edge peak and  $\text{Cr}^{3+}$  species do not, the relative fraction of  $\text{Cr}^{6+}$  can easily be followed by plotting the pre-edge peak intensity as function of time, see Figure 2, right. Storage in air environment induces a slight conversion of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  but this process is accelerated under irradiation with the monochromatic synchrotron beam.



**Figure 2:** Normalised Ni K transmission XANES spectra for the Ni reference compound BN pellets (bottom vertically shifted for clarity).