

## PRELIMINARY EVALUATION OF INNER SHELL SPECTROSCOPY AS AN ANALYTICAL TOOL FOR THE ANALYSIS OF POLYCYCLIC AROMATIC COMPOUNDS IN ENVIRONMENTAL SAMPLES

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### ABSTRACT

*Photoabsorption spectra have been measured for several polycyclic aromatic hydrocarbons (PAHs) and polycyclic aromatic compounds (PACs) using synchrotron radiation at the Brazilian Synchrotron Light Source (LNLS), covering the carbon, the nitrogen as well as the oxygen 1s-edges. A new sample preparation method was tested and applied successfully specially for the less volatile compounds. Our data showed good agreement with previously published results. New photoabsorption spectra of PAHs and PACs were recorded and will be presented. A street dust sample was analysed by NEXAFS and the results compared with previously published data on PAH identification by high-resolution gas chromatography-mass spectrometry.*

### 1. INTRODUCTION

Photoabsorption spectroscopy has been successfully applied to the study of complex  $\pi$ -systems, like polycyclic aromatic hydrocarbons (PAHs) and polycyclic aromatic compounds (PACs). In the absorption process a core electron may be excited into an empty state. As a consequence a fine structure is observed in the photoabsorption spectrum, which is related to the system under investigation. The photoabsorption spectrum is divided into two regions: the first region near the absorption edge, called NEXAFS (Near-edge X-ray Absorption Fine Structure) or XANES (X-Ray Absorption Near-Edge Structure) region, which will be concerned in this work and the so-called EXAFS (Extended X-ray Absorption Fine Structure) region, which starts about 50 eV above the edge and extends over many hundreds of eV. Depending on the symmetry of the final state involved in the transition it is possible to distinguish between two types of resonances in the photoabsorption spectrum: the  $\pi$  and  $\sigma$  resonances. The  $\pi$  resonances are in general characterised by narrow peaks and correspond to transitions into unoccupied molecular orbitals with  $\pi$ -symmetry, whereas the broad bands above the ionisation

threshold correspond to  $\sigma$ -like states. The importance of using NEXAFS to study the electronic structure by probing the unoccupied electronic states of organic molecules, and also the possibility of obtaining information on molecular orientation of adsorbed and condensed systems on metal surfaces have been previously and extensively discussed. Very good compilations can be found elsewhere [1,2].

Polycyclic aromatic hydrocarbons (PAHs) are of concern since many of them exhibit well known pro-carcinogenic and/or mutagenic properties to humans and experimental animals [3,4]. PAH formation, sources and fate have been reviewed [5-9]. Although some PAHs are of technological interest as intermediates or precursors of widely used substances, such as dyes [8], they are mostly found in the environment as organic pollutants already described in all environmental compartments [8]. In many samples of interest PAHs occur in complex mixtures containing isomers and associated with aliphatic hydrocarbons and other classes of polycyclic aromatic compounds (PACs) of toxicological importance such as PAH derivatives (nitrated-PAHs, quinones and ketones) and heterocyclic aromatic amines. PAH determination is therefore laborious and involves several analytical steps (sample extraction, clean up, concentration etc.) usually followed by chromatographic analysis [7-11]. The main goal of this work is to develop a methodology for the study of PAHs and PACs in complex matrices through photoabsorption spectroscopy.

This work was performed at the SGM beam line from the Brazilian Synchrotron Light Source (LNLS). In the first part of this paper, we present NEXAFS data obtained for different PAHs and PACs measured at the C, N and O 1s-edges (K-edges). Photoabsorption spectra obtained at the carbon K-edge for two PAHs (tetracene and chrysene) and their binary mixture are also discussed together with some preliminary results on the evaluation of NEXAFS as an analytical tool for PAH in a complex environmental sample consisting of street dust collected at Niterói City, Rio de Janeiro State, Brazil.

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## 2. EXPERIMENTAL

A simple procedure for sample preparation was developed and tested. It consists of dropping and evaporating very small volumes of high purity dichloromethane (Absolv - Tedia, RJ, Brazil) solutions of the target compounds over an aluminium support which, on its turn, was mounted on a sample manipulator and housed inside a vacuum chamber, with a base pressure of approximately  $10^{-9}$  Torr. This procedure allows blank correction, since the same solvent was used in all experiments and the investigation of up to 12 compounds without venting the system. It has worked successfully especially for the less volatile compounds.

Photoabsorption spectra (NEXAFS) of several PAHs and PACs (AccuStandard, CT, USA and Aldrich Chemical Co., WI, USA) were measured at the Brazilian Synchrotron Light Source (LNLS - Laboratório Nacional de Luz Sincrotron), located at the city of Campinas, São Paulo. The SGM beam line that covers a photon energy range from 250 to 1000 eV was used to obtain all NEXAFS data reported in this work. Spectra of several compounds with molecular weights ranging from 128 to 384 a.m.u. were recorded at the carbon (270 – 330 eV), nitrogen (390 – 440 eV) and oxygen (520 – 550 eV) 1s-edges. The spectral resolution was about 0.4 eV at the carbon edge. The spectra were recorded by measuring the total electron current at the sample ( $I$  signal) simultaneously with the signal of a gold grid ( $I_0$ ), which monitor the photon flux decay with time. Spectra for the aluminum support ( $I_s$ ) were also measured. The final data represent a plot of the ratio  $I/I_s$  normalized to the  $I_0$  signal against the photon energy. In order to increase the signal a positive potential of normally + 300 eV was applied to a metallic disk positioned in front of the sample. Energy calibration was performed through comparison of the coronene NEXAFS spectrum with previous data [14].

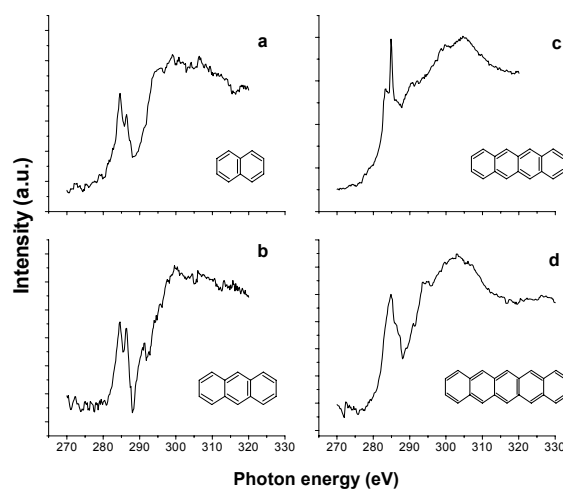
A street dust (SD) sample was treated as previously described [17] and analysed by NEXAFS in the same way as individual PAHs. Briefly, the SD sample was ultrasonically extracted with  $\text{CH}_2\text{Cl}_2$ . The extract was concentrated in rotary evaporator, centrifuged and further evaporated, under high purity  $\text{N}_2$ , after toluene addition. Concentrated extract was submitted to clean up on  $\text{SiO}_2$  SPE cartridges and the PAH rich fraction was eluted with hexane. The results obtained by NEXAFS were compared with previously published data on PAH identification by high-resolution gas chromatography-mass spectrometry (HRGC-MS) [17].

## 3. RESULTS AND DISCUSSION

### 3.1 SPECTROSCOPIC DATA

Carbon K-edge NEXAFS spectra of four linear HPAs, namely, naphthalene, anthracene, tetracene and pentacene obtained by monitoring the total current at the sample, so-called total electron yield (TEY) are presented in Figure 1(a-d). The spectra show several structures corresponding

to transitions from carbon 1s electrons to unoccupied molecular states. The sharp structures represent transitions from a C 1s electron to unoccupied molecular orbitals of  $\pi$  symmetry, whereas the broad bands above the ionisation threshold correspond to  $\sigma^*$  resonances [1]. Good agreement was observed with previously published data for tetracene [13] and pentacene [13]. However, poor spectra with low signal to noise ratios were recorded for the higher volatile compounds (naphthalene and anthracene), indicating that the sample preparation method is not suitable for high volatility PAHs which may sublime under ultra-high vacuum conditions ( $\sim 10^{-9}$  Torr).

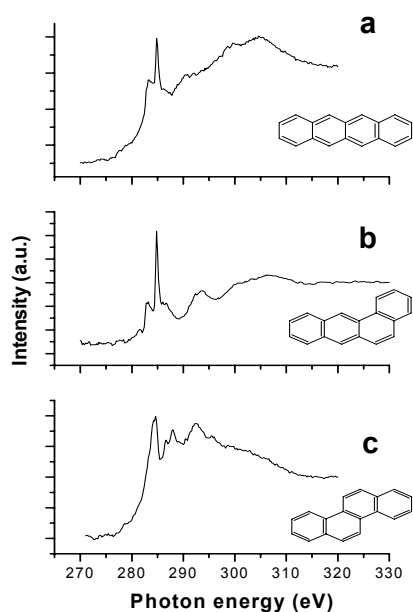


**Figure 1 - Carbon K-edge NEXAFS spectra of four linear PAHs: (a) naphthalene, (b) anthracene, (c) tetracene and (d) pentacene.**

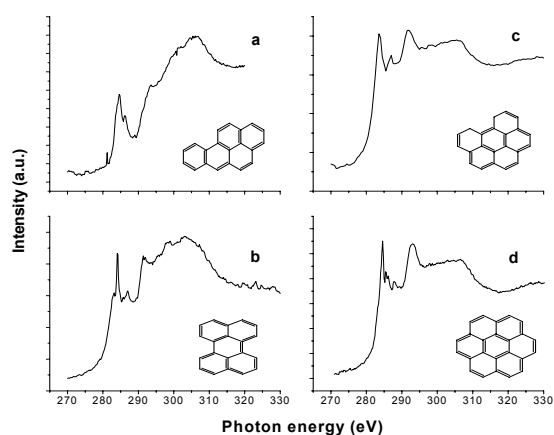
Figure 2 shows the NEXAFS spectrum of tetracene (Figure 2a) together with the spectra of two non-linear PAHs, benzo[a]anthracene (Figure 2b) and chrysene (Figure 2c). Although these PAHs are isomers (MW = 228 dalton) they present very different spectra with very sharp  $\pi$  resonances, suggesting strong differences in their unoccupied density of states, which can be used as a fingerprinting for identification purposes. The spectrum of chrysene (Figure 2c) is in good agreement with photoabsorption data previously reported by Oji *et al* [14] for vacuum deposited films onto a polycrystalline Cu substrate. The  $\pi^*$  and  $\sigma^*$  resonances are well resolved in the spectrum of Figure 2c. The sharp structures appearing below the ionization potential (IP), expected to be about 290 eV, represent transitions from a C 1s electron to unoccupied  $\pi^*$  orbitals, whereas the broad bands above it correspond to  $\sigma^*$  resonances. This is, within our knowledge, the first time that NEXAFS spectrum of benzo[a]anthracene (Figure 2b) is recorded.

Figure 3 shows NEXAFS spectra of four condensed PAHs obtained at the carbon K-edge. The spectra of perylene (Figure 3b) and coronene (Figure 3d) are also in very good agreement with data of Oji *et al* [14]. To our knowledge it is the first time that C K-edge photoabsorption spectra of

benzo[a]pyrene (Figure 3a) and benzo[ghi]perylene (Figure 3c) are reported. The isomeric PAHs perylene (Figure 3b) and benzo[a]pyrene (Figure 3a) also showed pronounced differences in their photabsorption spectra.



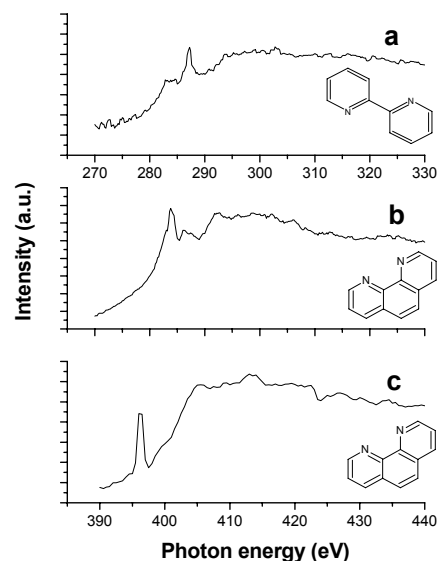
**Figure 2 - Carbon K-edge NEXAFS spectra of three isomeric PAHs: (a) tetracene, (b) benzo[a]anthracene and (c) chrysene.**



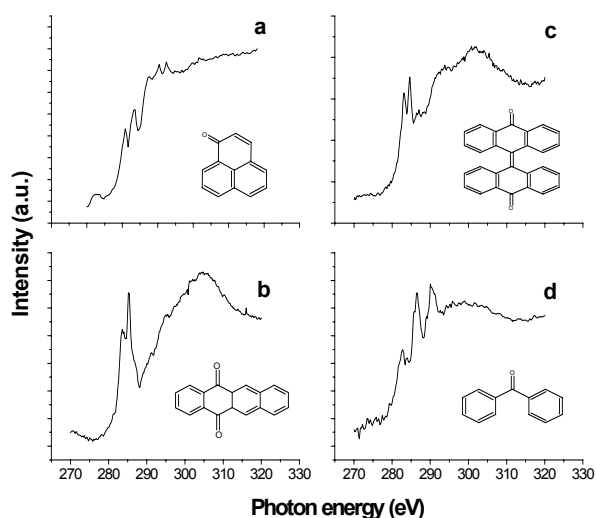
**Figure 3 - Carbon K-edge NEXAFS spectra of: (a) benzo[a]pyrene, (b) perylene, (c) benzo[ghi]perylene and (d) coronene.**

Investigation of nitrogenated PACs was also conducted at the SGM beam line of LNLS (Figure 4). The photoabsorption spectra of 2,2'-bipyridil (Figure 4a) and 9,10-phenanthroline (Figure 4b) measured at the carbon K-edge are shown together with the spectrum of 9,10-phenanthroline (Figure 4c) recorded at the nitrogen K-edge. The expected  $\pi$  e  $\sigma$  resonances are clearly shown. The carbon K-edge NEXAFS spectra of oxygenated PACs, namely phenalenone, naphthacenequinone, bianthrone and benzophenone are reported in Figure 5. As shown for PAHs and nitrogenated PACs it is also possible

to observe sharp structures in these spectra corresponding to  $\pi$  transitions, followed by  $\sigma$  resonances.



**Figure 4 - NEXAFS spectra of nitrogenated PACs: (a) 2,2'-bipyridil and (b) 9,10-phenanthroline obtained at the carbon K-edge and (c) 9,10-phenanthroline obtained at the nitrogen K-edge.**



**Figure 5 - Carbon K-edge NEXAFS spectra of oxygenated PACs: (a) phenalenone, (b) naphthacenequinone, (c) bianthrone and (d) benzophenone.**

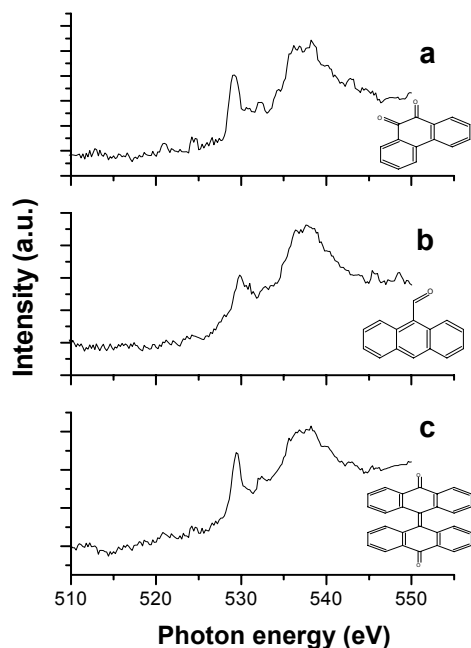
The oxygen K-edge photoabsorption spectra of three oxygenated PACs (9,10-phenanthrenequinone, 9-anthracenaldehyde and bianthrone) are shown in Figure 6. Again it is possible to observe strong contributions from both  $\pi^*$  and  $\sigma^*$  resonances to the spectra at the O K-edge. With the exception of bianthrone [15], no data were found in the literature for the nitrogenated and oxygenated PACs presented in Figures 4-6

The assignment of PAHs and PACs spectra represents a challenge to molecular quantum chemical calculations due to their complex electronic  $\pi$  systems. *Ab initio* calculations are being carried out with the aim of assisting NEXAFS data assignments for PAHs and PACs. Good results for the simplest system naphthalene have been already obtained [16].

### 3.2 ADDITIVITY OF SPECTRA

The occurrence of PAHs in environmental samples is in almost all cases characterized by very complex mixtures containing isomers, even alkylated PAHs and derivatives such as ketones, quinones, nitro etc in a wide range of molecular weights.

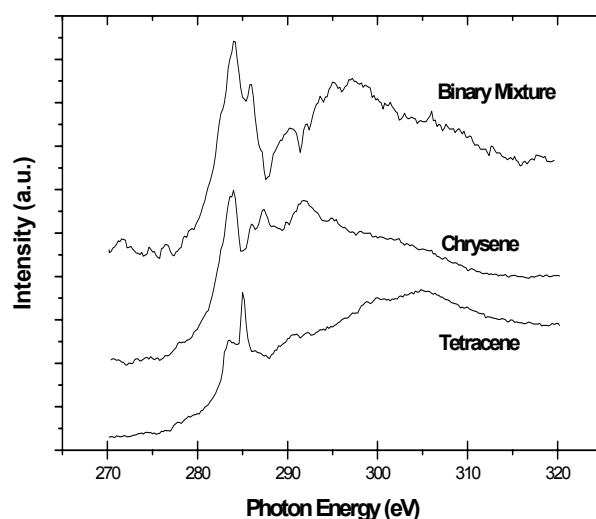
In order to evaluate NEXAFS as a technique for the study of PAH mixtures, binary mixtures of the tetracyclic tetracene and chrysene (MW = 228 dalton) were studied at the SGM beam line of LNLS. The C 1s NEXAFS spectra of tetracene and chrysene together with a mixture containing about the same quantities of these compounds are shown in Figure 7. The spectra of chrysene presents a sharp peak at approximately 285 eV followed by weaker structures while, on the other hand, for tetracene, the most intense peak corresponds to the second structure presented in the spectrum.



**Figure 6 - NEXAFS spectra of: (a) 9,10-phenanthrenequinone, (b) 9-anthracenaldehyde and (c) bianthrone obtained at the oxygen K-edge.**

In the spectrum of their binary mixture, it is possible to observe the contribution from both PAHs, especially in the  $\pi$  resonance region. The first peak of the mixture is larger when compared to the individual PAHs exhibiting a shoulder in the lower energy side of the spectrum. This occurs most probably due to the contribution from three

different  $\pi$  structures to this peak: one from chrysene and two from tetracene. The shoulder can be assigned as the first tetracene structure. The second peak from chrysene can be easily seen in the spectrum of the mixture. It seems to be the major contribution to the second structure observed in the mixture. Similar methodology has been successfully applied in the determination of nitrogenated classes of compounds in petroleum asphaltene [12].



**Figure 7 - C 1s NEXAFS spectra of tetracene, chrysene and their binary mixture.**

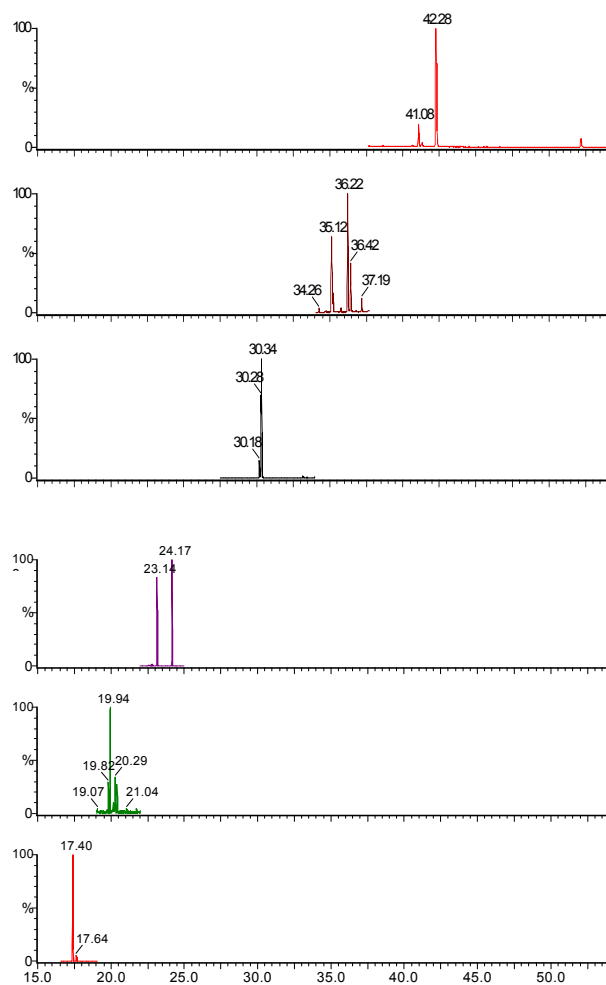
In the next step of this work more complex mixtures will be concerned. Quantitative relationship between individual PAHs and their mixtures will be studied in order to evaluate individual contributions to the mixture spectra. *Ab initio* calculations are being carried out with the aim of assisting NEXAFS data deconvolution and assignments [16].

### 3.3 ENVIRONMENTAL SAMPLES

HRGC-MS data for street dust (SD) collected at Niterói City are shown in Figure 8. Single ion monitoring chromatograms of the SD extract are shown in Figure 8a-f (17). Fifteen PAHs were identified: phenanthrene (17.40 min) and anthracene (17.64 min) (Figure 8a); 2-methylphenanthrene (19.94 min) (Figure 8b); fluoranthene (23.14 min) and pyrene (24.17 min) (Figure 8c); benzo[a]anthracene (30.18 min) and chrysene (30.28 min) partly resolved from triphenylene (30.34 min) (Figure 8d). Benzo[b]fluoranthene (34.26 min), benzo[k]fluoranthene (35.12 min), benzo[e]pyrene (36.22 min), benzo[a]pyrene (36.42 min) and perylene (37.19 min) are shown in Figure 8e. Indeno[1,2,3-cd]pyrene (41.08 min), benzo[ghi]perylene (42.28 min) and coronene (52.19 min) are shown in Figure 8f.

Figure 9 shows the NEXAFS spectrum obtained for the SD sample measured at the C-K edge. Very strong features can be observed in the  $\pi$  region, which are expected for

systems containing poly-aromatic structures. These are probably related to different transitions from carbon 1s electron to unoccupied molecular orbitals of the various PAHs concerned, since at least fifteen compounds were identified from the chromatographic analysis. A deconvolution methodology is being implemented in order to analyse such complex spectrum [17]. These results point to the viability of the use of the photoabsorption technique to recognize polycyclic aromatic structures in complex matrices. Further work is being carried out in the development of a methodology for PAH characterisation in raw extracts and solid samples.

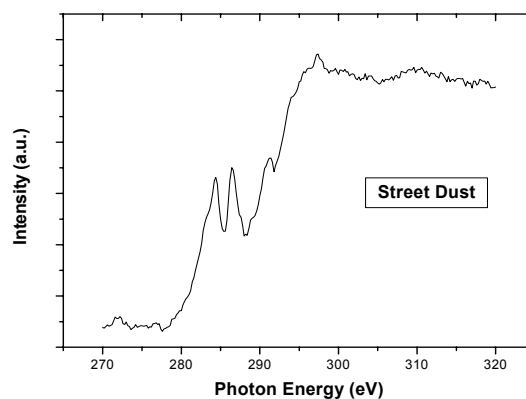


**Figure 8 - SIM chromatograms showing the peaks of the PAHs identified in a street dust sample collected at Niterói City, Rio de Janeiro State, Brazil (from down to top): a)  $m/z = 178$ , b)  $m/z = 190+192$ , c)  $m/z = 202$ , d)  $m/z = 228$ , e)  $m/z = 252$  and f)  $m/z = 276+278+300$ .**

#### 4. CONCLUSIONS

Photoabsorption spectra for a number of PAHs and PACs were measured at the C, N and O K-edges using synchrotron radiation from the Brazilian storage ring (LNLS). A new sample preparation method was

introduced. Good reproducible data was obtained demonstrating its applicability. NEXAFS spectra of several PAHs and PACs were recorded for the first time. Isomeric PAHs showed remarkable differences in their photoabsorption spectra which can be used as an identification tool. The developed method showed good capability as an analytical tool for the analysis of environmental samples but more studies are needed to evaluate its robustness. The next step of this work consists of studying other mixtures (binary, ternary, etc.) of PAHs and environmental sample extracts through photoabsorption spectroscopy in order to verify the potentialities of this technique as a non-destructive tool for the PAH and PAC analysis in complex matrices. Further work is being conducted on spectra assignment and deconvolution through *ab initio* calculations.



**Figure 9 - C 1s NEXAFS spectrum of a street dust sample collected at Niterói City, Rio de Janeiro State, Brazil.**

#### 5. ACKNOWLEDGMENTS

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