Chemical Analysis of Used Three-Way Catalysts by Total Reflection X-ray Fluorescence

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The methodology developed for evaluating, by total reflection X-ray fluorescence, the main elements in used three-way catalysts for cars after more than 59 000 km is described. The analytical method does not require chemical manipulation of the samples, is quick (30 min for sample preparation and 10 min for analysis), precise (between 1% and 10% of variation coefficient), and simple. The two catalytic monoliths contained in the cartridge of a car with more than 59 000 km have been analyzed. The mass relationships between the detected elements and Si, a component of the cordierite ceramic substrate, have been used to follow the axial and radial profiles of the elements. Information concerning the loss of active elements and the retention of contaminating elements as a consequence of the working conditions was attained by comparison between the results obtained for the used catalyst (59 000 km) with those of a fresh catalyst (0 km). The interface effect between the first and the second catalytic bricks was also studied.

Since 1993, Directive 94/12/EEC has compelled car manufacturers to decrease the amounts of hazardous NOx, unburned hydrocarbons, and CO in exhaust gas emissions. To satisfy this regulation a catalytic cartridge has become the widely adopted solution. The installation of a catalytic cartridge at the exit of the spark ignition engine considerably reduces the toxic emissions.¹ Since 1973, Directive 70/220/EEC has compelled car manufacturers to decrease the levels of CO, unburned hydrocarbons, and NOx in exhaust gas emissions. To satisfy this regulation a catalytic cartridge has become the widely adopted solution. The installation of a catalytic cartridge at the exit of the spark ignition engine considerably reduces the toxic emissions.¹ The cylinder arrangement of the car is the very complex chemical system. Often it consists of two monolith ceramic bricks, with a bee honeycomb-like structure, situated as shown in Figure 1.

Monoliths are based on cordierite, and this material is coated with a wash coat that contains the active components [CeO2–ZrO2 mixed oxides, platinum group, alumina, and other minor additives. Natural cordierite can contain 52 well-known different crystalline phases, as shown in the JCPDS database of the International Centre for Diffraction Data (Newtown Square, PA 19073-3273). These crystalline phases are usually magnesium aluminosilicates, which can have as minor constituent elements C, Na, Mg, Ca, Ti, Fe, Li, Bi, Cu, K, or hydrate H2O. The wash coat components are capable of transforming the three types of more pernicious emissions (NOx hydrocarbons, and CO), which gives rise to the name three-way catalysts (TWC) for the catalyst brick. TWC deteriorate under the harsh conditions to which they are subjected: high temperatures, high flow rates, and deposition of poisons. Although significant research effort has been devoted to study the deposition of poisons on TWC,² these studies must be updated and the information revisited because the nature and composition of the catalysts and the fuel formulation is rapidly changing.³ Moreover, the legislation is becoming more stringent,³ and consequently, the durability of the catalyst must be enhanced if the increasing low levels of emissions are to be fulfilled during the lifetime of the catalysts (between 80 000 and 100 000 km).

Knowledge of the retention of contaminants and of the loss of active elements is one of the key aspects that will result in the design of more durable catalyst cartridges. The study of the retention of contaminants by TWC has been conducted mainly by different analytical methods: SEM-EDS probe,⁴ X-ray fluorescence,⁵ and LIBS.⁶ The contaminants present in the greatest concentrations are P, Ca, S, Pb, and Zn (P, Ca, and Zn arising from lubricants and Pb and S from fuel).⁴ Axial and radial profiles of contaminants have been mainly described for the front brick of the catalytic system.⁵,⁶ The flow rate and flow pattern (turbulent across the first millimeters of the monolith and laminar in the rest), along with the gradient of temperatures existing within the brick, have been reported to explain such profiles.⁸,⁹

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The authors of this work are currently involved in a research project aimed at studying the causes of deactivation of real TWC and the possibility of implementing regeneration methodologies. It is clear that a precise knowledge of the deposition profiles of contaminating elements is essential for the achievement of this goal. A reliable, precise, and fast technique is required. Moreover, for a more precise quantification technique, ICPSM is a suitable candidate. The simplicity, rapidity, and accuracy of analysis by TXRF also makes this a suitable technique for monitoring the correctness of microwave digestion at the high pressures required by ICPSM analysis. In the work described here, the axial and radial concentration profiles of the main components and contaminants of catalyst monoliths have been studied by TXRF over the complete catalyst cartridge (front and rear bricks). The technique of total reflection X-ray fluorescence (TXRF) is well known and widely accepted by the scientific community. The general characteristics and potential applications of this technique have been described by Prange and Tölß. The work by Fernandez-Ruiz et al. on the direct analysis of solid samples by TXRF demonstrated that this technique can be applied to analyze the mass relationships between the elements with catalytic and environmental importance in car catalysts. The advantages of this technique in comparison to the SEM-EDS probe, LIBS methodology, and conventional XRF are that the limits of detection of TXRF are 3 orders of magnitude higher than in XRF/SEM-EDS, due to the absence of a matrix effect. Moreover, the amount of sample needed for the analysis is very small (10 mg) and this can be recovered after analysis. On the other hand, the analyses by SEM-EDS and LIBS are superficial and local and these techniques are therefore confined to microregions of the catalyst (from a few square micrometers to several hundreds of square micrometers), which can be very useful to obtain a microscopic map of the elements within very confined regions but fails to give the macroscopic and averaged results than are often required. In the case of the LIBS technique, the sample cannot be recovered after analysis, unlike in TXRF.

The axial study was also conducted in the rear monolith. Although front and rear monoliths are in close contact, the discontinuity in the flow features (the flow pattern changes from laminar to turbulent at the entrance of the second monolith and then, after several millimeters, back to laminar) could influence the retention of contaminants. To the best of our knowledge the study of the discontinuity effect on the retention of contaminants has not previously been carried out by TXRF.

**EXPERIMENTAL SECTION**

**Preparation of the Samples.** The study was carried out on the two catalytic bricks extracted from the exhaust system of a Ford Focus 1.6i run for more than 59 000 km: the front brick was placed upstream and the rear monolith downstream. A fresh catalyst from a brand new Ford Focus 1.6i with 0 km was used as a blank. Different samples were taken from the front (F) and rear (R) cylindrical monoliths at different axial and radial positions. To achieve this, the bricks had to be cut into different pieces (FI, front inlet; FO, front outlet; RI, rear inlet; RO, rear outlet) as indicated in Figure 2, where I and O also refer to the upstream and downstream positions. The powder material obtained during the cutting process was used as a representative sample of the average for a preliminary qualitative study of the matrix.

The samples obtained were subjected to the following preparation process prior to analysis by TXRF. First, 10 mg of each sample was ground in an agate mortar to a powder of <30 μm particle size. The powder was then further ground for 20 min in a vibrating micropulverizer consisting of a ball and an agate base (Fritsch GmbH, Oberstein, Germany). Subsequently, 1 mL of high-purity water was added to the powder. The mixture was then poured into a test tube in which up to 2 mL of high-purity water was added. The sample was homogenized for 10 min by ultrasonic desegregation in order to overcome possible agglomeration of particles. Finally, the particle size distribution in suspension was checked by using QELS until the required distribution of less than 10 μm of particle average diameter was achieved as Fernandez-Ruiz showed.

Two microliters of the suspension was taken and added. The sample was homogenized for 10 min by ultrasonic desegregation in order to overcome possible agglomeration of particles. Finally, the particle size distribution in suspension was checked by using QELS until the required distribution of less than 10 μm of particle average diameter was achieved as Fernandez-Ruiz showed.

**Instrumentation.** The TXRF analysis was performed using a Seifert EXTRA-II spectrometer (Rich Seifert & Co., Ahrensburg, Germany), equipped with two X-ray fine focus lines, Mo and W anodes, and a Si(Li) detector with an active area of 80 mm² and a resolution of 157 eV at 5.9 keV (Mn Kα).

An X-ray tungsten source was used for P determination in the TXRF analysis. The radiation was filtered with a Cu foil of 10-μm thickness in order to optimize the energy range (0–10 keV) used in the analysis. An X-ray molybdenum source was used for analysis of the rest of the detected elements, and this was filtered with a 50-μm Mo foil prior to analysis. The excitation conditions used were a potential difference of 25 kV and a variable intensity (between 5 and 25 mA) to yield a count rate of ~5000 counts/s.
in the spectra acquired with the tungsten source and a potential difference of 50 kV and a variable intensity (between 5 and 30 mA) to yield a count rate of ~5000 counts/s in the spectra acquired with the molybdenum source.

Quasi-elastic light scattering spectroscopy (QELS) was used for determination of the in-suspension particle size distribution of the analyzed samples. The QELS system used in this study was the AutoSizer IIc (Malvern Instruments Ltd.), equipped with a He-Ne 5-mW laser, a photomultiplier, and a processing electronic system controlled by the Malvern AutoSizer computer package.

**Qualitative and Interference Study.** After the preparation process, the TXRF spectra of the powders obtained by cutting the fresh (0 km) and used (59 000 km) monoliths were acquired during 1000 s in two energy ranges, 0–10 and 0–20 keV.

Figure 3 shows the spectra acquired from the fresh and used bricks in the energy range 0–20 keV. The presence of the following fluorescence X-ray lines can clearly be seen: Al K, Si K, Zr L, Pb M, Rh L, Ca K, Ti K, Ce L, Nd L, Fe K, Ni K, Hf L, Zn K, Pb L, Pt L, Sr K, and Zr K. If we compare the spectra of the fresh and used blocks between the lines for Ti K and Ce L, it can be seen that the increase in intensity in the valley can be explained by the presence of the La L line. On the other hand, the difference in intensity observed between the Ce L lines in the fresh and used blocks can only be explained in terms of the presence of Nd L lines. This result is consistent with the well-known use of lanthanum and neodymium oxides as commercial additives.

The analysis of phosphorus is very important in this study because it is an expected contaminant from the automobile lubricant. On the other hand, there is significant overlap between the P K line and lines coming from important constituents of the catalysts or contaminants (Al K, Si K, S K, Zr L, Sr L, Pb M, K K, and Ca K lines). To confirm the presence of P, we used the filtered least-squares (FLS) peak deconvolution method to decompose the acquired spectra. The spectra were acquired in the energy range of 10 kV. The elements Al K, Si K, S K, Zr L, Sr L, Pb M, K K, and Ca K were used in the deconvolution method. We subsequently evaluated the residual of the deconvolution process. The FLS process was carried out on the used catalyst (Figure 4a), where P is expected, and in the fresh catalyst (Figure 4b), where P is not expected.

Figure 4a shows the presence of an unassigned intensity in the deconvolution process around the P K peak maximum when the P K profile was not included. In addition, if we include the P K profile, we can observe the correct deconvolution of the envelope. Figure 4b does not show a contribution by P in any of the two cases, as one would expect.

**Semiquantitative Analysis.** One of the stoichiometric components of cordierite is Si. This element is always present in the catalyst samples. On the other hand, it is not likely that the Si concentration in the catalyst will vary much as the car catalyst is used. For this reason, we used the Si concentration as a reference, taking its value as 100 relative mass units. Our study focused on the following elements: Si, Al, Ce, and Rh as constituents and P, Ca, Ti, Ni, Zn, and Pb as probable contaminants. As will be shown below, Pt was detected in several samples of the used catalyst whereas it was not detected in the fresh sample. This element will therefore be considered as a contaminant from the point of view of the composition of the blank sample (fresh catalyst). This means that it is a contamination deposited during the working of the TWC. Traces of Pt arising from the re-forming catalysts used.

Figure 3. TXRF spectra of the average fresh catalyst (dot) and used catalyst (line).

Figure 4. (a) Process for the verification of the existence of P in the TXRF spectrum of the used catalyst. (b) Process for the verification of the absence of P in the TXRF spectrum of the fresh catalyst.
in refineries to improve the octane number of gasoline have been detected in gasoline$^{18}$ and will accumulate in the catalytic monolith. Although Pt can also be a component of TWC, since is very active in removing toxic emissions, the term contamination is applied to Pt deposition to highlight this additional source.

Table 1. Study of Variability of the Elements Analyzed by TXRF$^a$

<table>
<thead>
<tr>
<th>element</th>
<th>used-1</th>
<th>used-2</th>
<th>used-3</th>
<th>used-4</th>
<th>used-5</th>
<th>mean</th>
<th>SD (n=5)</th>
<th>CV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Al</td>
<td>89.45</td>
<td>93.67</td>
<td>93.28</td>
<td>91.44</td>
<td>92.72</td>
<td>92</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Ce</td>
<td>13.01</td>
<td>12.97</td>
<td>13.33</td>
<td>13.70</td>
<td>13.50</td>
<td>13.3</td>
<td>0.3</td>
<td>2</td>
</tr>
<tr>
<td>Rh</td>
<td>0.43</td>
<td>0.48</td>
<td>0.41</td>
<td>0.37</td>
<td>0.40</td>
<td>0.41</td>
<td>0.04</td>
<td>10</td>
</tr>
<tr>
<td>P</td>
<td>1.90</td>
<td>2.20</td>
<td>1.85</td>
<td>1.82</td>
<td>2.10</td>
<td>1.97</td>
<td>0.17</td>
<td>9</td>
</tr>
<tr>
<td>Ca</td>
<td>0.86</td>
<td>0.96</td>
<td>0.86</td>
<td>0.81</td>
<td>0.84</td>
<td>0.87</td>
<td>0.06</td>
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<tr>
<td>Ti</td>
<td>1.00</td>
<td>0.93</td>
<td>0.93</td>
<td>1.04</td>
<td>1.02</td>
<td>0.98</td>
<td>0.05</td>
<td>5</td>
</tr>
<tr>
<td>Ni</td>
<td>0.035</td>
<td>0.034</td>
<td>0.038</td>
<td>0.036</td>
<td>0.035</td>
<td>0.034</td>
<td>0.002</td>
<td>6</td>
</tr>
<tr>
<td>Pt</td>
<td>0.071</td>
<td>0.078</td>
<td>0.084</td>
<td>0.082</td>
<td>0.080</td>
<td>0.079</td>
<td>0.005</td>
<td>6</td>
</tr>
<tr>
<td>Zn</td>
<td>0.60</td>
<td>0.63</td>
<td>0.60</td>
<td>0.62</td>
<td>0.63</td>
<td>0.62</td>
<td>0.02</td>
<td>2</td>
</tr>
<tr>
<td>Pb</td>
<td>0.33</td>
<td>0.34</td>
<td>0.33</td>
<td>0.36</td>
<td>0.35</td>
<td>0.34</td>
<td>0.01</td>
<td>4</td>
</tr>
</tbody>
</table>

$^a$ The units are expressed in percent vs Si.

Table 2. Evaluation of the Differences in Relative Concentration (%) between Used Catalyst and Fresh Catalyst with Their Associated Band Error$^a$

<table>
<thead>
<tr>
<th>element</th>
<th>$C_{\text{fresh}}$ (rmu)</th>
<th>$C_{\text{used}}$ (rmu)</th>
<th>$\Delta C$ (rmu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>100 ± 1</td>
<td>100 ± 1</td>
<td>ref</td>
</tr>
<tr>
<td>Al</td>
<td>96 ± 3</td>
<td>90 ± 3</td>
<td>-6 ± 4</td>
</tr>
<tr>
<td>Ce</td>
<td>9.5 ± 0.3</td>
<td>8.3 ± 0.3</td>
<td>-1.2 ± 0.4</td>
</tr>
<tr>
<td>Rh</td>
<td>0.7 ± 0.1</td>
<td>0.4 ± 0.1</td>
<td>-0.3 ± 0.1</td>
</tr>
<tr>
<td>P</td>
<td>0.38 ± 0.08</td>
<td>3.1 ± 0.7</td>
<td>2.7 ± 0.7</td>
</tr>
<tr>
<td>Ca</td>
<td>1.15 ± 0.05</td>
<td>1.13 ± 0.04</td>
<td>-0.02 ± 0.06</td>
</tr>
<tr>
<td>Ti</td>
<td>0.98 ± 0.04</td>
<td>0.99 ± 0.04</td>
<td>0.01 ± 0.06</td>
</tr>
<tr>
<td>Ni</td>
<td>0.019 ± 0.002</td>
<td>0.056 ± 0.006</td>
<td>0.037 ± 0.006</td>
</tr>
<tr>
<td>Pt</td>
<td>nd</td>
<td>0.065 ± 0.003</td>
<td>0.065 ± 0.003</td>
</tr>
<tr>
<td>Zn</td>
<td>0.120 ± 0.002</td>
<td>0.54 ± 0.01</td>
<td>0.42 ± 0.01</td>
</tr>
<tr>
<td>Pb</td>
<td>0.004 ± 0.001</td>
<td>0.41 ± 0.01</td>
<td>0.41 ± 0.01</td>
</tr>
</tbody>
</table>

$^a$ The sample evaluated was FI in both cases. rmu, relative mass units; nd, not detected.

been shown to be accumulated during the use of the car because their increase is smaller than the associated band error.

**Detection Limits.** The detection limits (DL) associated with the evaluated elements Si, Al, Ce, Rh, P, Ca, Ti, Ni, Pt, Zn, and Pb were calculated using eq 2, as reported by Klockemkämper,$^{11}$

$$DL = \frac{3M}{A} \sqrt{B/R}$$

where $M$ is the element mass, $A$ and $B$ are the areas of the peak and background, respectively, in counts per second for each element, and $r$ is the acquisition time in seconds according to the IUPAC definition.

Experimental determination of the detection limits was achieved using ICPS or AAS single elementary patterns of known concentration (M ercke KgaA, Darmstadt, Germany). The detection limits obtained were as follows: $DL_{Si} = 635$ pg, $DL_{Al} = 954$ pg, $DL_{Ca} = 72$ pg, $DL_{Rh} = 14$ pg, $DL_{P} = 517$ pg, $DL_{Zn} = 50$ pg, $DL_{Ti} = 32$ pg, $DL_{Ni} = 7$ pg, $DL_{Pt} = 8$ pg, $DL_{Zn} = 5$ pg, and $DL_{Pb} = 6$ pg.

If we consider that the quantity of sample in question deposited on the flat carrier is ~5 µg, we obtain the following concentration detection limits:

- $DL_{Si} = 127$ µg g$^{-1}$,
- $DL_{Al} = 191$ µg g$^{-1}$,
- $DL_{Ca} = 14.4$ µg g$^{-1}$,
- $DL_{Rh} = 2.8$ µg g$^{-1}$,
- $DL_{P} = 103$ µg g$^{-1}$,
- $DL_{Pt} = 10$ µg g$^{-1}$,
- $DL_{Zn} = 14.4$ µg g$^{-1}$,
- $DL_{Ti} = 6.4$ µg g$^{-1}$,
- $DL_{Ni} = 1.4$ µg g$^{-1}$,
- $DL_{Pt} = 1.6$ µg g$^{-1}$,
- $DL_{Pb} = 1$ µg g$^{-1}$,
- and $DL_{Pb} = 1.2$ µg g$^{-1}$.

The relative sensitivity calibration curve used in this study was obtained in the same way as described by Fernández-Ruiz and

Capmany, the only difference being that the solution pattern used in the calibration was prepared with the same ICPS or AAS single elementary patterns used in the determination of the detection limits.

**RESULTS AND DISCUSSION**

**Wash Coat Constituent Elements.** After fixing the instrumental conditions, we proceeded to carry out a systematic study of the radial and axial deposition profiles in the used and fresh catalysts. Figure 5 shows the axial profiles of some of the wash coat constituent elements. Al, Ce, and Rh were selected as representative elements of the wash coat.

Figure 5 shows the axial dependence of the relative concentrations of Al, Ce, and Rh. The first conclusion is that the sample has significant inhomogeneity in terms of the elemental composition. This fact is an unavoidable consequence of the industrial process of impregnation of the cordierite bricks by the wash coat. The increasing concentration along the axial coordinate of the bricks could also be a deliberate strategy of the manufacturer to improve the catalytic performance. On the other hand, the concentrations of these three elements are consistently higher in the fresh catalyst than in the used catalyst, although this could also indicate loss by attrition during function. As a matter of fact, several works have shown that noble metals and wash coat components of TWC suffer from attrition and are released through the exhaust pipe into the environment. Roadside dust samples collected from broad-leaved plants contained anomalously high concentrations of Pt and Pd, and these have been related to their emission from car exhaust pipes. Therefore, from the environmental point of view, these elements can be considered as pollutants. These elements are in the wash coat layer that impregnates the cordierite bricks. It is reasonable to believe that this layer is susceptible to deterioration under the continuous variations of temperature and very high gas flow rate to which it is subjected. From this point of view, the fractured micrometric wash coat particles can be dragged through the channels of the catalyst and be expelled into the environment.

Figure 6 shows the radial profiles obtained for the same elements, i.e., Al, Ce, and Rh.

![Figure 6. Radial deposition profile of the constituent elements Rh, Al, and Ce.](image)

Figure 5. Axial deposition profile of the constituent elements Rh, Al, and Ce.

fresh catalyst than in the used one, a situation in agreement with the hypothesis outlined above. Moreover, if we consider the profile of the levels FO-00 and FO-59 for Al and Ce, we can see that the difference in the concentration is greater as the radial distance decreases. Theoretically, the distributions of pressure and temperature of the gases that penetrate the catalytic cartridge present a parabolic symmetry.\(^8\) In this situation, the central region of the catalyst is the area that is affected to a greater extent by changes in pressure and temperature, and therefore, from the catalytic point of view it is this area that should be degraded more quickly. The Rh profile does not offer any additional information because the error bands overlap.

**Contamination Elements: P, Ni, Pt, Zn, and Pb.** Figure 7 shows the axial profiles of the contaminant elements P, Ni, Pt, Zn, and Pb. In the axial profiles of the five elements evaluated as pollutants, two clearly different areas exist. These areas correspond with each of the catalytic bricks that form the catalytic cartridge. In all cases, it is in the front monolith in which the highest quantities of pollutants are absorbed. The rear monolith gives rise to a smaller level of retention than the first one, apart from the behavior of the elements Pb and Zn. In addition, it is worth highlighting the important effect on the quantities of retained elements that exists in the interface between the two bricks. The distance between the two bricks is only \(\sim 0.1\) mm, but the retained quantities decrease dramatically. In percent versus Si units, P changes from 1.47 to 0.81 (a decrease of 32\%), Ni goes from 0.03 to 0.02 (a decrease of 33\%), Pt goes from 0.08 to 0.01 (a decrease of 87\%), Zn goes from 0.30 to 0.23 (a decrease of 23\%), and Pb goes from 0.23 to 0.21 (a decrease of only 9\%). A change in the flow regime from laminar to turbulent could occur in the interface, and this could be the origin of the fall in the retention of contaminants. It is important to stress that all the contaminants (except Zn and Pb) progressively reach a concentration level in the rear monolith that is similar to the value of the fresh sample, a fact that indicates the final region of the rear monolith is free of contamination. Previous regions of the catalyst system have retained all the contamination. However, the Pb and Zn concentrations in the end section of the rear monolith are considerably higher than in the fresh brick. This can be explained by the ease of volatilization of Zn and Pb compounds at the high temperatures to which the catalyst is subjected. Zn and Pb are continuously transported by the gas flow in a retention equilibrium dominated by the volatilization of their compounds. This situation results in these compounds being emitted into the environment. Finally, the radial profile of the contaminant elements is shown in Figure 8.

For the polluting elements, we can see that the radial behavior is opposite to that obtained for the constituent elements. If we consider profile FI-59, we can appreciate that the elementary concentrations grow as the radial distance increases and their evolution has an approximately parabolic form. This fact seems to contradict the geometry of the catalytic system of a car (Figure 1), where the flow of combustion gases impacts on the central region of the catalytic block. Under these conditions, the most reasonable behavior would be that the elementary concentrations were maximum for small radial distances and minimum for large
CONCLUSION

This work shows that TXRF is a very useful technique to evaluate the constituents and contaminant elements in used TWC catalytic matrixes. The method requires very small quantities of sample, and the low detection limits obtained allow the measurement of concentrations in the parts-per-million range for all the elements studied. P, Ca, Zn, Pb, and Pt were detected and these are deposited in the TWC when working under real conditions. The method does not require chemical manipulation, eliminating the uncertainties associated with the recovery problems in the acid digestion processes. The simplicity, rapidity, and accuracy of the analysis make TXRF a suitable technique for monitoring the diffusion profiles of concentration in these types of material. On the other hand, the anomalies detected in the radial and axial profiles of contaminants and constituents have been studied. A strong axial gradient was observed for the contaminants. The behavior and the interphase effect of some elements were studied. These effects should be studied more thoroughly to find a satisfactory explanation. The study also shows that Zn and Pb, and very likely Al, Ce, and Rh, are emitted into the atmosphere in the exhaust pipe gases and must be considered as pollutants as much as NO\textsubscript{x}, unburned hydrocarbons, and CO. From the environmental point of view, we have demonstrated that the elements Al, Ce, and Rh can be considered as potential pollutants in the current TWC catalysts for gasoline. The elements Zn and Pb should continue to be considered as potential pollutants. Our current investigations aim to find a method for the absolute quantification of these elements by combining the acquired knowledge on TXRF and the techniques of high-pressure microwave digestion and ICPMS for the elements of environmental and catalytic interest.

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