# Elemental characterization of tar by energy dispersive X-ray fluorescence of the three most consumed cigarettes brands in Peru

**V. A. G. Rivera**
National University of San Marcos
**Carlos Giovanni Molinari Cheme** (carlos.molinari@unmsm.edu.pe)
National University of San Marcos
**Diego A. Flores C.**
National University of San Marcos

**Research Article**

**Keywords:** EDXRF, Tar cigarettes, lung cancer, harmful elements to the lungs, Peru

**Posted Date:** March 14th, 2022

**DOI:** https://doi.org/10.21203/rs.3.rs-1401930/v1

# Abstract

According to the World Health Organization (WHO),85% of deaths from lung cancer were attributable to tobacco use in 2018 (WHO, 2020). However, this data is from the European region and there is a lack of studies related in developing countries such as Peru. In this frame, we employed the nuclear technique of energy dispersive X-ray fluorescence (EDXRF) in order to analyzed 3 of the most consumed brands of cigarettes in Peru were analyzed. To do so, an artificial experiment array was carried out to simulate the human lungs of not only an active but a passive smoker as well. With these results, this research was able to find the elemental chemical composition of the tar that it is impregnated to the lungs of the consumer for each brand and give a glance about the presence of the most harmful of elements.


# Introduction

Since 2001, when the World Health Organization (WHO) start promoting anti-smoking campaigns to the world (Scha et al., 2001), more research about the consumption of cigarettes were made but principally in developed countries. These studies were fitted to the realty of this part of the world and a clear example is the high presence of Po210 isotope in tobacco cigarettes at Europe due to the contamination of Chernobyl incident many years ago (Ali et al., 2020; Melitsko, 2018; Papastefanou, 2009). Nevertheless, many countries in South America did not do much investigation on the matter and only took the guidelines recommendations from WHO, even though this organization made these guidelines based on research done mostly only in developed countries without substantial research about other realities such as the one in South America. With this in consideration and the lack of research done on this topic in Peru, an investigation to analyze the composition present in the tar attached at the lungs becomes important to provide useful information not only about the composition but the harms that can provide to the consumer and the society as well. It is important to mention that in Peru does not exist any studies about the presence of isotope Po210 in tobacco cigarettes or other dangerous components. Additionally, it is known that in Peru exists different kind of soils with metals in its composition which can be harmful to humans. These metals could be Zinc, Titanium or Copper which may produce long-term respiratory diseases, change the alkalinity on the blood or even cause lung cancer(Stellman, 1998).

To start an investigation about this topic, the first thing to do is to define how is Tar propagation through the cigarette consumption (Caliri et al., 2021; Iede et al., 2017; Mider, 1956; Schaefer et al., 2013). To get the answer to this question it is necessary to define the environments where it is consumed and who are affected by the different types of cigarettes. So here it is found that when a smoker consumes such products, the person near is affected as well even though this indirect consumer is not smoking directly. Therefore, to obtain the full impact of whatever the composition of the product is, the target public must be defined not only with the person who is smoking but the person near as well and maximize this secondhand smoking because this way the study can get the worst-case scenario possible from where the damage is the highest and the possible solutions can include the widest scenarios.

For these reasons, the study focusses on obtain and characterize samples from the recreated mechanism of an active smoker and from the breathing of a secondhand smoker as well. The impact of this approach is more accurate to engage not only the composition and the time this last but also to the human health that is transferred to the public health.

# Methodology

For this study, three of the most consumed brands in Peru (Impuesto Selectivo al Consumo aplicable a los Cigarrillos, 2017) were analyzed by using 100 cigarettes for each brand (H, P and L) to recreate the week average consumption of an active and a passive smoker.

### Experimental Setup

To simulate not only the smoking process but also the secondhand smoking, the following steps and systems were created: first the samples were extracted by filtering the cigarette smoke with isopropyl alcohol contained in two sealed Erlenmeyer Flasks connected each other and one connected to a vacuum machine, so all the smoke go through the flasks and the tar was contained there as much as possible to recreate human lungs. Then, to simulate a passive smoker, it was used another similar arrangement extracting the smoke from outside the cigarette by its own with an acrylic bell-shaped. After the process of containing the tar was done, the samples were separated from the alcohol using a bain-marie technique by heating the alcohol to a temperature of 85°C, it started to boil but the other components did not because they have a boiling point above 100°C (Nicotine's boiling point is 247°C). Finally, it remained only the tar and all the components analyzed by EDFXR.

The samples were putted on petri dishes for the EDFRX analysis (300 seconds of analysis each sample). The equipment used was the X-123SDD X-Ray Spectrometer with a Mini-X tube, and the data was obtained through with Amptek DppMCA software and analyzed with Origin.

### Analysis by EDXRF

The elemental composition analysis was performed using a portable EDXRF AMPTEK instrument (X-123SDD X-Ray Spectrometer). This instrument uses an X-ray tube with an Au anode, that operated at 30 kV and about 30 μA. This instrument allows the characterization of elements with Z values greater than 12 and with a resolution of 3 decimals. The performance of the array has been checked using reference samples. The estimated uncertainty in these measurements of the elemental concentrations is about 10% and it is important to point out that the equipment is more sensible around the gold anode energy (Cabrejos, 2015). The measurements were taken 5 times for each sample and the graphics obtains corresponds to the mean of these takings, with an instrumental error of $\pm 1\backslash\%$.

### Experimental Results

Due to the limited funding of our own, the number of cigarette packs (20 cigarettes each) was 5 for each brand. This affected the amount of tar extracted for each brand which subsequentially limited the concertation of each element as it can be seen in some of the small peaks in the spectrum. Reason why some elements have pronounced peaks even though they are small ones. At the same time, this sample also reflects very well qualitatively the concentration of each element that the consumer (passive and active) is taken into his or her body in weekly bases.

### Active Smoker

Figure 1 shows the results for the brands H, P and L. The peaks correspond to the characteristic elements present in the samples for an active smoker. Also, it is noticeable that the concentration of each element found is related it to the number of counts so the difference among one brand to the others can be seen here and a qualitative analysis can be made. Most of the spectrums are confirmed by the $K_\alpha$ energies level except for Thorium (Th) which is the peak of $L_\alpha$ and the $K_\beta$ shell of Zinc (Zn). The machine use a gold anode and it is detected as a superposition of a peak (around 9.713 KeV) attached to the $K_\beta - Zn$, this energy belongs to the $L_\alpha$ shell of Gold (Cabrejos, 2015). It because of this, that the peak of gold is not consider in the analysis of the characterization of the tar samples.

The corresponding $K_\alpha$ for each element found is showed in Table 1. The $\mathrm{K}_\beta$ shell of Zn intensity is explainable due to the proximity of this energy to the gold anode of the equipment; therefore, because of the resonance we see an enhancement in the $\mathrm{K}_\beta$ signal of the Zn. From Fig. 1 also can be notice that even though, Titanium's peak is almost imperceptible due to the small sample size took, it is considered in the following table due to the well-marked peak.

Table 1
Detected element with its corresponding $K_a$ energy shell.

| Element | $K_a$ (KeV) |
|---|---|
| S | 2.309 |
| Cl | 2.622 |
| Ar | 2.958 |
| K | 3.314 |
| Ca | 3.692 |
| Sc | 4.093 |
| Ti | 4.512 |
| Fe | 6.405 |
| Cu | 8.046 |
| Zn | 8.637 |
| Se | 11.224 |
| Rb | 13.396 |

In order to identify without doubt the Ti presence, it must be analyzed the range of energy from 4 to 5 Kev ($K_\alpha = 4.512\mathrm{KeV}$ for Ti) as it was displayed on Table 1 (Bruker, 2015). The results expose not only that Ti is present in at least one of the samples for an active smoker but also reveal the brand with the highest levels to the lowest of it as it can be seen in Fig. 2.

### Passive Smoker

For the other case measured as the intuition may tell, secondhand smoking has less amount of the same elements found for an active smoker, but the spectrums were the same. However, the concentration order for the brand which has highest to the lowest corresponding a passive smoker change as the results in Fig. 3 shows.

The samples could be characterize using Table 1 as it was used to identify the elements in Fig. 1. Like it occurred before in the spectrums of active smokers, the peak of Th corresponds to the $L_\alpha$ energy and $K_\beta$ energy of Zn was one of the highest. This same peak is a little bit wider than the rest of them, this is because of the $L_\alpha$ energy shell corresponding to the gold anode from the X-ray tube that was detected as it occurred in Fig. 1, but it is not considered for the analysis and removed from the characterization of the samples. In the graphic the Ti peak had a low intensity in comparison with the other peaks, so it is shown with different scale on Fig. 4 shows.

## Discussion

The results show that the three brands have the same chemical elements but in different concentrations and this could be seen by looking of the counts per peaks. The identified peaks are from the $K_\alpha$ energies of each element and their exact energies for each one of them are shown in Table 1. From these results obtained, it can be well stablished that Ti was not noise from the measurement but the presence of the element itself. This was possible not only with the software used but also due to the experimental set up made. Even though the concentrations in the samples taken are small due to the number of cigarettes used, the set up made possible to obtain the most of it and this way the Ti was able to be detected.

Additionally, we found some metals such as Ti, Cu, Fe, Se and Zn. These elements are very hazardous to the lungs causing ulcers (cooper), irritation (selenium) and, they can cause cancer just by inhalation on long terms as well (Stellman, 1998). The FDA (Kux, 2012) published a list of harmful and potentially harmful constituents in tobacco products and tobacco smoke, in contrast with this study the high concentration of Se, also for the passive and active smoker, provides a good look of the presence of this chemical element in the Peruvian cigarettes market which can be linked to respiratory problems that could be more harmful in areas with less oxygen as in the Andean region of the country. Due to the EDXRF machine capacity, elements with Z number below 12 could not be detected. However, elements above that as the Cl found in the samples, could be part of harmful chemical compositions with other elements that were not detected due to its Z < 12 number, such as chlorinated dioxins/furans (CDF)(EPA, n.d.) or vinyl chloride $\left(C_2H_3Cl\right)$. From these two compounds, the second one is carcinogen but the first one is additionally a reproductive or developmental toxicant agent (EPA, n.d.) Therefore, several of the elements found correspond to some of the harms described in other studies in developed countries that were used and published by WHO to warn about the dangers of cigarettes consumption. (Schar et al., 2001). In Figs. 1 and 3, can be noticed that the brand order of the intensity spectrum for an active and a passive smoker change (see Table 2). From this same comparison it can be noticed that even though there are differences between the two types of smokers, these ones are not that big. Focusing on Cl and Se for example, the differences change but they remain small. It is important to point out that for brand P looking at Cl due to that it can be part of a reproductive or developmental toxicant agent as well as a carcinogen one, the active smoker has the highest point of its intensity peak 455.302 counts and the passive one of the same brands has this point with 556.335 counts, as it is showed the difference is 711.534 counts. Here, the passive smoker has the highest Cl peak differing from the other two brands, which draws the attention of this research. For one of the other elements mentioned before because is a respiratory toxicant, the Se has its highest point of intensity 6720.855 counts for the active smoker and the passive one has it at 8032.059 counts, with a difference of 1311.204 counts. As it is showed, the highest peak correlate to the passive smoker for brand P which shows an untypical behavior among the brands used.

To contrast more the data obtained, in Table 2 it is showed the highest intensity of the peak in each element for each brand for an active smoker and passive smoker as well. This intensity is measured in counts of the detection and here it is showed that for two of the brands, even though the intensity changes for a secondhand smoking, there is still a consumption of the same elements. In case of the third one (brand P) the intensity of the passive smoker for many elements is higher than the active one.

Table 2
Comparative for an active and passive smoker for each element, ±1% error..

| | Brand | Element | Intensity (counts) | | Brand | Element | Intensity (counts) |
|---|---|---|---|---|---|---|---|
| Active | P | S | 230.992 | Passive | P | S | 225.277 |
| | | Cl | 455.302 | | | Cl | 556.335 |
| | | Ar | 1845.419 | | | Ar | 951.764 |
| | | K | 454.504 | | | K | 4611.679 |
| | | Ca | 330.480 | | | Ca | 5022.111 |
| | | Sc | 251.236 | | | Sc | 929.997 |
| | | Ti | 428.858 | | | Ti | 393.538 |
| | | Fe | 1329.956 | | | Fe | 1415.386 |
| | | Cu | 1969.385 | | | Cu | 2212.731 |
| | | Zn ($K_\alpha$) | 4698.907 | | | Zn ($K_\alpha$) | 5083.165 |
| | | Zn ($K_\beta$) | 10997.954 | | | Zn ($K_\beta$) | 12874.321 |
| | | Se | 6720.855 | | | Se | 8032.059 |
| | | Th ($L_\alpha$) | 1701.021 | | | Th ($L_\alpha$) | 1992.947 |
| | | Rb | 1391.846 | | | Rb | 1825.064 |
| | H | S | 370.611 | | H | S | 283.530 |
| | | Cl | 1270.630 | | | Cl | 559.096 |
| | | Ar | 1053.012 | | | Ar | 958.175 |
| | | K | 6346.783 | | | K | 827.698 |
| | | Ca | 1752.370 | | | Ca | 1752.509 |
| | | Sc | 413.585 | | | Sc | 389.678 |
| | | Ti | 338.259 | | | Ti | 268.817 |
| | | Fe | 910.376 | | | Fe | 850.946 |
| | | Cu | 1628.851 | | | Cu | 1452.474 |
| | | Zn ($K_\alpha$) | 3767.712 | | | Zn ($K_\alpha$) | 2725.857 |
| | | Zn ($K_\beta$) | 10361.913 | | | Zn ($K_\beta$) | 9012.954 |

| Brand | Element | Intensity (counts) | Brand | Element | Intensity (counts) |
|---|---|---|---|---|---|
| | Se | 7137.539 | | Se | 5615.171 |
| | Th ($L_\alpha$) | 1881.112 | | Th ($L_\alpha$) | 1406.669 |
| | Rb | 1685.106 | | Rb | 1302.492 |
| L | S | 754.712 | L | S | 322.071 |
| | Cl | 1863.185 | | Cl | 522.524 |
| | Ar | 1388.649 | | Ar | 853.640 |
| | K | 8788.801 | | K | 1852.641 |
| | Ca | 1400.733 | | Ca | 1461.208 |
| | Sc | 257.397 | | Sc | 311.720 |
| | Ti | 350.823 | | Ti | 408.269 |
| | Fe | 1113.591 | | Fe | 1308.195 |
| | Cu | 2112.303 | | Cu | 1317.006 |
| | Zn ($K_\alpha$) | 3602.033 | | Zn ($K_\alpha$) | 2404.639 |
| | Zn ($K_\beta$) | 13189.454 | | Zn ($K_\beta$) | 7945.928 |
| | Se | 9109.469 | | Se | 4785.523 |
| | Th ($L_\alpha$) | 2409.729 | | Th ($L_\alpha$) | 1173.533 |
| | Rb | 2149.541 | | Rb | 1069.121 |

Is important to mention that the chemical process from which the tar is extracted due the consumption of cigarette will be always the same for an active smoker and a passive one, the amount of tar produce due to this reaction is nearly constant since the human body do not take part on it beyond the velocity ratio of the consumption. However, the reaction of each human body from the whole to the cellular level with this amount impregnated in the lungs, for each brand and whether it is an active smoker or a passive one will differ in each organism so the same amount will be able to harm more to some people than others, this is due to the different reactions every human body have (Samet, 2002). In this sense, our results are a simulation from the experimental setup made and allow to determine the characteristics peaks of Tar due to the cigarette consumption.

## Conclusion

The experimental set up worked and made possible to obtain the elements that due to the small sample size otherwise could have been lost. Furthermore, it can be well established that due to the high interaction found of $K_\alpha$ and $K_\beta$ Zn energies levels lead to conclude that it could be more presence of Zn in the tar samples than other elements identified and it's an irritant for the lungs. The FDA categorize Se as a respiratory toxicant agent and the intensity of this element is high in the detection made so it leads to future studies about this presence found for the Peruvian market. Additionally, the FDA categorize the CDF family as a carcinogen and a reproductive or developmental toxicant agent, this compounds characteristically have Cl in their chemical composition, so this conduct the study to suspect that the Cl peaks are part of this CDF family described by the FDA (Kux, 2012). Due that this research focused on the chemical elements due the nuclear technique used so further studies about the chemical compounds and behavior could be made using as a starting point this study. In addition, this work can be used as a start point for medical research focusing on these elements due to their presence in tar so their repercussions on the human body can be better understood based on samples that were taken from the current market in Peru. To prevent the presence of this elements in future cigarettes it is recommended that they should study the soil before they start planting.

# Declarations

## Acknowledgement

We want to express our deep gratitude to the Group of Nuclear Physics (GFN-UNMSM) and Dr. Jorge Bravo from the laboratory of Soil science, archaeometry and new materials (Ciencia del suelo, arqueometría y nuevos materiales – UNMSM) to make this research possible.

## Disclosure statement

No potential conflict of interest was reported by the author.

## Authors contributions statement

Carlos Giovanni Molinari Cheme and Diego A. Flores C. conducted the experiments, analyzed the data, prepared the figures, performed the mathematical calculations, prepared the samples, V.A.G.Rivera, Carlos Giovanni Molinari Cheme and Diego A. Flores C. prepared the manuscript, Carlos Giovanni Molinari Cheme. and Diego A. Flores C. designed the experimental setup, V.A.G.Rivera supervised the project, V.A.G.Rivera, Carlos Giovanni Molinari Cheme and Diego A. Flores C. discussed the results and contributed to finalizing the paper.

## Competing interests

The authors declare no competing interests.

# References

1. Ali, R., Zhang, Z., Bux Soomro, M., Gogan, I.C.W., Soomro, H.R., 2020. Tobacco control via quick response code and mobile health technologies: Empirical-evidence of the health belief model theory. Human Systems Management 39. https://doi.org/10.3233/HSM-190629
2. Cabrejos J.A.B., 2015. Energy dependence of the production of escape peaks in energy dispersive X-ray fluorescence spectroscopy. Revista de Investigacion en Fisica UNMSM 18.
3. Caliri, A.W., Tommasi, S., Besaratinia, A., 2021. Relationships among smoking, oxidative stress, inflammation, macromolecular damage, and cancer. Mutation Research - Reviews in Mutation Research. https://doi.org/10.1016/j.mrrev.2021.108365
4. EPA, n.d. Dioxins and Furans.
5. Iede, M. al, Nunn, K., Milne, B., Fitzgerald, D.A., 2017. The consequences of chronic cannabis smoking in vulnerable adolescents. Paediatric Respiratory Reviews. https://doi.org/10.1016/j.prrv.2016.11.001
6. Impuesto Selectivo al Consumo aplicable a los Cigarrillos, 2017. Lima.
7. Kux L., 2012. Harmful and Potentially Harmful Constituents in Tobacco Products and Tobacco Smoke; Established List.
8. Melitsko, S., 2018. Poverty and smoking: assessing the financial impact of tobacco purchases on households´ budgets in Argentina. Tobacco Induced Diseases 16. https://doi.org/10.18332/tid/84631
9. Mider G.B., 1956. Some developments in cancer research. Journal of Chronic Diseases 4, 296–320. https://doi.org/10.1016/0021-9681(56)90032-7
10. Papastefanou, C., 2009. Radioactivity of tobacco leaves and radiation dose induced from smoking. International Journal of Environmental Research and Public Health 6, 558–567. https://doi.org/10.3390/ijerph6020558
11. Samet J.M., 2002. [Risks of active and passive smoking]. Salud pública de Mexico 44 Suppl 1, S144-60.
12. Schaefer, D.R., Adams, J., Haas, S.A., 2013. Social Networks and Smoking: Exploring the Effects of Peer Influence and Smoker Popularity Through Simulations. Health Education and Behavior 40. https://doi.org/10.1177/1090198113493091
13. Schar, E.H., Gutierrez, K.K., 2001. SMOKING CESSATION MEDIA CAMPAIGNS FROM AROUND THE WORLD. RECOMMENDATIONS FROM LESSONS LEARNED.
14. Stellman J.Mager., 1998. Enciclopedia de Salud y Seguridad en el Trabajo. Vol. 2. Ministerio de Trabajo y Asuntos Sociales.
15. WHO, 2020. Tobacco use causes almost one third of cancer deaths in the WHO European Region [WWW Document]. URL https://www.euro.who.int/en/health-topics/disease-prevention/tobacco/news/news/2020/2/tobacco-use-causes-almost-one-third-of-cancer-deaths-in-the-who-european-region

# Figures

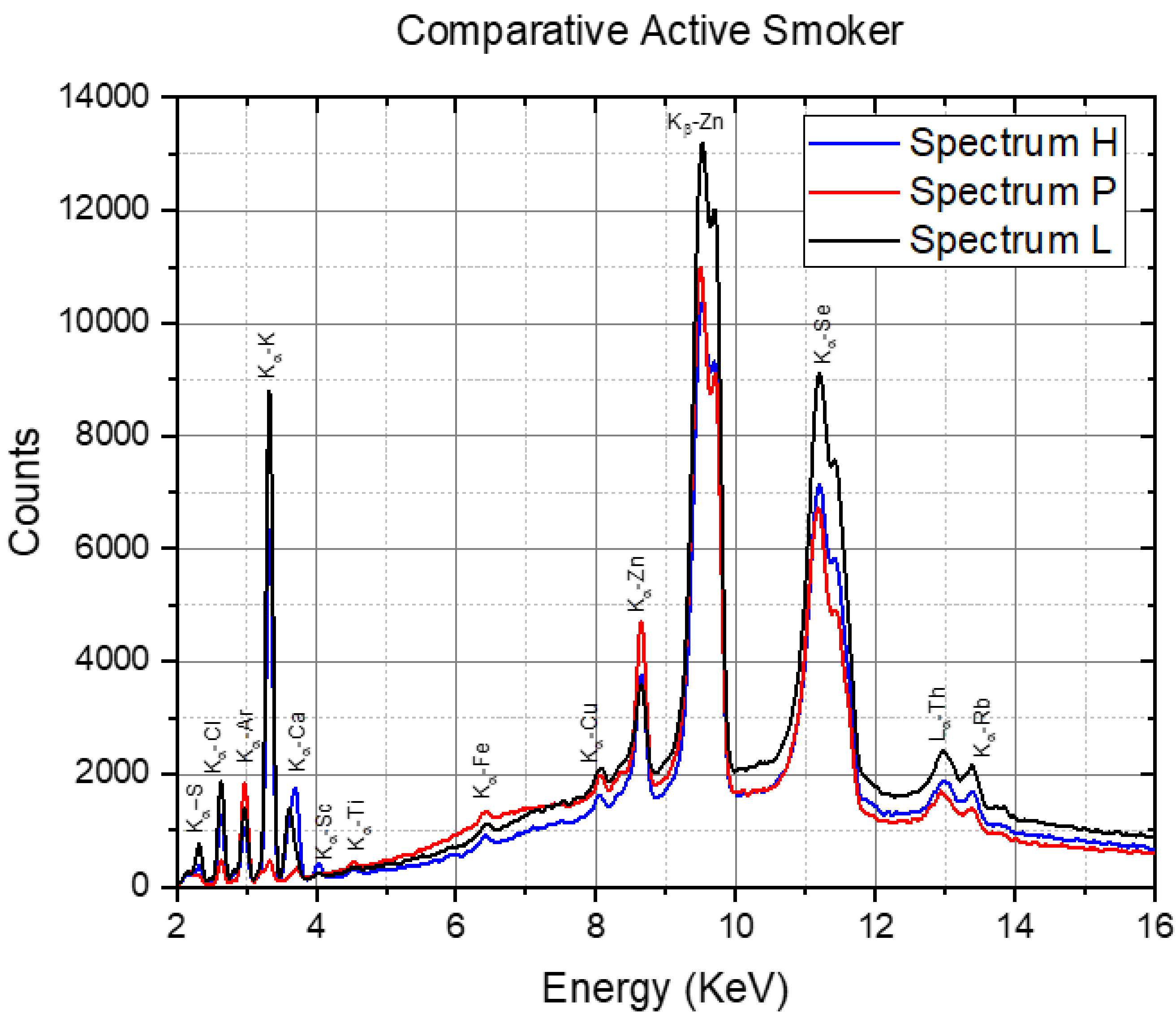


Figure 1

EDFRX spectrums of the samples took for an active smoker in bands worked, under the same experimental conditions. The data was taken mainly from $K_a$ shells but also $K_\beta$ shell of Zn due to the characteristic energy proximity to the gold anode and the $L_a$ of Th because it's in the machine energy range of detection. Also, it is noticeable that the concentration of each element found is related with the number of counts and brand L is higher in most elements than the other brands.

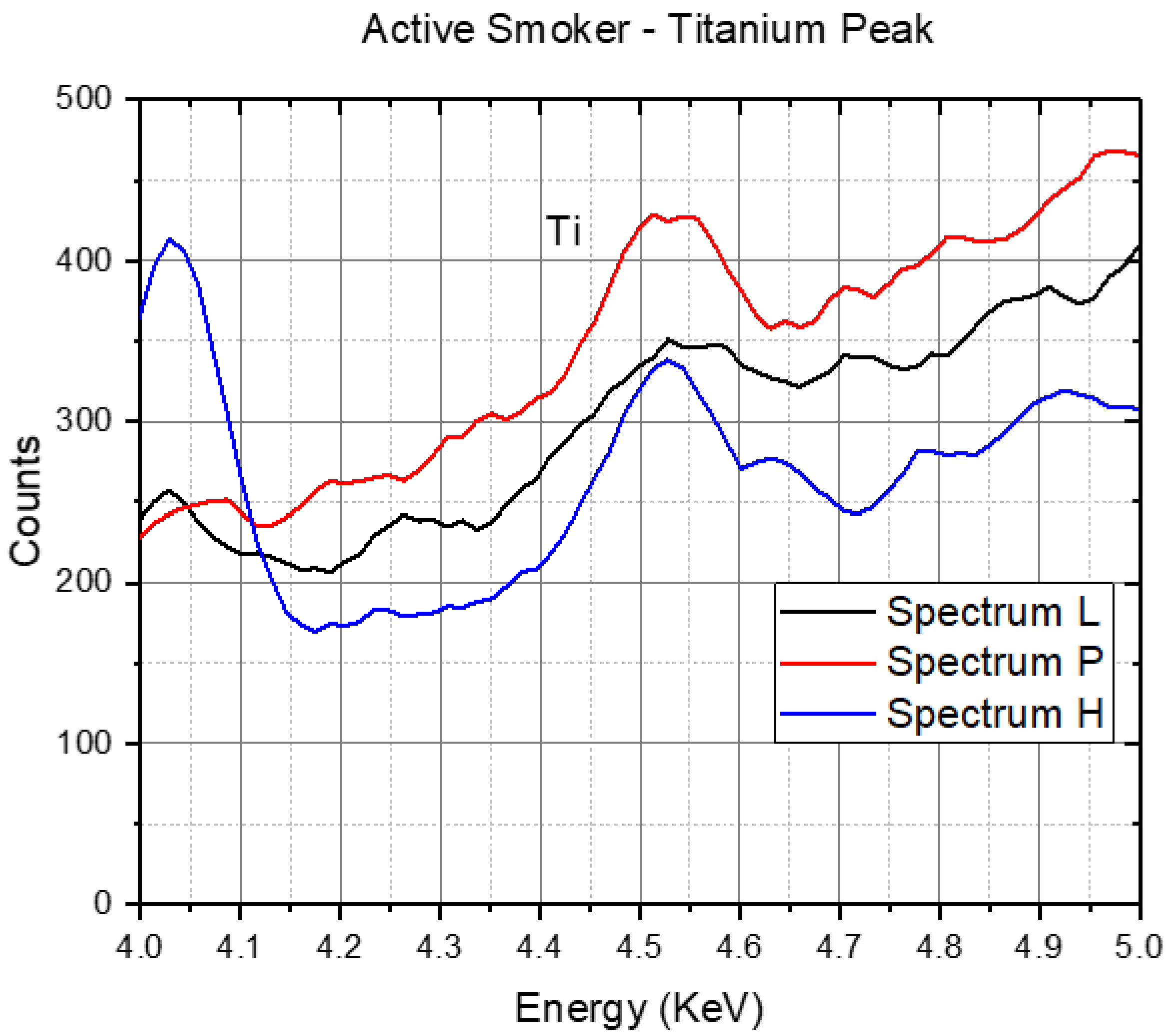


Figure 2

Ti peak reveal that the brands, where the most pronounce peaks are P and H. The difference on the wide in these peaks may occur due to the loss of photon energy.

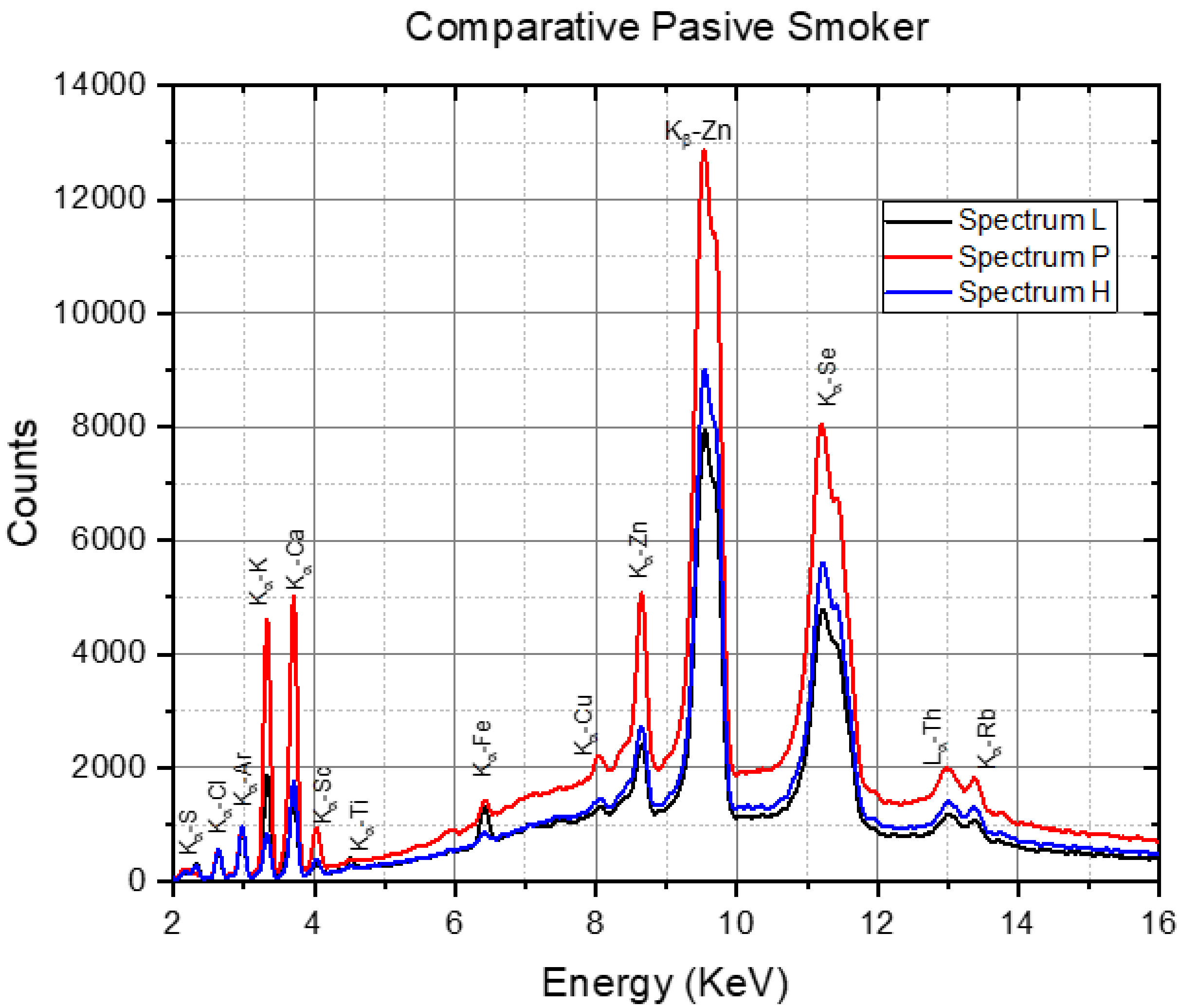


Figure 3

EDFRX Spectrums of the samples took for a passive smoker or secondhand smoking in brands worked (L, P, H). The data was taken mainly from $K_\alpha$ shells but also $K_\beta$ shell of Zn and $L_\alpha$ of Th. These results confirm that the composition inhaled by a person next to a smoker is the same of an active smoker but in a lower quantity (less photons were emitted in some peaks). Also, it is noticeable that the concentration of each element found is related with the number of counts and in this case brand P is higher in most elements than the other brands, which was found different of an active smoker.

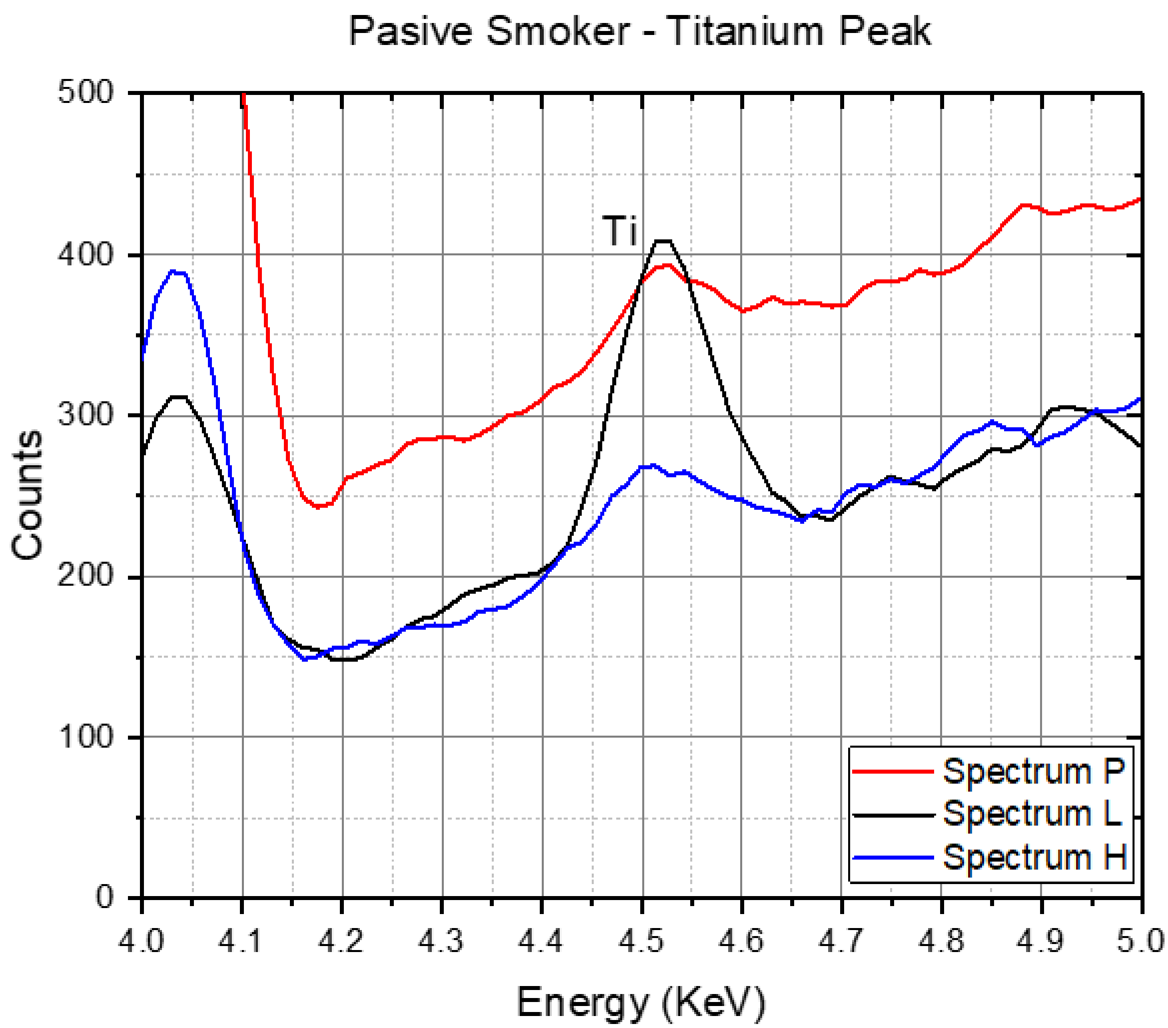


Figure 4

This graphic reveal that the brand with the most pronounce Ti peak is L. The difference on the wide in these peaks may occur due to the loss of photon energy