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Non-destructive determination of 15 major and minor elements in Murchison and Allende meteorites using µXRF

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ABSTRACT

µXRF can efficiently and non-destructively aid the understanding of the chemical structure of the Murchison and Allende meteorites. In this study, was determined 15 major and minor elements (Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Fe, Zn) at meteorites carbonaceous chrondrite. Based on the results obtained in this work, a brief comparative synthesis was made between the analysis of our results with some works selected from the scientific literature that use destructive analytical techniques to obtain these chemical elements. The comparative analysis demonstrates that the results were satisfactory and therefore, the use of µXRF appears to be efficient as a non-destructive analytical technique for the chemical analysis of these rare artifacts, which are the meteorites.

KEYWORD: µXRF, Murchison, Allende, chondrite meteorite

INTRODUCTION

Meteorites are excellent study materials because they are historical astrophysical artifacts that possess the chemical, physical and all geological evolution present in their materials. In this way, the abundance of chemical elements present in these materials is extremely relevant for Astrobiology and Planetary Sciences because they retain unique information about the natural processes that occurred at the beginning of the Solar System. The analysis by the analytical technique of µXRF can help in the determination of elemental compositions present in these meteorites in a non-destructive way (NASCIMENTO-DIAS, B. L. *et al*, 2018).

Essentially, the analyses and characterization of meteorites are mostly done by destructive techniques and wet chemical methods (JAROSEWICH, 1990). In general, such methods require, in addition to a sample preparation, a large amount of material. Moreover, the sensitivity in these terms of these techniques restricts the possibility of obtaining data, mainly due to the physical composition of the analyzed materials being modified after all.

Essentially, the data provided by µXRF and analysis generated by it, allows us to non-destructively determine the presence of various chemical elements in these rare samples, in fragments or semi-microscopic samples around 10 mg. In addition, since it is a non-destructive technique, if the user has an interest, it can be combined with other techniques to obtain additional data and more information about the analyzed sample, without running the risk of the sample being damaged or to compromise any information to be generated in the future while using other techniques. This method of obtaining meteorite information in this way is of extreme relevance for the understanding, for example, for identifications and classifications of chondrites meteorites (MAYNE, EHLMANN, DAVIAU, 2011; DAVIAU, R.G. MAYNE, A.J. EHLMANN, 2012; DUNN, 2015) and the search for determination of the chemical composition of meteorites (KAYE and CHAPPELL, 1987).

In this way, it can be observed that µXRF can bring great advantages to obtain important information of these materials, which can still be grouped and combined with other complementary techniques, thus playing a fundamental role in several areas such as planetary sciences, geosciences, astrobiology and materials science (NASCIMENTO-DIAS, OLIVEIRA and ANJOS, 2017).

The advantage of the µXRF technique is mainly related to having no problem with the amount of material available for the analysis to be limited. Moreover, another point is that meteorites are mostly heterogeneous and most destructive techniques do not allow the integrated visualization of the arrangement of the chemical elements present in the meteorites. In this way, this methodology benefits us by providing the composition of the main elements present in the meteorite structure and possible minor and trace elements.

Thus, the data generated by µXRF will be presented so that, afterwards, a brief synthesis of comparative analysis will be made between the analysis of our results with some works selected from the scientific literature that use destructive analytical techniques to obtain these chemical elements.

MATERIALS AND METHODS

MURCHISON METEORITE (CHONDRITES CARBONACEOUS CM2)

On September 28, 1969, during a meteor shower, at 10h 45min, near the town of Murchison, Victoria, Australia, it was witnessed the fall of the largest carbonaceous chondrites already observed of type II and that today takes the name of the city in who fell. It has been observed since its entrance into the atmosphere, tearing the sky in a glowing form, similar to a ball of bright fire until the moment of its fall. As it descended, it fragmented so as to break into three pieces before disappearing, leaving only a cloud of smoke that exuded a very strong smell associated with acetone and / or other possible organic compounds. The details of the fall and an initial description are given by (LOVERING *et al*, 1971).

Many specimens of this meteorite were found in an area of more than 13 square kilometers, with individual masses of up to 7 kg. A fragment, weighing 680 g, crossed a roof and fell into a haystack. The total mass collected was greater than 100 kg. In addition, several details pertinent to the terrain in which the fragments were scattered were collected. A chemical analysis was reported by Jarosewich (1971) and a short description was published by Ehmann *et al* (1970). A somewhat more detailed description was given by Fuchs, Jensen and Olsen (1970) prior to the 1970 meeting of the Meteoritical Society.

The Murchison meteorite in **Figure 1** is classified as carbonaceous chondrite. However, Murchison is specifically recognized as belonging to the CM2 group, which is the most abundant type of carbonaceous chrondrite, and 446 meteorites of this group have been found to date in the Meteoritical Bulletin Database. Its composition draws attention because countless different amino acids, sugars, alcohols, carboxylic acids and even nucleic acids have already been detected (METEORITICAL BULLITIN, 2017).

Figure 1 – Murchison Meteorite used in this work

Source – The Author

The development of this work was carried out by the analysis of the fragment of the $1mm^2$ Murchison meteorite, given by Dr. Maria Elizabeth

Zucolotto, from the National Museum of Rio de Janeiro (UFRJ), who confirmed the authenticity and correspondence to the mineralogy and description found in the (METEORITICAL BULLETIN, 2017) .

ALLENDE METEORITE (CHONDRITE CARBONACEOUS CV3)

The Allende meteorite in **Figure 2** had its fall observed in the city of Allende, Mexico, on February 8, 1969. The Allende is classified as a carbonaceous chondrite of the group of meteorites CV3, that is, it has highly defined condyles of 1mm or greater in diameter, olivine compounds rich in magnesium.

The most striking feature of CV3 chrondrites is the presence of large irregular inclusions in their gray matrix called CAI (Calcium and Aluminum Inclusions). In addition, the Allende and the meteorites of this group have a smaller amount of water in their interior in relation to the other carbonaceous meteorites and, because of this, end up being more resistant to the weathering of the terrestrial environment (CLARKE JR *et al*, 1971).

Figure 2 – Allende Meteorite used in this work

Source – The Author

The Allende meteorite is considered a reference standard because it was collected after the witnessed fall. Several samples were also prepared and then distributed to several laboratories for analysis and comparison.

Our Allende meteorite sample was 2 cm^2 long and was provided by Professor Maria Elizabeth Zucolotto of the National Museum of Rio de Janeiro (UFRJ), who confirmed that the sample corresponds to the mineralogy and textured description in the Meteoritical Bulletin (2017).

Finally, it can be said that the Allende is the most famous example of this type of carbonaceous because its entrance into the atmosphere was observed and fall in Mexico in 1969, spreading about 2 tons of material in Chihuahua. Samples of this meteorite may also be requested for the meteorite division of the Smithsonian National Museum of Natural History in Washington, USA, to be used as the standard.

μXRF

The analyses of the elementar chemical composition present in the Murchison and Allende meteorites were carried out using a μXRF commercial System (M4 Tornado by Bruker-Nano) at UERJ. This system has Rh anode X-ray tube, Polycapillary X-ray optics focus (spot sizes < 25 μm for Mo-K_α) and XFlash silicon drift X-ray detector (energy resolution FWHM <135 eV at 250,000 cps for Mn-K_α and 30 mm^2 active detector).

The automated scanning performed on both samples provided the safe detection of 15 chemical elements (Mg, Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Fe, Cu, Zn) present in Murchison and Allende, without the necessity of having been made suitable or prepared of the analyzed sample, that is, in a totally non-destructive manner.

The acquisition of the XRF spectrum was done in a vacuum of 20 mbar from parameters adjusted so that the measurements were taken in a standardized way. The parameters used were the current in 600 μA, voltage of 40 kV, and in 2 cycles that had a total duration of 2 h 25 min.

The low Z XRF spectra were obtained using a 12.5 μm aluminum filter and to obtain the high Z XRF spectra the 630 μm aluminum filter was used. The use of the second filter has the purpose of attenuating the noise a bit mainly in the region above 6.40 keV. Thus, XRF scanning in the meteorites was made shortly after we acquired these parameters that followed as patterns throughout the scan of the sample analyzed.

RESULTS

The qualitative determination of the chemical elements present in a both meteorites were done in a non-destructive way, that is, it did not result in the damage of the sample or in the possible loss of some future information, if it is analyzed again.

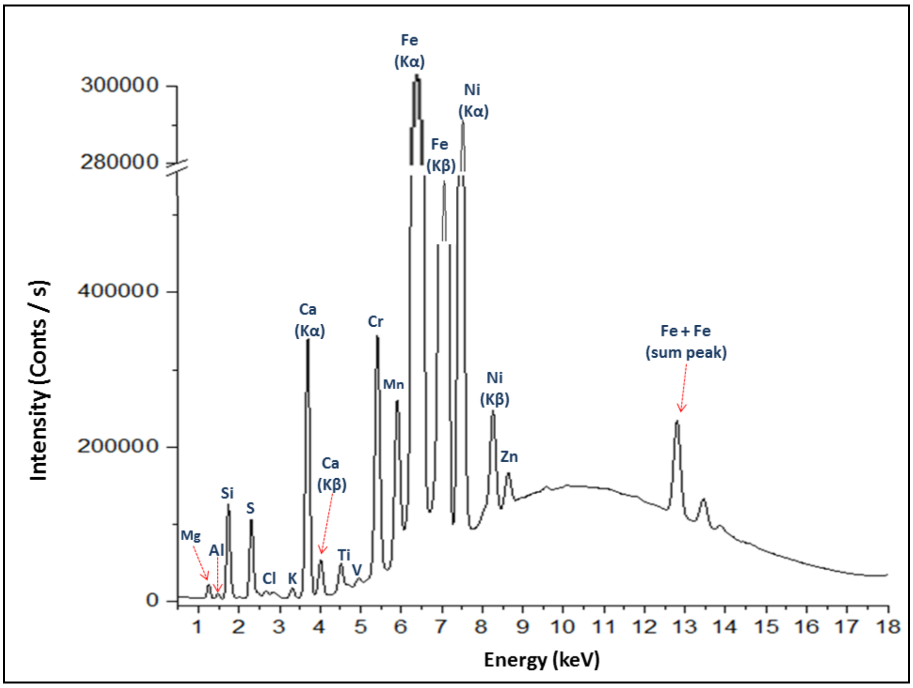
Essentially, the analysis performed was based on simple and well-known physical principles that chemical elements emit characteristic radiations when subjected to an appropriate characteristic excitation and that is specific for each atom of the periodic table, thus not having the possibility of having two atoms with the same characteristics.

The results obtained using the μXRF technique provided spectra that show peaks that are related to the K_α energy lines detected during the scanning process. The detected elements were: Mg (1.25 keV), Al (1.49 keV), Si (1.74 keV), S (2.31 keV), K (3.31 keV), Ca (3.69 keV), Ti (4.51 keV), V (4.95 keV), Cr (5.41 keV), Mn (5.90 keV), Fe (6.40 keV), Ni (7.48 keV), Cu (8.05 keV) and the Zn (8.64 keV).

MURCHISON METEORITE (CHONDRITE CARBONACEOUS CM2)

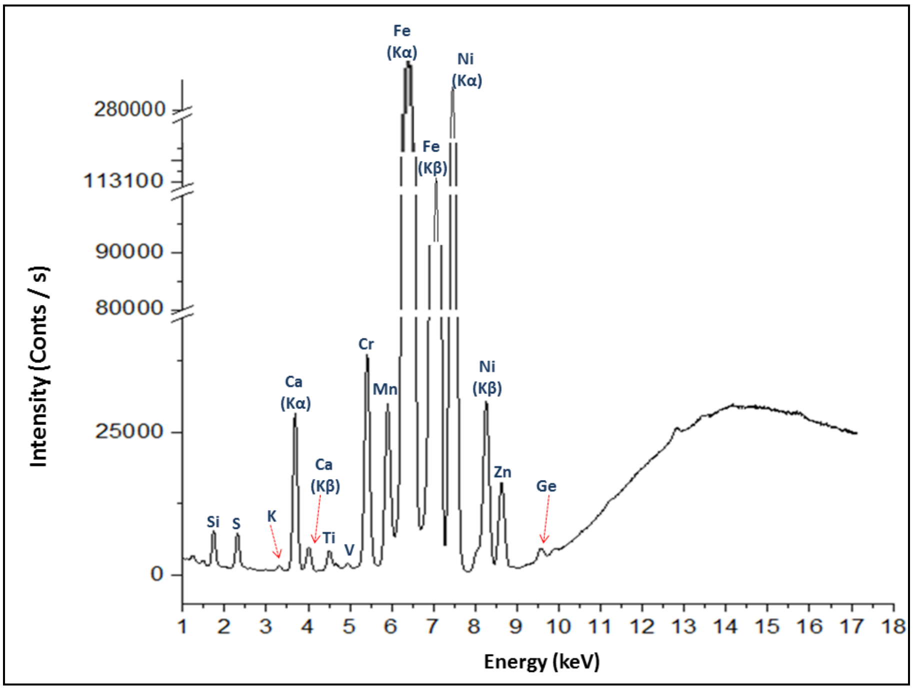
In **Figures 3 and 4** are presented the μXRF spectra of the Murchison meteorite, in which it is possible to observe the result obtained from the peaks of the elements (Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Zn and Ge) detected.

Figure 3 – Total spectrum XRF for low atomic numbers Z of the Murchison meteorite



Source – The Author:

Figure 4 – Total spectrum XRF for high atomic numbers Z of the Murchison meteorite

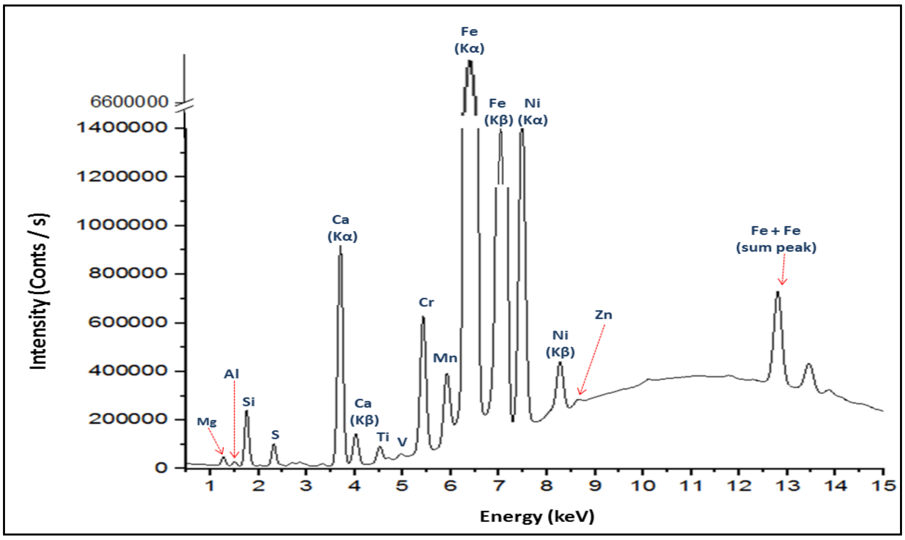


Source – The Author

ALLENDE METEORITE (CHONDRITE CARBONACEOUS CV3)

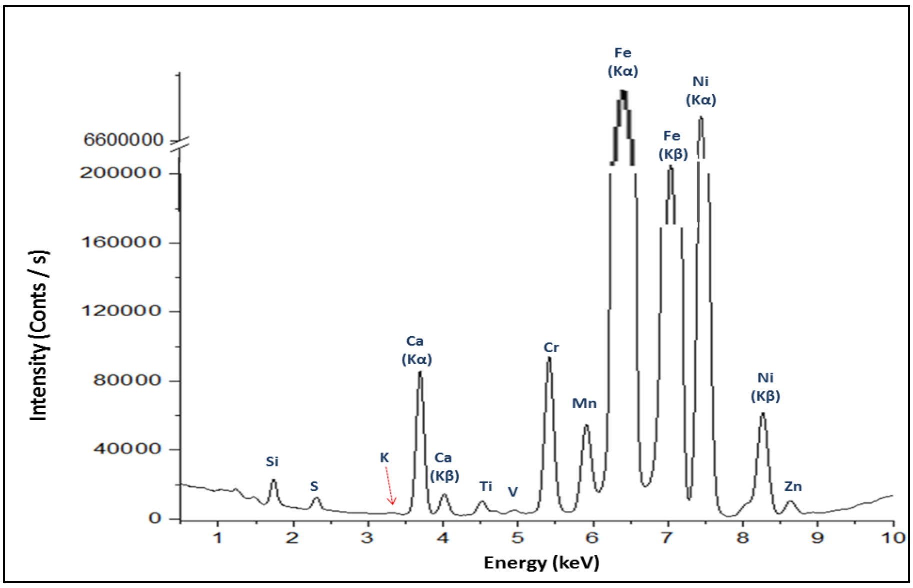
The spectra of µXRF of the Allende meteorite are shown in **Figures 5 and 6**, where it is possible to observe the result obtained from the peaks of the elements (Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Ni and Zn) detected.

Figure 5 – Total spectrum XRF for low atomic numbers Z of the Allende meteorite



Source – The Author

Figure 6 – Total spectrum XRF for high atomic numbers Z of the Allende meteorite



Source – The Author

DISCUSSION

Based on the analysis of the results of the elemental chemical composition obtained by µXRF, a brief comparative synthesis was performed. The comparative analysis was done with some other works selected from the scientific literature.

Essentially, the analyses and characterization of meteorites are mostly done by destructive techniques and wet chemical methods that require, besides a sample preparation, a large amount of material. In this way, we selected works that use this analytical methodology to ascertain the efficiency of the results obtained in our work.

According to the published values from the available literature, in relation to the Murchison meteorite, it was verified the detection of 11 elements (Na, Mg, Al, P, S, K, Ca, Cr, Mn, Fe and Ni) (SHOWALTER, WAKITA and SCHMITT, 1972; NAKAMURA, 1974, KALLEMEYN and WASSON, 1981; GRADY *et al*, 1987; WLOTZKA *et al*, 1989; BURGESS, WRIGHT, PILLINGER, 1991; DREIBUS *et al,* 1993). This investigation was carried out from a compilation composed of data derived from chemical analyzes made mainly by ICPMS e INAA.

Considering these data available in the literature and comparing with data that were non-destructively obtained by µXRF, it is possible to observe a good efficiency of the fluorescence technique in the detection of elemental chemical composition. Among the eleven elements found in the literature, 10 were detected in this work (Mg, Al, P, S, K, Ca, Cr, Mn, Fe and Ni). In addition 5 other elements were detected (Si, Ti, V, Zn and Ge) and besides presenting a good efficiency, also shows to have a good sensitivity for the detection of chemical elements. The comparison of results obtained from the elemental chemistry composition of the Murchison meteorite made in our non-destructive work by µXRF in relation to the results generated by destructive analytical techniques are presented in **Table 1.**

Table 1 - Comparative analysis between the results of the Murchison meteorite

Murchison (this work)	**Murchison** Literature[a]	**Murchison** Literature[b]
--------	Na	Na
Mg	Mg	Mg
Al	Al	Al
Si	--------	--------
P	P	P
S	S	S
K	K	K
Ca	Ca	Ca
Ti	--------	--------
V	--------	--------
Cr	Cr	Cr
Mn	Mn	Mn
Fe	Fe	Fe
Ni	Ni	Ni
Zn	--------	--------
Ge	--------	--------

Source – (a) Kallemeyn and Wasson, (1981); (b) Wolf, Compton and Gagnon (2012)

According to the available literature with published values related to the Allende meteorite, the chemical analyzes are mainly done by ICPMS e INAA. By the compilation of data derived from these analyzes, it was also possible to verify the detection of 11 elements (Na, Mg, Al, P, S, K, Ca, Cr, Mn, Fe and Ni) (JAROSEWICH, CLARKE JR. and BARROWS, 1987; WOLF, COMPTON and GAGNON, 2012).

Among the elements found in the literature, 10 were detected here (Mg, Al, P, S, K, Ca, Cr, Mn, Fe and Ni). Futhermore, were detected morer 5 other elements (Si, Cl, Ti, V and Zn) in this work.

Essentially, this shows a good efficiency of the µXRF technique and a good sensitivity for analysis of elemental chemical composition. Thus, based on these data available in the literature and comparing with data that were non-destructively obtained by µXRF, it is possible to notice a very significant efficiency of the fluorescence technique in the detection of chemical elements present in the structural composition in the Allende meteorite.

The comparison of the results obtained from the elemental chemistry composition of the Allende meteorite made in our non-destructive work by µXRF in relation to the results generated by destructive analytical techniques are presented in **Table 2.**

Table 2 – Comparative analysis between the results of the Allende meteorite

Allende (this work)	**Allende** Literature[a]	**Allende** Literature[b]
--------	Na	Na
Mg	Mg	Mg
Al	Al	Al
Si	--------	--------
P	P	P
S	S	S
Cl	--------	--------
K	K	K
Ca	Ca	Ca
Ti	--------	--------
V	--------	--------
Cr	Cr	Cr
Mn	Mn	Mn
Fe	Fe	Fe
Ni	Ni	Ni
Zn	--------	--------

Source: (a) Jarosewich, Clarke Jr. and Barrows (1987), (b) Wolf, Compton and Gagnon (2012)

CONCLUSION

The comparative analysis demonstrates that the results generated from our methodology based on the use of µXRF as an analytical technique in the Murchison and Allende meteorites was quite satisfactory.

The µXRF in both analyzes demonstrated > 80% in relation to the results obtained with the conventional techniques of the scientific literature in the detection of major and minor elements. Also, it was possible to notice a greater sensitivity of µXRF in the analysis of elemental chemical composition, which was able to detect additional elements that were not detected in the literature of destructive analytical techniques.

In addition, the methodology adopted was simple and was shown to be non-destructive because there was no need for any sample preparation. Thus, it is possible to conclude that it is quite valid to use the µXRF technique as a non-destructive analytical technique to obtain elemental chemical determination in meteorites.

Determinação não destrutiva de 15 elementos maiores e menores em meteoritos de Murchison e Allende usando µXRF

RESUMO

Buscou-se demonstrar como a utilização da µXRF pode auxiliar de maneira eficiente e não destrutiva à compreensão da estrutura química dos meteoritos condritos carbonáceos Murchison e Allende. Fundamentalmente, em nossos resultados foi possível determinar 15 major and minor elementos (Mg, Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Fe, Cu, Zn), os quais aparecem em ambos os meteoritos condritos carbonáceos. Além disso, através da técnica de µXRF também foi possível obter dados qualitativos relativamente precisos sobre onde e como cada um desses elementos químicos está relacionado com os meteoritos Murchison e Allende. Dessa forma, baseado nos resultados obtidos, foi feita uma breve síntese comparativa entre as análises de nossos resultados com alguns trabalhos selecionados da literatura científica que utilizam técnicas analíticas destrutivas para obtenção desses elementos químicos. A análise comparativa demonstra que os resultados gerados foram satisfatórios e assim, a utilização da µXRF aparenta ser eficiente como técnica analítica não destrutiva para análise química desses artefatos raros que são os meteoritos.

PALAVRAS-CHAVES: µXRF; Murchison; Allende; Meteorito Condrito.

Determinación no destructiva de 15 elementos mayores y menores en meteoritos de Murchison y Allende usando µXRF

RESUMEN

Buscamos demostrar cómo la utilización de la µXRF puede ayudar de manera eficiente y no destructiva a la comprensión de la estructura química de los meteoritos condados carbonáceos Murchison y Allende. En la mayoría de los casos, en nuestros resultados se pudo determinar 15 mayor y menor elementos (Mg, Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Fe, Cu, Zn), los cuales aparecen en ambos los meteoritos condados carbonáceos. Además, a través de la técnica de µXRF también fue posible obtener datos cualitativos relativamente precisos sobre dónde y cómo cada uno de esos elementos químicos está relacionado con los meteoritos Murchison y Allende. De esta forma, basado en los resultados obtenidos, se hizo una breve síntesis comparativa entre los análisis de nuestros resultados con algunos trabajos seleccionados de la literatura científica que utilizan técnicas analíticas destructivas para la obtención de esos elementos químicos. El análisis comparativo demuestra que los resultados generados fueron satisfactorios y así, la utilización de la µXRF parece ser eficiente como técnica analítica no destructiva para el análisis químico de estos artefactos raros que son los meteoritos.

PALABRAS CLAVE: µXRF; Murchison; Allende; Meteorito condrito.

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