



Chemical characterization of extraterrestrial sample return: a versatile platform @UnivAQ

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Abstract The main analytical techniques useful for the comprehensive chemical characterization of relevant specimens available from extraterrestrial sample return missions, also considering, among others, the instrumental facilities available at the “Centro di Microscopia” of the University of L'Aquila (UnivAQ), are described. Different qualitative and/or quantitative approaches may be used in view of the different amounts, origin (terrestrial, extraterrestrial, synthetic, etc.) and type (organic, inorganic or hybrid matrices) of the authentic samples. ICP-MS and GC-MS, X-Ray, ATR-FTIR and micro-FTIR, Raman, UV-Vis spectroscopies, TEM or SEM, with X-Ray elemental analysis - EDX microscopies are among the most important characterization techniques, either destructive or non-destructive, employed for this specific end. Finally, two selected case studies have been discussed.

Key words. Astrochemistry – Methods: Laboratory: Solid State – Methods: Laboratory: Molecular – Techniques: Spectroscopic

1. Introduction

The knowledge of mankind on the chemical composition of the universe is still rather limited. The analysis of the samples coming back from extraterrestrial missions, allows researchers around the world to work with the state-of-the-art analytical techniques available in connected laboratories, here on Earth (ex-situ), thus addressing extremely complicated aspects, especially related to investigations on extra-terrestrial organic matter. In this way, this level of detailed sample characterization provides the variety and accuracy, in organic analysis, that are restricted in spacecraft-based exploration missions, due to the limitations of the on-board (in-situ) instrumentation. Moreover, in case of extraterrestrial (ET) sample return, is not uncommon to obtain odd results due

to the risk of sample contamination (Court et al. 2012). Apart from this aspect, whenever it is possible to obtain ET samples, extra care is needed to avoid sample destruction and loss during the investigation process, preferring non-destructive techniques that possibly require as low amount of sample as possible. In this respect, here we present the wide analytical possibilities present at UnivAQ, covering extremely sensitive techniques, requiring a minor amount of material, united with a good sample recoverability, a critical and relevant issue for ET sample return.

2. Analytical techniques @UnivAQ

The analytical possibilities available at the University of L'Aquila involve techniques for

either organic or inorganic materials. Being the samples very limited in availability, non-destructive techniques are preferred, whenever possible. Starting with the ones that allow good and relatively easy sample recovery, electron microscopy allows excellent spatial resolution ranging from millimeter fractions down to tens of nanometers. Scanning Electron Microscopy (SEM) in particular, requires minimal level of sample pre-treatment united with a full recoverability of the sample. Together with morphological analyses, Energy Dispersive X-ray analysis (EDX) allows a full recognition of the sample elemental composition and the possibility of analyzing the elemental distribution in a certain area of the sample (Figure 1 - Palomba et al. (2001)). However, X-ray mapping performed with this kind of technique is not able to determine light elements (C, N, O) with sufficient accuracy. In this respect, spectroscopies are usually able to recognize the presence of these elements, discriminate the chemical bonding among them and roughly estimate their relative amount. FT-IR spectroscopy in particular is sensitive to different chemical bonding of organic species, while X-ray Photoelectron Spectroscopy (XPS) is sensitive not only to chemical bonding but is also able to reveal the presence of any element and distinguish the occurrence of different oxidation state within the element itself. The advantage of the systems present at the “Centro di Microscopie” is the possibility of performing micro-FTIR, namely focusing the probe onto specific areas of the sample and building spectral maps to reveal differences in diverse points of the sample (Palomba et al. (2001); Rotundi et al. (2007); Rotundi et al. (2008); Dionnet et al. (2020)) without the need of a large scale facility (Raynal et al. 2000). In addition to FT-IR spectroscopy, sensitive to changes in dipole moment of chemical bonds, Raman spectroscopy is often complementary to FT-IR, since it detects molecular vibrations that imply a change in polarizability, making it a useful tool in identification of scarcely polar and apolar molecules, such as condensed aromatic rings. Many minerals present crystalline habits that may need to be revealed. This is even more important in case of materials with

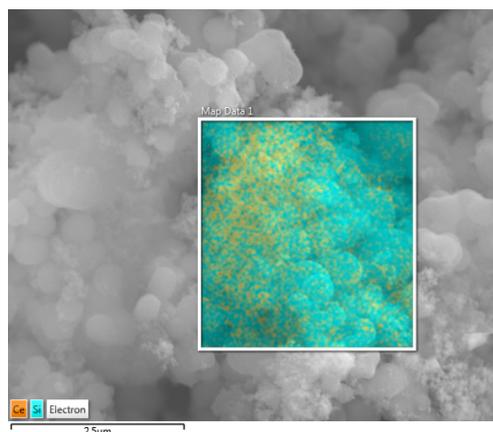


Figure 1. SEM image with EDX mapping for ceria (orange)-silica (blue) hybrid material.

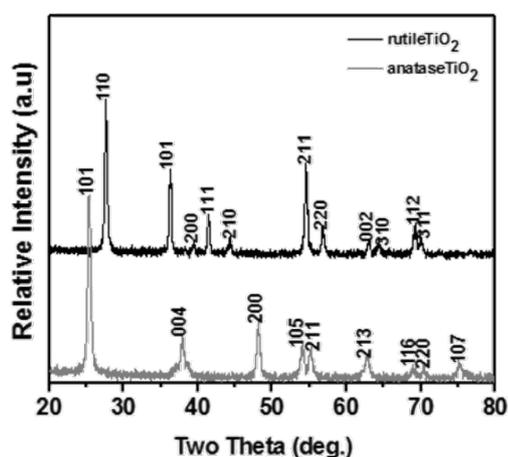


Figure 2. XRD for two different polymorphs of titania (anatase and rutile). Adapted from (Shaikh et al. 2016).

same chemical composition but different crystal structures (polymorphs). One of the most common examples are rutile and anatase, both polymorphs of titanium dioxide (Figure 2). X-Ray Diffraction (XRD) is able either to recognize and distinguish known lattices or to assign proper crystal structures to unknown samples. The techniques mentioned so far are non-destructive, therefore favorable for such delicate and precious samples. However, the goal of preserving the materials for further analyses is not always achievable. Dealing with

fully complex organic samples that need identification of several chemical species contemporarily (i.e. proteins, aminoacids or functionalized conjugated/aromatic systems), the most sensitive analytical technique is Nuclear Magnetic Resonance (NMR - Chan et al. (2020)). However, in case we are in the presence of a mixed organic-inorganic system, a pretreatment to remove the inorganic fraction is needed, thus impeding the recoverability of the initial sample. The same problem appears whenever the quantification of the organic fraction of a hybrid system is needed. In this case Thermogravimetric Analyses (TGA) is employed to measure the weight loss of the investigated material by eliminating the organic part in oxidative environment. Often isotopic composition is crucial in defining the terrestrial or extraterrestrial origin of the samples (Gargano et al. 2020). One of the most isotope-sensitive techniques is Mass Spectrometry (MS); furthermore, this technique coupled with an inductively coupled plasma (ICP-MS), for the atomization of the samples, allows the use of a minimal amount of sample to detect and quantify a wide variety of inorganic elements with all the relative isotopes. The drawback in this technique is the low sensitivity towards lighter elements and the ones present in Earth atmosphere (i.e. C, N, O).

2.1. Case studies

After having widely described the main analytical techniques available in our laboratories, we present two case studies for model fully inorganic or fully organic samples, to be considered as reference analysis protocol for these categories of materials. Naturally, non-destructive techniques will always be preferred and prioritized with respect to destructive ones. Considering interplanetary dust particles composed by different metal oxides and intermetallics, the first analysis to be considered is SEM-EDX one. This would allow to obtain morphological information coupled with a rough estimation of the elemental distribution present in the sample. Afterwards, XRD would be employed to identify the crystalline phases present, compatibly with the el-

ements identified previously. The background of XRD patterns is also able to give information about eventual amorphous phases in the samples. XPS analyses could provide more precise information about elemental composition and oxidation state of the various components of the sample. Being sensitive to all elements, this technique would also detect traces of organic species on the surface of the samples through the presence of C, N or O signals. Finally, if data about the isotopic composition might be of pivotal importance, sufficiently to opt for partially sample sacrifice, ICP-MS could return a quantitative picture of elemental and isotopic composition and ratio. Moving to a totally organic sample, it might be useful consider the case of polyaromatic functionalized disordered carbon particles. As for the aforementioned case, electron microscopy, either in transmission or in scanning mode, coupled with EDX detector is the perfect tool to identify sample morphology and elemental composition, even with an intrinsic scarcer accuracy towards light elements. Surface spectroscopy, such as XPS, is the most accurate non-destructive technique able to recognize light elements and differentiate them according to different chemical bonding. The limit of this technique is the penetration depth of the probe, since electrons can escape only few nanometers underneath the surface of the materials. For bulkier samples, FT-IR guarantee a better penetration sampling, maintaining a good level of discrimination among possible functional groups present. In case the sample condensed aromaticity is predominant, the polarizability of the sample might be non-sufficient for IR spectroscopy; however, the problem could be overcome by employing Raman spectroscopy, the most sensitive technique for carbon-based materials characterization. Despite the good characterization level achievable with non-destructive techniques, if in the sample are present chiral species, tautomers or the same chemical unit repeated in different numbers (i.e. different hydrocarbon chains length), the only measurements able to unravel them is by performing NMR experiments. As known, the organic compounds may contain a mixture of C-, O-, and N-bearing macromolecular car-

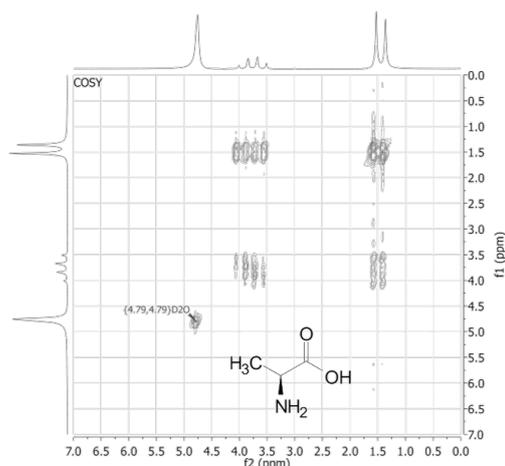


Figure 3. ^1H - ^1H COSY NMR spectrum of L-Alanine. Adapted from (Zivkovic et al. 2017)

bon materials exhibiting a wide range of structural order, as well as aromatic, ketone, imine, and/or imidazole compounds. The NMR spectroscopy is really precious when aminoacids or other bio-based molecules/chemical species are present (Figure 3).

Finally, applications of chemometrics in the optimization of different types of analytical methods, along with the possibility to perform multivariate analysis of experimental data, may represent a clear added value for the optimization of the required information extraction. This kind of expertise is also available at our department.

3. Conclusions

The return of samples from extraterrestrial sources is an essential step in understanding the origin and evolution of our neighbouring planets. Furthermore, a strong synergy is needed in order to bring together different scientific expertise and a wide availability of analytical techniques as much complementary as possible between them, apart from economical concerns. In this paper, we presented the analytical equipments available as a versatile platform, at the University of L'Aquila. They are not only extremely effective for everyday

samples, but may be crucial in the future in the analyses of extraterrestrial samples return. Indeed, the wide variety of non-destructive techniques allows an excellent level of accuracy in characterizing samples of every nature (organic, inorganic, hybrid). However, in case these analyses are not sufficient to unravel the properties of the investigated materials, the destructive techniques employed are developed to work with the minimal amount of sample (in the range of few mg), yet with high sensitivity and excellent experimental accuracy.

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