

## Basque Infrastructure for the Integral Study of Materials from Cultural Heritage (BISMaCH)

### FIXLAB

#### Description



IBeA research group has many instrumentation that can be use in the study of Heritage Science, such as several Raman systems, portable ones and a laboratory Raman microscope, portable and laboratory mid-FTIR instrumentation (to work in transmittance, diffuse reflectance and ATR mode), a portable LIBS system, a portable near infrared instrumentation, a portable X-Ray fluorescence system together with a laboratory X-Ray fluorescence imaging system. Together with spectroscopic techniques IBeA research group has a system to perform ion chromatography and ICP-MS for soluble salt test. Almost all the instrumentation is located in the same laboratory inside the new Casiano building that belongs to the Scientific Park of the University of the Basque Country. The laboratory implements all the small instrumentation for sample preparation (Cross-section preparation, IR pellet preparation, fume hoods in the laboratory, microwave assisted digestion, focused ultrasound assisted extraction, etc). It is important to highlight that the facility implements laboratory and portable devices for all techniques. This means that if there could be any size constrain at the time of analyzing a sample by using laboratory devices, it could be possible the analysis by using the portable devices that do not present any geometrical constrains.

The most important characteristic of this facility is the chance of combining several complementary instruments in the analysis of the same sample, obtaining valuable information, and going further than the use of a single technique. This approach always warranties the success of the analysis, providing at the same time elemental, molecular and structural information of the sample. However, independent from the instrumentation, the most important feature of the facility is the expertise of the more than 10 doctors working in the laboratory on cultural and natural heritage (archaeology, architectural archaeology, art analysis, environmental interaction with cultural heritage, degradation studies, etc), each of one being specialist in more than one instrument.

#### Fields of application

Cultural heritage  
 Archaeology, Art, Architecture, Industrial heritage,  
 decorative arts

#### Materials

Inorganic and organic  
 pigments, metals, ceramic, mural paintings, stone,  
 binders

#### Equipment

##### Laboratory Raman Imaging System (532 nm, 633 nm and 785 nm):

The InVia Raman spectrometer (Renishaw) is coupled to a Leica upright confocal microscope. The system uses a 532 nm laser with a maximum power of 50 mW and a 1800 lines/mm diffraction grating. The Rayleigh radiation is filtered with an Edge filter, providing a cut-off of  $60\text{ cm}^{-1}$ . The signal is recorded with

a Peltier cooled CCD detector, being the mean spectral resolution about  $1\text{ cm}^{-1}$ . The system has another two excitation laser: 785nm and 633 nm. The InVia Raman spectrometer can be carried out surface analysis by mapping point-by-point and in a multiplexed mode (Streamline Raman imaging). It is also possible to focus on single sample grains. In order to avoid excessive noise in the spectra, the equipment is installed in an anti-vibratory table and in a temperature controlled room.

#### **Portable Raman Systems (532 nm and 785 nm):**

The RA100 spectrometers (Renishaw) are provided with a 785 nm laser and coupled to a videocamera with objectives of 5X, 20X and 50X if needed. The Rayleigh radiation filter provides a cut-off of  $150\text{ cm}^{-1}$ , being the mean spectral resolution about  $2\text{-}4\text{ cm}^{-1}$ .

The two BWTEK portable Raman spectrometers (785 and 532 nm) are linked through a dual microspectroscopy and a high resolution motorized tripod. The specific characteristics of the portable spectrometers are similar. The equipment implements controller software of the laser power (from 0% to 100% of the total power), being the nominal laser power of the instrument  $330\text{ mW} \pm 15\%$  at the source and  $255\text{ mW} \pm 15\%$  at the surface of the analyzed sample. Regarding the tripod, the probe of the InnoRam spectrometer can be mounted on it that implements 4x, 20x or 50x objectives. They allow focusing the laser on a 10-200 nm spot in diameter, depending on the used objective. It is provided with a micro-video camera which allows focusing for exhaustive studies of the samples.

#### **Laboratory FTIR System:**

Jasco FT/IR 6300 is an Infrared Fourier based spectrometer which covers a range between 7800 and  $350\text{ cm}^{-1}$  using a Peltier cooled DLATGS detector. It can provide a mean spectra resolution of up to  $1\text{ cm}^{-1}$ , even though the normal working spectral resolution is  $4\text{ cm}^{-1}$ . With this system it is possible to acquire spectra in transmittance, ATR and reflectance mode.

#### **Portable IR Systems:**

ASD Inc. FieldSpec4 Hi-Res spectroradiometer. FieldSpec4 Hi-Res is a high resolution spectroradiometer which works in the 350-2500 nm range. It has three detectors: VNIR (silicon covering the range between 350 and 1000 nm), SWIR1 (InGaAs photodiodes covering the range between 1001 and 1800 nm) and SWIR2 (InGaAs photodiodes covering the range between 1801 and 2500 nm). The normal working spectral resolution is  $4\text{ cm}^{-1}$ . With this system it is possible to acquire spectra in reflectance mode.

The DRIFT device (Agilent) is provided with a ZnSe beam splitter and a Deuterated Tri-Glycine Sulphate (DTGS) detector. The Michelson interferometer has a maximum resolution of  $4\text{ cm}^{-1}$  and a maximum spectral range of  $4000\text{ - }600\text{ cm}^{-1}$ .

#### **Laboratory EDXRF Imaging System:**

The M4 TORNADO micro energy dispersive X-ray fluorescence ( $\mu\text{-ED-XRF}$ ) spectrometer is able to detect elements with atomic number (Z) higher than 10 (starting from sodium). It implements two Rh tubes powered by a low- power high voltage (HV) generator and cooled by air. One of the tubes is able to operate at voltages in the range of 10-50 kV and currents in the range of 100-700 mA. This first tube is mounted on a mechanical collimator that allows performing measurements under a lateral/spatial resolution (spot) of 1 mm. There is a second Rh tube which is able to operate between 10-50 kV and 100-600 mA. This polycapilar lens is able to achieve a lateral resolution of 25 mm for the Mo Ka-line. The detection of the fluorescence radiation emitted by the elements is performed by an energy-dispersive SDD detector with  $30\text{ mm}^2$  sensitive area and energy resolution of 142 eV for the Mn Ka line. The system allows to work under vacuum conditions in order to improve the detection of lighter elements ( $Z < 16$ ). For that purpose, a MV 10 N VARIO-B diaphragm pump will be used establishing the vacuum inside the chamber of the instrument at 20 mbar. The system performs punctual analysis but also surface analyses by providing the spatial distribution of the elements (EDXRF imaging).

#### **Portable EDXRF System:**

The EDXRF system is a hand-held X-MET5100, EDXRF spectrometer (Oxford Instruments, UK) equipped with a rhodium, anode X-ray tube (operating at 45 kV). The analyzer has a high resolution silicon drift detector. The measurements are usually taken in 50 s accumulation time. The system is controlled with a PDA attached to the body of the equipment.

#### **Portable LIBS System:**

The portable EasyLIBS IVEA system employs a pulsed Nd:YAG laser, with the possibility to dual pulse mode, and emits at the fundamental wavelength of 1064 nm. The laser energy per pulse on the sample is higher than 25 mJ with a repetition rate of 1 Hz and the duration of laser pulse is 4–5 ns. The gun goes connected to a computer and to three spectrometers corresponding to the Ultraviolet (UV) spectral range (196–419 nm), the Visible (VIS) spectral range (420–579 nm), and that of the Near Infrared (NIR) (580–1000 nm) (Czerny-Turner Ocean Optics HR 2000 +).

#### **Ion Chromatography system:**

The quantification of the anions and cations of the soluble salts is carried out using a Dionex ICS 2500 ionic chromatograph with a suppressed conductivity detector ED50. An IonPac AS23 (4x250 mm) column and IonPac AG23 (4x50 mm) pre-column is used for separation of anions (fluoride, chloride, sulfate and nitrate). The quantification of cations (sodium, calcium, potassium, ammonium and magnesium) is conducted by using an IonPac CS12A (4x250 mm) column and IonPac CG-12A (4x50 mm) pre-column by Vertex. 5 mM Na<sub>2</sub>CO<sub>3</sub>/0.8 mM NaHCO<sub>3</sub> buffer and 25 mA suppression current at 1 ml min<sup>-1</sup> flow is set for the analysis of the anions. This means that carbonate system cannot be analysed. In the case of cations, 20 mM CH<sub>4</sub>SO<sub>3</sub> as mobile phase and 75 mA of suppression current at 1 ml min<sup>-1</sup> flow are used.

#### **ICP-MS system:**

Metals are determined and quantified by means of an Elan 9000 ICP-MS (PerkinElmer), provided with a Rytan cross-flow nebulizer, a Scott-type double pass spray chamber and standard nickel cones. Preparation of calibrates is carried out using standard solutions from Alfa Aesar, Specpure and analysis are done inside a class 100 clean room. Argon (99.999%) is used as carrier gas in the ICP-MS measurements.

#### **Potential Results**

BISMaCH infrastructure a multi-technique laboratory, among others, for the diagnosis of the state of conservation of artworks and building materials, the study of the materials used in artworks, the damages produced by pollutants in building materials, decorative artefacts and wall paintings. The combination of analytical and diagnostic techniques is necessary to have the whole picture of the artwork under analysis. Depending on the objective of the study, we select the analytical techniques that will provide the most appropriate and valuable results, combining molecular and elemental information. We can analysis organic and inorganic materials, metals, stones, soluble salts, cellulose, pigments, etc.

#### **References**

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### Sample or service requisites

In the case of Raman spectroscopy, the samples can be analysed without any sample preparation, but due to geometrical constrains large samples cannot be analysed by Raman imaging. In those cases a sampling step and sample preparation could be needed. Another alternative could be the use of portable Raman system provided with fibre optic probes. The acquisition time depends on the sample/compound type, ranging from 5 seconds up to 30 minutes (but usually less than 5 minutes). The only drawback of the technique is the possibility of sample burning due to high laser powers and fluorescence that can make useless the Raman analysis. If Raman imaging or mapping is needed, sample preparation will be compulsory to provide a flat surface. This means sampling step, cold resin embedding and surface polishing.

In the case of FTIR, in transmittance mode the samples have to be prepared as a KBr pellet. This means that 0.5mg of sample has to be grinded in an agate mortar mixed with 150mg of KBr, put the mixture in a die and press under 7-10 tons to form a pellet. For ATR and reflectance analysis, the samples can be measured without any sample preparation, but due to geometrical constrains a prior sampling step could be needed. ATR and reflectance analysis is very suitable for powders. The time of analysis is quite short (1 to 3 minutes). In transmittance mode the detection limits are high. In the case of NIR system, there is no geometrical constrains because it use a probe and there is no need to do any kind of sample preparation. The time of analysis is quite short (1 to 3 minutes).

In the case of EDXRF imaging, the samples can be analysed without any sample preparation, but due to geometrical constrains large samples cannot be analysed. In those cases a sampling step and sample preparation could be needed. Another alternative could be the use of portable EDXRF system, which does not need any kind of sample preparation and has no geometrical constrains. The acquisition time depends on the sample/compound type and size, ranging from 1 minute up to 8 hour (but only in the case of EDXRF imaging analysis). If EDXRF imaging or mapping is needed, sample preparation will be almost compulsory to provide a flat surface. This means sampling step, cold resin embedding and surface polishing. The detection limits depend on the chemical element. In the case of the portable EDXRF, the acquisition time depends on the sample/compound type and size, ranging from 50 seconds up to several minutes (but only in few cases). The detection limits depend on the chemical element, but as it is an open system, light elements cannot be detected (except S, Si, Na and Al).

For the LIBS analysis there is no geometrical constrains because it use a probe and there is no need to do any kind of sample preparation. The time of analysis is quite short (1 to 3 minutes). It is important to highlight that this technique can give a mark on the surface due to the laser ablation of the sample. In almost all cases, this mark is not visible to the naked eye, but this issue has to be considered.

**For further details please contact the provider.**



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