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Chemical characterization techniques of dental biomaterials: a review

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Abstract: The aim of this review article is to investigate the various chemical analyses techniques commonly used to identify the identity of a material or the identity of its components to achieve a qualitative analysis. Also, a quantitative analysis is performed afterwards to figure out the quantity of the material's chemical constituents. The materials are probed, measured, and determined using a variety of analytical methods, techniques, and tools. This characterization is important in detecting materials' properties and thereby the appropriate choice of the dental material according to its use. Criteria for technique selection also include penetration depth and mean free path, resolution, detection limits, potential damage to the specimen, and specimen preparation requirements; our goal is to maximize information while minimizing damage.

Keywords: chemical analysis; characterization; spectroscopy; principle; scanning; microscopy.

I. Introduction

Chemical characterization techniques involve the identification of a material and the identification and quantification of its chemical constituents. as part of an assessment of the overall properties and the suitable application of the materials. It involves a measurement of the level of a leachable substance from the material, surface topographic analysis, microstructure and elemental analysis of unknown material according to its atomic configuration. Criteria for technique selection also include penetration depth and mean free path, resolution, detection limits, potential damage to the specimen, and specimen preparation requirements; our goal is to maximize information while minimizing damage. Within (microanalysis) it is necessary to identify trace components down to extremely low concentration (parts per trillion in some cases) and several techniques specialize in this aspect. In other cases, a high degree of accuracy in measuring the presence of major components might be the issue. Usually, the techniques that are good for trace identification are not the same ones used to accurately quantify major components. Therefore, the aim of this review to highlight the most commonly used techniques for both qualitative and quantitative analyses for dental materials (1).

1. Inductively coupled plasma spectroscopy (ICP):

ICP is an elemental analysis technique that uses an argon (Ar) plasma (ICP) to convert the sample into ions that are then measured using a mass spectrometer (MS), figure 1. It is a powerful characterization technique, capable of precisely identifying and measuring all elements in the periodic table and detecting up to 20 different trace elements simultaneously down to 1-10 ng of analyte element per liter in solution.

Plasma, referred to as the fourth state of matter, is a collection of positively charged particles, negatively charged particles (e.g., electrons) and excited species moving in random directions. When the temperature of a solid substance is increased at a fixed pressure, it is converted to liquid and then to gas. On further heating, the gas molecules start moving in random directions and when it is sufficiently heated, the atoms are ionized into freely moving charged particles and thus enter the plasma state (2).

ICP-MS is similar to inductively coupled plasma optical emission spectroscopy (ICP-OES), but ICP-OES uses an optical spectrometer to measure the light emitted from elements as they pass through the plasma, whereas ICP-MS measures the elements (ions) directly. Both techniques provide fast analysis of multiple elements in a sample, but ICP-MS provides much lower detection limits than ICP-OES, so it's a better choice for trace element analysis (3).

ICP-MS is typically used to analyze samples that are liquids (such as water) or that can be dissolved, or acid digested, to give a liquid. It is very versatile and can easily measure organic solvents, detect extremely small (nano)particles, or be connected to accessories that allow direct analysis of solid materials or gases.

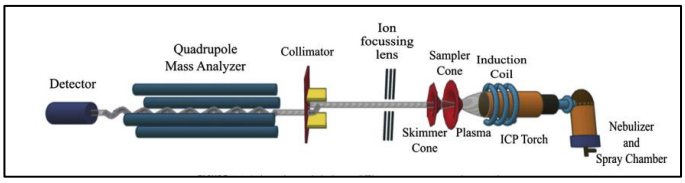


Figure 1. Inductively coupled plasma (ICP) mass spectrometer schematic diagram.

Principle of ICP:
There are six fundamental compartments of ICP-MS, figure 2:

1. The sample introduction system
2. Inductively coupled plasma
3. Interface
4. Ion lens
5. Mass analyzer
6. Detector.

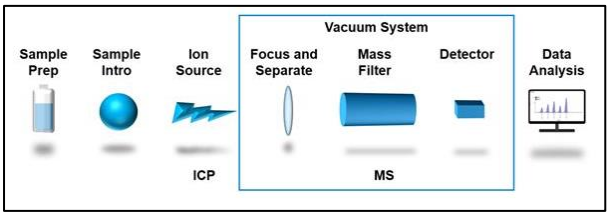


Figure 2. fundamental compartments of ICP-MS instrument.

1. Sample introduction system

ICP-MS is usually used to measure liquid samples. Liquid sample is pumped into a nebulizer, where the liquid is converted into a fine spray or aerosol mist using a jet of argon gas, figure 3. The aerosol mist passes through a spray chamber, where the larger droplets are removed. The fine droplets are carried by the argon gas flow to the ICP plasma torch. Because liquid sample analysis is more convenient, solid samples are often converted to liquids using acid digestion to dissolve the sample matrix, or acid extraction to extract the analytes into a solution for analysis (4).

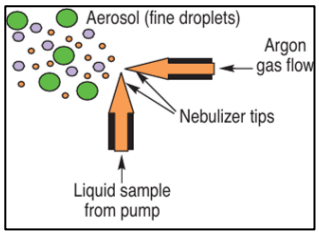


Figure 3. converting the liquid sample to aerosol mist.

Common diluents include dilute acids (e.g. hydrochloric acid) or alkali (e.g. ammonium hydroxide). Deionized water has been used as a diluent, however some elements are unstable in pure water, therefore acidic or alkaline diluents are preferred in most cases. Disadvantages of using dissolution media such as loss or contamination problems, dissolution medium causes loss of some elements and damage for the nebulizing system and plasma torch (4).

Solid sample analysis

A laser ablation (LA) device can be connected to an ICP-MS to perform direct solids analysis by LA-ICP-MS, figure 4. LA-ICP-MS involves placing the sample into a chamber on a special mount, then focusing a high energy beam from a pulsed laser onto the sample surface. Solid particles ablated and vaporized from the sample surface and swept up with a gas stream (usually helium) and carried to the ICP torch, where they are decomposed, dissociated, atomized, and ionized in the same way as for normal aerosol droplets. LA-ICP-MS is sometimes used for bulk (whole sample) analysis in applications such as quality control of metals, alloys, glasses, and ceramics where digesting the material might be difficult. In LA-ICP-MS the laser can be focused to a beam size of only a few microns, so analysis of small samples or a very tiny part of a larger sample is possible.

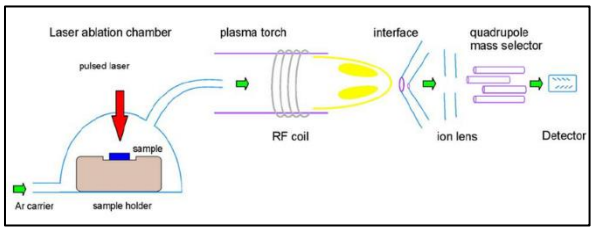


Figure 4. *Laser ablation ICP-MS*

1. Plasma (ICP) to convert the elements in the sample aerosol to ions

The plasma torch consists of concentric quartz tubes the inner tube containing the sample aerosol and Ar support gas and the outer tube containing an Ar gas flow to cool the tubes. The energy is provided by a radio frequency (RF) generator operating at about 1.5 KW produces an oscillating current in an induction coil that wraps around the tubes creating an oscillating magnetic field.

2. Interface region:

The generated ions are then extracted through the interfacial region which is a pair of coaxial nickel (or platinum) cones separate the plasma from the mass spectrometer vacuum chamber, figure 5. The movement of electrons and ions in the torch generate a tremendous amount of heat (10,000K) leads to a complete fragmentation of every sample molecule, leaving only their detectable, atomic constituents (5).

3. Ion lens

It focuses and guides the ion beam and prevent photons and other neutral species (such as non-ionized matrix components) from reaching the detector ◎ maximize transmission and therefore sensitivity◎ into the quadrupole mass analyzer. These uncharged particles would cause a high background signal, so they must be prevented from passing through the vacuum system and reaching the detector. This is usually achieved by positioning a 'photon-stop' in the ion path, or by deflecting the ion beam off-axis while the photons and neutrals, being uncharged, continue in a straight line and so are removed from the ion beam, figure 6.

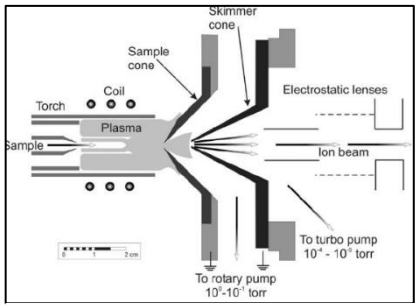


Figure 5. interfacial region cones.

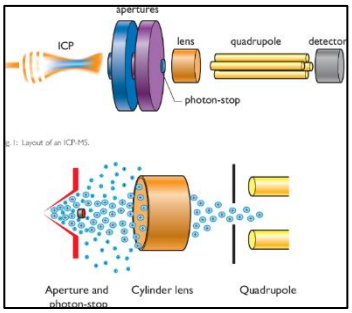


Figure 6. Ion focusing lenses

4. Mass spectrometer

Quadrupole is essentially a mass filter, separating ions based on their m/z ratio. A quadrupole consists of four parallel cylindrical metallic rods positioned in a square array. Radio frequency alternating current (AC) and direct current (DC) potentials are applied to the rods◎ electric field in the center through which ions pass.

6. Detector
7. Data processing

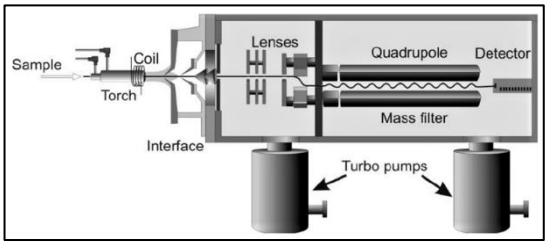


Figure 7. Quadrupole in ICP.

For conventional quantitative analysis, the software calculates the concentration of each element in the unknown samples by comparing the measured counts in the sample to the counts in a known-concentration reference solution.

Advantages of ICP:

1. It provides the broadest elemental coverage, extremely low detection limits (<0.1 part per trillion 'ppt') for nearly all the elements it can measure, and wide measurement range.
2. Multi-elemental technique.
3. Simple specimen preparation.
4. High throughput (about 40 specimens per hour).
5. Liquid and solid sample introduction systems.
6. Relatively small sample volumes required (typically 1-3 mL for solution mode).
7. Capable of isotope ratio measurement.

Disadvantages of ICP:

1. Equipment & Operating cost (argon).
2. Could not detect H and He; below the mass range of the mass spectrometer), Ar, N, and O (which are present at high level from the plasma and air), and F and Ne (which can't be ionized in an argon plasma).
3. Occurrence of interferences (e.g. polyatomic ions).

N.B. Polyatomic ions form in the high-temperature plasma, either due to incomplete atomization or from recombination reactions during the extraction of ions into the mass spectrometer. These ions may be derived from the sample matrix, reagents used for sample preparation, plasma gases (argon) or entrained atmospheric gases. For example, in samples containing chloride (or where hydrochloric acid is used during sample preparation), chlorine oxide (35Cl16O) and argon chloride (40Ar35Cl) are formed in the plasma. These ions share the same m/z ratio as vanadium (51V) and arsenic (75As) respectively. The presence of chloride may therefore lead to erroneous results for these analytes (4).

Dental example using ICP cumulative curve for ion release, figure 8 (6).

2. X-ray fluorescence spectroscopy (XRF):

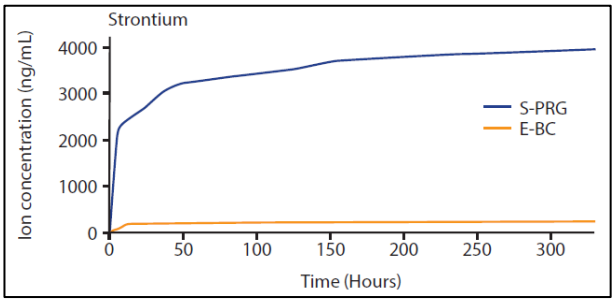


Figure 8. Comparison of average cumulative ion release of strontium over time in the prototype S-PRG sealer (S-PRG) and EndoSequence BC sealer (E-BC).

XRF is a non-destructive analytical technique used to determine the elemental composition of a wide variety of sample types including solids, liquids and loose powders. XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) x-ray emitted from a sample when it is excited by a primary X-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent X-rays "fingerprint" that is unique for that specific element, which is why XRF spectroscopy is an excellent technology for qualitative and quantitative analysis of material composition (7).

X-ray fluorescence process:

A solid or a liquid sample is irradiated with high energy X-rays from a controlled X-ray tube.

1. When an atom in the sample is struck with an X-ray of sufficient energy (greater than the atom's shell binding energy), an electron from one of the atom's inner orbital shells is dislodged.
2. The atom regains stability, filling the vacancy left in the inner orbital shell with an electron from one of the atom's higher energy orbital shells.
3. Electron drops to the lower energy state by releasing a fluorescent X-ray. The energy of this X-ray is equal to the specific difference in energy between two quantum states of the electron. The measurement of this energy is the basis of XRF analysis, figure 9 (7).

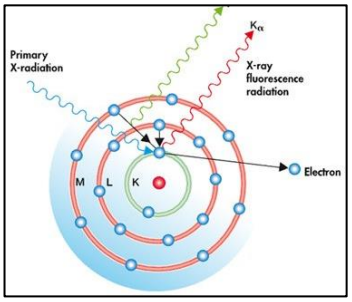


Figure 9. process of XRF radiation

Interpretation of XRF:

When X-ray energy causes electrons to transfer in and out of these shell levels, XRF peaks with varying intensities are created and will be present in the spectrum, a graphical representation of X-ray intensity peaks as a function of energy peaks.

The peak energy (x-axis) identifies the element; as the energy increases the atomic weight of the element increases, this is because the electrons of the heavier elements are bound tighter. While the peak height/intensity (y-axis) is generally indicative of counts which is the number of x-rays one can see that iron is present in a large quantity compared to the other elements because of the high number of counts, figure 10 (8).

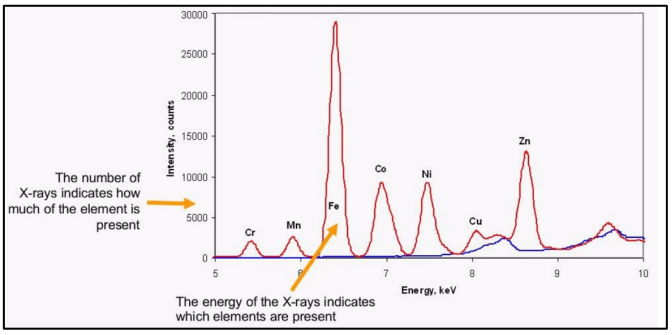


Figure 10. interpretation of XRF graph radiation

Types of XRF instrumentation:

Traditionally, XRF instrumentation is divided into two types according to how they discriminate the energies of the X-ray photons arising from the sample: Wavelength dispersive X-ray fluorescence (WDXRF) & energy dispersive X-ray fluorescence (EDXRF), figure 11.

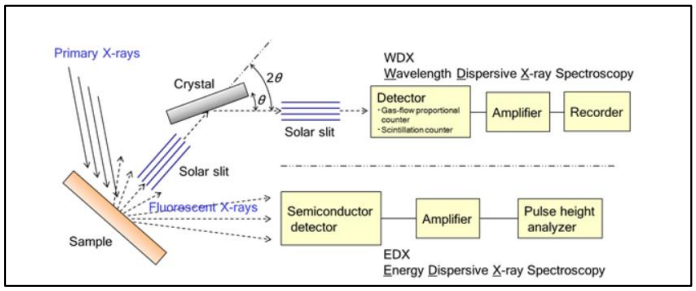


Figure 11. difference between WDXRF and EDXRF

EDXRF has a time advantage, as all elements are measured simultaneously, lower price, portable, relies on a semiconductor detector. WDXRF measures the elements one after another, has a high-resolution system and sensitivity (utilizing a crystal to disperse the fluorescence spectrum into individual wavelengths of each element, providing high resolution and low background spectra for accurate determination of elemental concentrations). Crystal material used is for example a synthetic thin film multilayer crystal giving higher sensitivity and resolution. Collimators further improve resolution by providing different angular divergences to restrict unwanted secondary x-rays from reaching the detector (9).

Advantages of XRF:

1. XRF is a rapid process.
2. Non-destructive.
3. XRF allows for simple sample preparation in the open-air nature of the instrument, and it has low running costs.
4. Wide elemental range for analysis.

Disadvantages of XRF:

1. Limited depth of penetration of X-rays does not exceed 1 mm (inhomogeneous samples are not analyzed accurately).

Poor sensitivity to light elements (Al, Mg); this problem is partially eliminated, for example, by purging the chamber with a sample with helium.

As an alternative, WDXRF can handle more complex samples, but it is more expensive, more time-consuming and requires more expertise to operate (10).

Example on XRF analysis representation, figure 12:

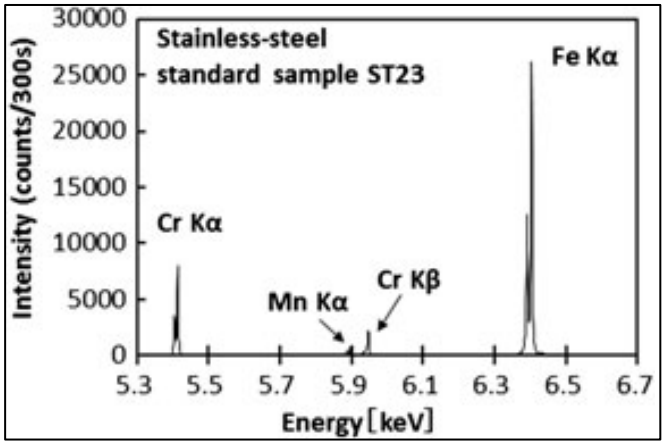


Figure 12. X-ray fluorescence spectrum of a stainless-steel standard sample (ST23: Fe 64%, Cr 22%, Ni 10%, Mn 1.6%, etc.; JFE Techno-Research Corp.) obtained with the polychromatic simultaneous wavelength dispersive Xray

3. Energy dispersive x-ray spectroscopy (EDX):

EDX spectroscopy is involved in the detection of elemental analysis or chemical characterization of a sample by using scanning electron microscope. EDX can detect elements from boron (atomic number 5) upwards.

Basic principle:

An electron beam strikes conducting solid sample's surface to eject 'core' electrons from an atom leaving a vacancy forming atom ionization, figure 13. Atom ionization occurs only when the amount of energy of the inbound electron is large enough to knock an inner orbital electron. In short, this energy from electron exceeds the binding energy of the shell, which is generally known as critical excitation energy. Consequently, a higher energy electron fills this vacancy & release energy (unique to each element) to reach a stable condition. This principle is known as Moseley's Law, which determined that there was a direct correlation between the frequency of energy released and the atomic number of the atom.

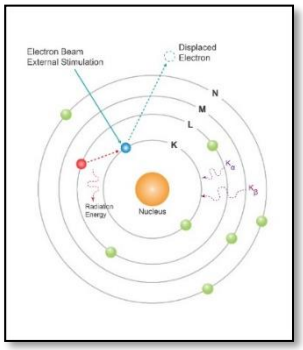


Figure 13. EDX principle

Sample preparation:

Size of the sample do not exceed 3-5 cm. Sample should be conductive for the electrons to react with. A highly polished surface is required for accurate quantitative analysis. Vacuum compatible materials (liquid could not be analyzed). Powder samples can be compacted into disks (11).

EDX apparatus consists of four basic components: the excitation source (electron beam or X-ray beam), the X-ray detector, the pulse processor, and the analyzer, figure 14. The X-ray detector converts X-ray energy into voltage electric signals. The pulse processor measures the detected signals and transfers them to the analyzer, where data is collected, processed and displayed as a spectra reporting the X-ray intensity versus energy

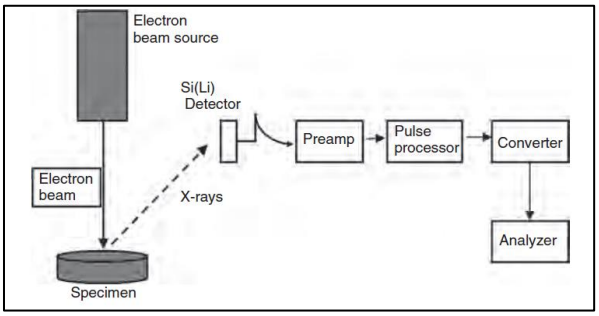
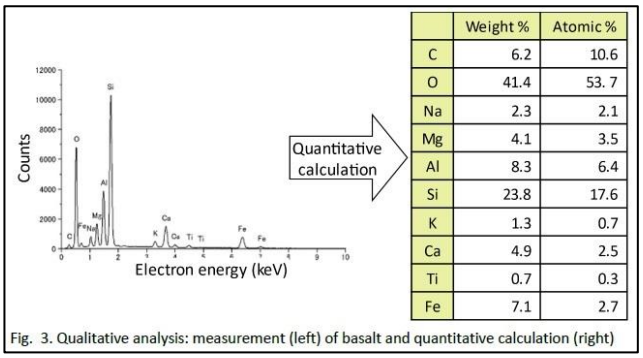


Figure 14. EDX apparatus.

Obtained data from EDX:



	Weight %	Atomic %
C	6.2	10.6
O	41.4	53. 7
Na	2.3	2.1
Mg	4.1	3.5
Al	8.3	6.4
Si	23.8	17.6
K	1.3	0.7
Ca	4.9	2.5
Ti	0.7	0.3
Fe	7.1	2.7

Fig. 3. Qualitative analysis: measurement (left) of basalt and quantitative calculation (right)

Figure 15. qualitative and quantitative analysis of EDX

Qualitative analysis is to identify elements contained in "unknown" materials using characteristic X-ray energies. Quantitative analysis is to identify the number of the emitted characteristic photons by the detector, figure 15. X-ray spectra are presented in a histogram with energy in keV on the x-axis and the number of counts on the y-axis

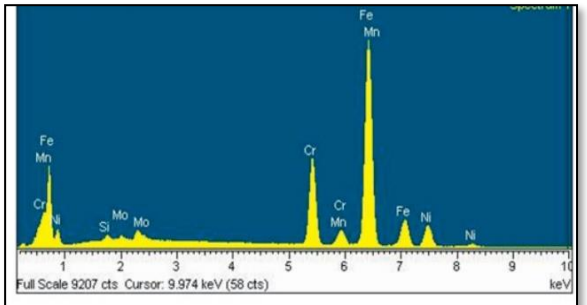
Advantages of EDX:

1. It has a very high mass sensitivity with a detection limit of 1000 ppm and excellent precision.
2. Surface sensitive: generate data from only the top couple of microns of SEM specimens.
3. It is a non-destructive technique.
4. The ability to scan areas and single spots; a large spatial range from about 1 mm2 to submicron2; elemental spectra are linked to image data generated by electron microscope; elemental maps, "dot maps," can be generated from the data.

Disadvantages of EDX:

1. Light elements below 11 atomic number is difficult to be analyzed (not a sensitive technique).
2. Surface roughness directly affects the results obtained. Therefore, samples must be carefully prepared to acquire surface smoothness.
3. Samples must be exposed to vacuum conditions, gases cannot be analyzed and liquids are limited to those that have very limited volatility and will not contaminate the system.
4. Non-conductive samples should be coated.
5. Insensitive method in bulk analysis.
6. Quantitative analysis of heterogonous materials often results in inaccurate data
7. Chamber dimensions often limit the size of samples.
8. The need for standards with a composition as similar as possible to the sample under investigation is a negative aspect when investigating new materials (13).

Dental example, EDX analysis of a stainless-steel alloy, figure 16:



Element	Weight %	Atomic %
Si	0.54	1.08
Cr	17.53	18.80
Mn	1.45	1.47
Fe	66.61	66.50
Ni	11.11	10.55
Mo	2.76	1.60
Totals	100	100

Figure 16. EDX spectrum suggests a stainless steel. The quantification results indicate that this is likely a 300 series and is a good match to alloy 316.

In both SEM/EDS and XRF, characteristic X-ray emissions are excited by an energetic source. The main difference between the techniques is the type of radiation used to excite the emissions. In SEM/EDS, it is an electron beam, whereas in XRF an X-ray beam excites the characteristic X-rays. Spectroscopy in both cases consists of measuring the energy of the emitted X-ray peaks, forming a spectrum that represents an elemental fingerprint of the sample. In XRF, because an X-ray source is used, the spectral background is lower, allowing small peaks to be recognized. This results in the ability to detect very low concentrations of an element. One technical limitation of a portable XRF is that light elements (P and below in the periodic table) are not detectable due to absorption of low-energy X-rays by air and the detector window. Thus, some elements making up the tooth and bone structure (P, O) are not detectable. This also applies to the principal components of the resin fillers in which the elements Si and O are not detectable, figure 17.

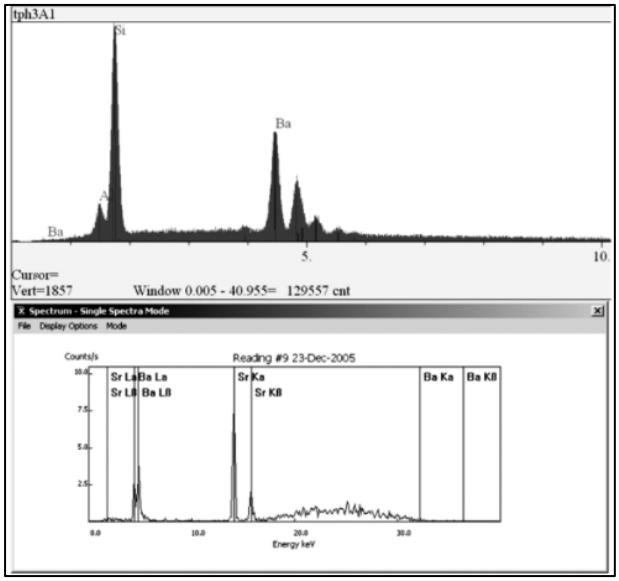


Figure 17. EDS spectrum (top) and XRF spectrum (lower) of TPH 3 resin. The silicon peak seen in the EDS spectrum does not appear in XRF spectrum, but Sr is seen in XRF spectrum due to the greater sensitivity of XRF.

The detection limit in EDS is around 1% concentration, whereas in XRF it is much lower: 10–100 p.p.m. for the elements of interest (0.00001–0.0001% concentration). Figure 17 shows an example of comparative analysis by the two techniques for the resin TPH 3. In the EDS spectrum, the Si peak is dominant, and Al and Ba are detected, while in the XRF spectrum, Ba and Sr are detected. Al will not be detected by XRF analysis as it is below P in the periodic table (14).

2. Conclusion

Chemical characterization techniques understanding is useful to identify the materials' properties and select the most appropriate analysis according to the type of the property needed to be tested.

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