We report a preliminary study on four orthodontic cements, including three glass-ionomer cements and a zinc-phosphate cement, carried out by thick target X-ray fluorescence (XRF) using a portable spectrometer. The aim of this study was to assess the potential of this method for the analysis of some biomaterials used in orthodontics. Due to the lack of reference materials and thick target nature of samples, and because most of the analyzed materials evidenced only one major element, only qualitative analysis was performed. The analyzed glass-ionomer cements unexpectedly evidenced Sr and La as major elements. Two of the analyzed glass-ionomer cements containing Sr also contained traces of Au, and they showed almost identical compositions. The materials contained in addition traces of Fe, Co and Zn. The roles of the detected elements are discussed. While XRF proved to be a valuable and simple method for the diagnosis of substituted glass ionomer cements, other analytical techniques should be used for more advanced characterization.

Key words: XRF analysis, portable spectrometer, standardless multielemental analysis, thick target, orthodontic cements, glass ionomer cements, zinc phosphate cement, specimen preparation, dentistry.

In a broad sense, dental cements are hard, brittle materials formed by reactions between a powder and a liquid. Among other, glass-ionomer cements contributed significantly to technical and clinical progress in orthodontics, due to their capacity to bind on the surfaces of teeth and of ceramic and metal brackets [1–3]. The interface interactions responsible for this remarkable binding strength are not completely understood and further investigation is needed [4]. Dental research greatly benefits of the atomic and nuclear surface and thin layer analysis methods for the study of dental materials’ composition, characteristics and interactions. In this approach, the elemental analysis is the first step, and X-ray fluorescence (XRF) is most popular among these techniques. It allows simple and sensitive multielemental analyses, it is completely nondestructive and covers a high dynamic range of concentrations, therefore can give at a glance a relevant image from major to trace elements [5, 6].

We recently applied standardless XRF using a portable instrument in a study of endodontic sealers; the potential and limits of the technique for dental materials' analysis were discussed in detail [7]. Previously we used XRF together with PIXE and ERDA in the analysis of a variety of dental composites [8]. Other authors proved that XRF of dental composites provides valuable information for forensic applications [9, 10]. By a different approach, we studied by XRF the diffusion of Ag⁺ ions from an AgNO₃ solution into dental enamel and the simultaneous release of Ca according to power functions of the incubation time (Preoteasa, Preoteasa and Gavrilus, unpublished, presented in [11]). Other authors demonstrated by XRF on teeth sex, age, pollution and smoking dependent differences [12] and the accumulation of lead in teeth of children from Pb-polluted industrial environments [13].

In the present study, we evaluate the potential of a portable energy-dispersive X-ray (EDX) XRF instrument for the standardless analysis of three glass ionomer orthodontic cements [1–3, 14, 15] in comparison with a conventional dental zinc-phosphate cement [16, 17].

The glass ionomer cements are formed by inorganic granules of the ion-exchangeable glass calcium fluoroaluminosilicate SiO₂–Al₂O₃–CaF₂–Na₃AlF₆–AlF₃–AlPO₄ and a polyelectrolytic organic acid. In aqueous environment, the organic acid releases H⁺ ions which attack the glass releasing thus Ca²⁺, Al³⁺ and F⁻ ions. The later react with the polyelectrolite and the dental tissue forming a strongly bound rigid matrix [1–3]. Accordingly, in a conventional glass ionomer cement energy-dispersive XRF can detect only Ca. However, in more advanced materials of this type the Ca²⁺ and Al³⁺ ions are partly substituted with other metal cations which improve their properties. If these substituent cations are heavier than Ca (Z > 20), they can be detected by energy-dispersive XRF, which, therefore, can bring relevant information. On the other hand, Zn can be readily detected by XRF in a conventional zinc-phosphate cement. In addition, the glass ionomer cements may contain other organic resin monomers which polymerize by light-curing or by chemical self-curing.

The following orthodontic dental cements were analyzed: Fuji Ortho LC light cured glass ionomer cement for orthodontic bonding (GC), Transbond Plus XT light cured adhesive for metal and ceramic brackets bonding to tooth surfaces (3M Unitek), Ketac Cem easily photopolymerizable resin modified glass ionomer (3M ESPE), and Adhesor conventional zinc-phosphate self-curing cement (Spofa Dental).

Disk-shaped samples with a flat surface were prepared from these materials by self-curing or by photopolymerization on polished glass plates. The solidification process was triggered chemically for the self-curing cements by mixing their
components. For the light-curing composites this was done photochemically, with intense blue light (420–500 nm) from a halogen lamp with glass fiber optics.

Measurements were made using a portable EDX-XRF spectrometer with X-ray tube having Ag anode and with semiconductor detector cooled with Peltier elements, namely an X-MET 3000 TX+ spectrometer (Oxford Instruments) with the tube operated at 40 kV and 0.006 mA anode current for 60 sec, having Si PIN diode detector. The energy resolution was of 275 eV for the Mn Ka line, sufficient for the present preliminary investigation. Such an instrument could analyze all elements from K to U, except those having characteristic radiation in the energy interval of anode’s radiation coherently and incoherently scattered by the samples. This interval is defined between the Compton scattered Kα line and the Rayleigh scattered Kβ line of the anode: Rh, Pd, Ag, Cd, In could not be analyzed well with the Ag anode (Kα ~22.2 keV, Compton ~20.6 keV, Kβ ~24.9 keV).

To evaluate the concentrations, the spectra were processed with the Alloy FP (Fundamental Parameters) program incorporated in the instrument, in the “thick sample” mode in order to make corrections for matrix effects. This program does not analyze Ca and lighter elements. The estimated relative concentrations of the characteristic X-ray lines were listed, but due to reasons mentioned below they should be looked with caution.

With the exception of Ketak Cem, the spectra of the analyzed materials evidenced only one major element accounting for about 95–99 % of the detected elements and one or two trace elements with < 1 % concentrations. Without proper reference materials, this singular character of spectra and the thick target nature of materials made quantitative analysis difficult, even in terms of relative concentrations. Therefore, although the spectra were processed with a dedicated program, we evaluated practically only orde r of magnitude concentrations and we limited ourselves to qualitative analysis.

Both Fuji Ortho LC and Transbond showed Sr as the major detectable element and traces of Fe by their K lines and, surprisingly, impurities of Au by its L lines (Fig. 1). Their spectra were practically identical and, therefore, they cannot be identified by brand using XRF. Most remarkably, Ketac Cem showed Ca (K lines) and La (L lines) in approximately 48–49 % relative concentrations of the detected elements, and Fe, Zn and Sr impurities at about 1 % levels. Thus all three glass ionomer orthodontic cements were substituted with “exotic” elements such as Sr and La. In fact this is a relevant characteristic for the developments of new glass-ionomer cements [2, 3, 18]. In Fuji Ortho LC and Transbond, Ca was not detected, therefore, given the similar chemical properties, we suppose that it was completely substituted by Sr, probably in the form of SrF₂. It is noteworthy that these two materials seem to contain no impurity, as Au an Fe might have been added with a purpose.
In Ketac Cem one can suppose that, given their similar oxidation states (3+, 2+), La substitutes probably a substantial fraction of Al in some of the later’s compounds from the ion-exchanging glass (Al$_2$O$_3$, Na$_3$AlF$_6$, AlF$_3$ and AlPO$_4$). The substitution of Ca ($Z = 20$) and Al ($Z = 13$) by Sr ($Z = 38$) and La ($Z = 57$) is made in view of increasing the radio-opacity of the material, which is necessary for the kind of applications of these cements in orthodontics [2]. Moreover, the same purpose explains the presence of the Au ($Z = 79$) at trace or minor level in Fuji Ortho LC and Transbond. The preparative technique consists in sintering ionomer glass particle with powder of Au which results in the formation of a ceramo-metallic powder [2]. The ceramo-metallic particles might contribute also to the improvement of the optical aspect of the materials (color, translucence) for physionomic purpose [19]. We may suppose that Au-sintered glass particles account for a fraction of the mineral filling in Ortho LC and Transbond and are at the origin of the observed Au L lines in the XRF spectra of these biomaterials.

Finally, the conventional zinc phosphate orthodontic cement Adhesor shows Zn as the major element (~99 %) and traces of Fe and, possibly, Co, both below 1 %.

Fig. 1 – XRF spectra of some orthodontic cements. The spectra were recorded with a portable energy-dispersive spectrometer equipped with an X-ray tube having an Ag anode. Fuji Ortho LC, Transbond Plus XT and Ketac Cem were glass ionomer cements, while Adhesor was a zinc phosphate cement. The artefactual lines in the spectra such as pile-up lines were not labeled.
It is obvious that both Zn and Au have a good biocompatibility: while Zn is an essential oligoelement and is ubiquitous in hard tissues like enamel, dentin and bone, Au is well tolerated because of its chemical inertia and is used since many decades for metallic works in dentistry.

The chemical and biological significance of the substitution of Ca by Sr in Fuji Ortho LC and Transbond is not obvious, but suggestions can be made based on their chemical properties [20]. Strontium salts have properties which are intermediate between those of barium and calcium. Strontium chloride is sometimes used in toothpastes for sensitive teeth. Strontium ranelate is used in the treatment of osteoporosis. As compared to Ca, the hydroxides and fluorides of Sr are somewhat more soluble [20]. It is plausible that substitution of CaF₂ by SrF₂ facilitates the release of F⁻ ions and the intake of Sr²⁺ ions in hydroxyapatite, resulting in a strong bond of the cement to enamel and dentine.

In Ketac Cem, lanthanum(III) apparently substitutes aluminum(III). Various recent dental restorative materials and ceramics contain certain lanthanides mainly for color and optical fluorescence [1]. However, using PIXE and PIGE we detected Yb in the form of YbF₃ microgranules embedded in the dental composites Tetric Ceram and Ariston for slow F⁻ release in the oral environment [8, 11, 21–23]. New roles for the iconic lanthanide, lanthanum, seem to be involved in Ketac Cem. In addition to the role of La in increasing the radiologic opacity by its high electron density, this rare earth may have also other functions. Thus La₂O₃ instead of Al₂O₃ improves the alkali resistance of glass, and the strong binding of the lanthanum with phosphates in LaPO₄ [24] may improve the mechanical properties of the cement as compared to the AlPO₄-containing standard glass-ionomer cement.

Note that in contrast to the other analyzed materials, Transbond had a strong blue color. The producer mentions “color changing for easier flash clean-up and better bracket reference” [25/20]. The Fe traces detected in Transbond may suggest that the intense blue color was achieved with Prussian Blue, Fe₇(CN)₁₈·xH₂O, or Fe₃[Fe(CN)₆]₃·xH₂O, where x = 14–16, which is an insoluble, non-toxic pigment used as an antidote for certain kinds of heavy metal poisoning, e.g., by thallium and radioactive caesium [26]. However, all the remaining three cements contained traces of Fe which were not accompanied by a blue color. It has been shown that traces of Fe could increase the bonding of some glass-ionomer cements to dentin [27].

In the case of Adhesor, the high Zn concentration is consistent to the zinc phosphate cement nature of the material. This evidences a completely different nature as compared to the glass ionomer cements. The presence of the Fe and Co traces could play a possible role for color or for strengthening adhesion to enamel and dentin.

Let as note finally that a preliminary analysis of one of the Au-containing glass-ionomer cements has been made by LA-ICP-MS at a spatial resolution of 100 μm. This method confirmed the results of XRF analysis, including the
presence of Au but, in addition, it showed that the sample is strongly heterogeneous on a 100 mm scale and the detected composition was different from point to point. This result emphasized the fact that XRF, which analyzes a sample of about 10 mm diameter, determines an average elemental composition. From this point of view, XRF is complementary to LA-ICP-MS which analyzes the local concentrations.

In brief, XRF analysis, even semi-quantitative or qualitative, evidenced relevant aspects in the elemental composition of the orthodontic cements, related mainly to unexpected exotic metals in the glass-ionomer cements. In fact the most important result of this preliminary study may be considered the diagnosis in these materials of substituted ion-exchanging glasses containing Sr and La, probably instead of Ca and Al. Also, detection of Au at trace or minor levels pointed to the presence of ceramo-metallic Au-sintered glass particles. However, two of the analyzed glass-ionomer cements showed almost identical Sr-dominated compositions and cannot be identified by brand using this simple technique. Trace elements like Fe, Co and Zn were also detected in the four orthodontic cements. The main advantage of XRF is its versatility, simplicity and speed, and it remains a valuable option for the analysis of glass ionomer cements containing substituents heavier than Ca ($Z > 20$). Other methods like LA-ICP-MS and SIMS, as well as PIXE, PIGE and ERDA, including their microbeam versions, should be used to analyze the elements contained in the glass-ionomer cements but invisible by XRF (e.g. F, Na, Al, Si, P) and to analyze their spatial distribution. This approach, as well as the possible biocompatibility implications of Sr and La, remain to be explored in further investigations.

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