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Study of filling material of dental composites: an analytical approach using radio-activation

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Abstract: The aim of this study is to carry out elemental analyses of dental composites acquired from different producers using photoactivation analysis (PAA). High energy electrons produced by an electron linear accelerator are absorbed by a tungsten disk (Bremsstrahlung converter) thereby producing high energy X-rays (bremsstrahlung). The dental composite materials under study were exposed to the bremsstrahlung radiation whereby radionuclides were produced through photonuclear reactions. Their radioactivities were measured using high resolution semiconductor spectrometers equipped with high purity germanium detectors (HPGe). The spectra were analysed using appropriate computer software. As a result, photonuclear reactions of 12 stable elements were detected in different dental composite species, and the elemental concentrations were calculated. For comparison, the dental composites were also investigated using scanning electron microscopy (SEM) and energy-dispersive X-ray fluorescence spectrometry (EDXRF). Various sizes and shapes of dental composites were observed using SEM. However, contents of dental composites, e.g. Mg, Ni, Ba and Sr were obtained by PAA whilst C, O, Al, S, Ba and Sr were detected by EDXRF spectrometry. The results for Ba and Sr obtained using the two techniques show considerable difference.

Keywords: Photoactivation analysis (PAA), dental composites, bremsstrahlung photons, semiconductor spectrometry, X-ray fluorescence spectrometry (EDXRF).

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1 Introduction

Dental composites are frequently used as restorative or adhesive material. These materials are produced by composing various concentrations of different elements and an organic matrix material; each brand shows different characteristics. Dental composites located between enamel and dentine may transfer foreign elements into organism. These decelerate biological, chemical and mechanical decline [1]. A knowledge of the presence or absence of key elements in dental composites is of vital importance. The accumulation of various chemical species including metal compounds in the living tissue is a normal natural process as long as the concentrations of these metal compounds remain at a “normal”, viz. biocompatible level. Elements in excessive concentration might have considerable toxic effects [2]. Therefore, elements, metal compounds in particular, need to be analyzed both in biological tissue and in medicaments. As pointed out by Suciu et al. [3], elemental analysis is used in medicine in a wide application range, from current clinical applications to the investigation of the structure and mechanisms in normal and pathological tissues and the development of new medical materials. Moreover, forensic analytical studies of dental material and dental composites have been carried out frequently to find evidence in criminal cases; the signature of component concentrations, trace metal compounds in particular, normally is selective for individuals with a high degree of probability. Nowadays, highly precise nuclear and atomic analysis methods for element analysis are frequently reported [2–9] in the scientific literature. One very powerful analysis method, photoactivation analysis (PAA), has hitherto not been applied in elemental analysis of dental composites.

For many years PAA has been used as a variable analytical tool in various scientific fields. Its basic principle has been described in detail elsewhere [10–12], thus it will be discussed only briefly here. The basis of PAA is photonuclear reaction. The material under study is exposed to high energy photon radiation, usually 10–30 MeV bremsstrahlung, mostly produced by an electron linear accelerator. The energy of the bremsstrahlung photons is transferred to the nuclei

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of elemental components of the exposed matter, thus converted, through photonuclear reactions, to radioactive species. The reactions can be of (γ,n), (γ,2n), (γ,γ′), (γ,p), (γ,np) type, primarily depending upon the energy of the incident activating photon quanta. The product nuclides can decay by emission of different nuclear particles and/or quanta. In almost all cases the photon emission (γ or X-ray fluorescence) is used for analytical evaluation. The photon spectra are obtained by appropriate radiation spectrometers, preferably equipped with high resolution semiconductor detectors. Photoactivation analysis can be performed mostly instrumentally, viz. without chemical processing, and frequently can be carried out non-destructively, thus it is notably time-saving. Using PAA, some low-Z elements, e.g. C, N, O, F and several other elements, e.g. Mg, Si, Ca, Ti, Ni, Sr, Y, Zr, Nb, Sn, Tl and Pb, can be determined at lower detection limits as compared to neutron activation analysis (NAA) [13]. Most of the elements of the Periodic Table can be analysed efficiently by PAA at high detection power. It has been reported in the international literature for many years [11].

PAA has many advantages compared with other methods. However, it requires considerably costly hardware equipment (a high energy activating photon source, e.g. an electron linac or a microtron, see Refs. [10, 11, 14] and high resolution gamma-ray spectrometry equipment). Furthermore, high-level qualification of the personnel is mandatory, in radiation safety issues in particular.

The aim of this study is to carry out elemental analyses of dental composites acquired from different producers by PAA using a clinical electron linear accelerator. In the following, we describe materials and methodology, and we present the results of our study.

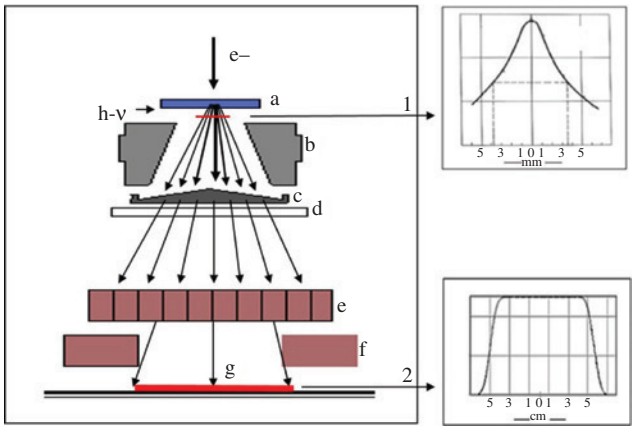


Figure 1: Schematic view of the cLINAC. (a) Bremsstrahlung converter; (b) primary collimator; (c) flattening filter; (d) ionisation chamber (bremsstrahlung dose meter); (e) X diaphragm; (f) Y diaphragm; (g) large sample exposure position ("Patient board"), 1: Bremsstrahlung profile upstream from the flattening filter (exposure position for small samples, used in the dental composite experiment), 2: homogenous bremsstrahlung field profile at level (g).

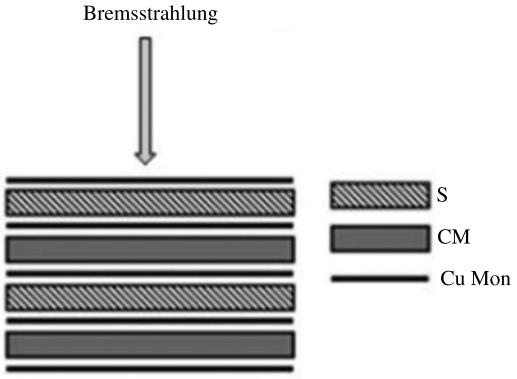


Figure 2: Irradiation scheme of samples (S), calibration materials (CM) and bremsstrahlung flux copper monitors (Cu Mon).

2 Materials and methods

A clinical electron linear accelerator (cLINAC) was used. It is schematically shown in Figure 1. The details are published elsewhere [15]. In this study, five different brand dental composites were investigated. The samples, calibration materials and bremsstrahlung flux monitors (thin copper sheet) were prepared and arranged as shown in Figure 2. The flattening filter was removed to reduce the distance between the tungsten converter and the items exposed to about 17 cm, thus enhancing the effective bremsstrahlung flux density. Therefore, the materials were placed about 17 cm downstream from the tungsten converter for higher flux delivery and irradiated with 18 MeV homogeneous bremsstrahlung photons. The cLINAC was modified to enable close exposure distance to the converter. The irradiation period was 2 h.

After irradiation and a cooling time of 2 h, the γ-ray emissions of the dental composites and calibration materials were counted by a coaxial n-type liquid nitrogen-cooled ORTEC HpGe detector and a coaxial p-type electrically cooled ORTEC HpGe detector. Materials were placed in front of the detector head at a distance of 5 cm

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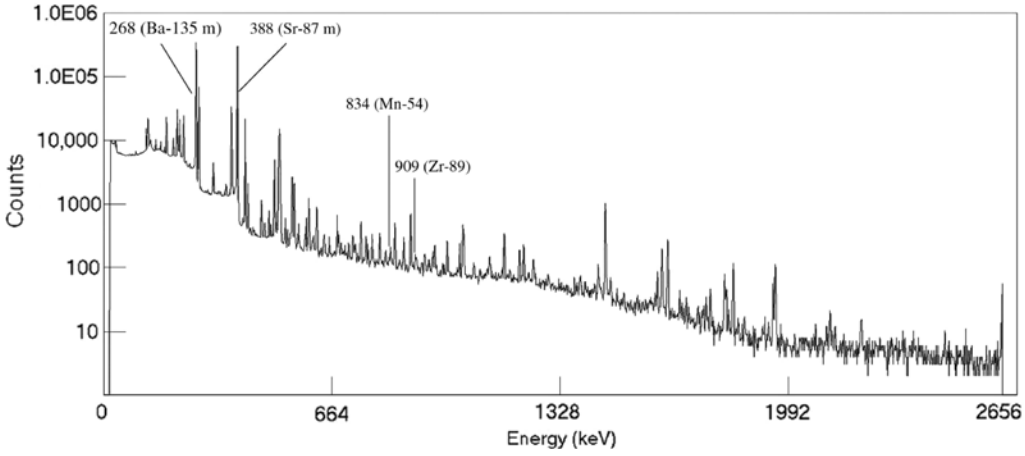


Figure 3: Gamma-ray spectrum of a dental composite after bremsstrahlung exposure.

to reduce dead time interference. Spectra were collected using MAESTRO-32 software [16]; see Figure 3.

Analytical results without bremsstrahlung flux correction are calculated by Eq. 1 [11].

$$c_S = \frac{c_{Cal} \cdot m_{Cal} \cdot P_S}{m_S \cdot P_{Cal}} \cdot \frac{e^{-\lambda(t_{dCal} - t_{dS})} - e^{-\lambda(t_{dCal} - t_{dS} + t_{cCal})}}{1 - e^{-\lambda t_{cS}}} \quad (1)$$

(index S, Cal refer to sample – and calibration material – related parameters, respectively.)
where:

c	Element contents (µg/g)
m	Mass (g)
P	Pulse number of the spectral signal; net peak integral
t_d	Decay period (s)
t_c	Spectrum collection period (s)
λ	Decay constant (s^{-1})

Initial conditions for the validity of Eq. 1 [12]:

Sample and calibration material
- are inactive prior to activation;
- are similar in size, shape and matrix composition;
- are exposed simultaneously;
- receive the same activating radiation dose;
- are measured with the same radiation spectrometer at identical counting geometry;
- emit similar integral radiation doses after activation.

Under the exposure conditions in our experiments, equal bremsstrahlung doses received by all items irradiated cannot be achieved. Thus, external radiation monitor foils were used to correct for different doses received by each sample and calibration material, respectively (see Figure 2). Generally copper (^{65}Cu) and nickel (^{57}Ni) have been used. All items exposed simultaneously should be geometrically congruent. In the present case copper monitors were used to correct for changing activating flux densities [11, 17], Thus, quantative evaluation in the present case was carried out using Eq. 2:

$$c_S = F_{corr} \cdot \frac{c_{Cal} \cdot m_{Cal} \cdot P_S}{m_S \cdot P_{Cal}} \cdot \frac{e^{-\lambda(t_{dCal} - t_{dS})} - e^{-\lambda(t_{dCal} - t_{dS} + t_{cCal})}}{1 - e^{-\lambda t_{cS}}} \quad (2)$$

The correction factor, obtained by the activity of the flux monitors, is defined by Eq's. 3 and 4.

$$F_{corr} = \frac{\bar{I}_{normMonCal}}{\bar{I}_{normMonS}} \quad (3)$$

where $\bar{I}$ is the averaged normalised count number of the monitors.

$$F_{corr} = \frac{(m_{Mon1S} + m_{Mon2S}) \cdot \left(\frac{I_{Mon1Cal} \cdot \lambda_{Mon}}{e^{-\lambda_{Mon} \cdot t_{dMon1Cal}} \cdot (1 - e^{-\lambda_{Mon} \cdot t_{cMon1cal}})} + \frac{I_{Mon2Cal} \cdot \lambda_{Mon}}{e^{-\lambda_{Mon} \cdot t_{dMon2Cal}} \cdot (1 - e^{-\lambda_{Mon} \cdot t_{cMon2Cal}})} \right)}{(m_{Mon1Cal} + m_{Mon2Cal}) \cdot \left(\frac{I_{Mon1S} \cdot \lambda_{Mon}}{e^{-\lambda_{Mon} \cdot t_{dMon1S}} \cdot (1 - e^{-\lambda_{Mon} \cdot t_{cMon1S}})} + \frac{I_{Mon2S} \cdot \lambda_{Mon}}{e^{-\lambda_{Mon} \cdot t_{dMon2S}} \cdot (1 - e^{-\lambda_{Mon} \cdot t_{cMon2S}})} \right)} \quad (4)$$

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The uncertainty of concentration of an element detected in a dental composite was calculated using the following equation [18].

$$\Delta c_S = c_S \sqrt{\left(\frac{\Delta c_{Cal}}{c_{Cal}}\right)^2 + \left(\frac{\Delta P_{Cal}}{P_{Cal}}\right)^2 + \left(\frac{\Delta P_S}{P_S}\right)^2 + \left(\frac{\Delta m_{Cal}}{m_{Cal}}\right)^2 + \left(\frac{\Delta m_S}{m_S}\right)^2 + \left(\frac{\Delta I_{Cu}}{I_{Cu}}\right)^2} \quad (5)$$

where:

Δc	Uncertainty of element content ($\mu g \cdot g^{-1}$ or %)
Δm	Uncertainty of mass (g)
ΔP	Uncertainty of net peak integral
ΔI	Uncertainty of count number of Cu monitors

The dental composites were investigated using QUANTA FEG 450 model [19] scanning electron microscopy (SEM) with energy dispersive X-ray fluorescence (EDXRF) spectrometry.

3 Results and discussion

Spectra were processed using the Gamma-W software [20]. As an example, the gamma-ray spectrum of a dental composite after bremsstrahlung exposure is shown in Figure 3. Detected reactions, radionuclides, their half-lives and characteristic gamma-ray energies as well as their intensities are listed in Table 1. The (γ,n) reaction type was detected for ^{88}Sr, ^{84}Sr, ^{52}Cr, ^{55}Mn, ^{75}As, ^{90}Zr, ^{93}Nb, ^{136}Ba, ^{140}Ce and ^{58}Ni. This reaction contributes most significantly to the total photoneutron cross section, called Giant Dipole Resonance (GDR), in the γ-ray energy range from 10 MeV up to about 30 MeV. If the bremsstrahlung energy is higher than the neutron binding energy a single neutron is emitted from the nucleus. The threshold of the (γ,n) reaction equals the binding energy of the neutron. Most of the elements in dental composites were detected by this reaction. The (γ,2n) reaction was detected for ^{79}Br. The threshold of the (γ,2n) reaction is almost two times higher than that of the (γ,n) reaction. Several metastable state activation products, e.g. ^{87m}Sr and ^{135m}Ba (see Table 1) were also generated through (γ,γ′) reactions ("Level excitation") at lower incident bremsstrahlung energies. However, the respective cross sections are very small, sometimes referred to as "Pygmy Dipole Resonance (PDR)". Therefore, these are overlain by far by (γ,n) reactions of neighbouring stable target isotopes, e.g. ^{88}Sr and ^{136}Ba [11].

A (γ,p) reaction was detected for Mg (^{25}Mg(γ,p)^{24}Na). Because the threshold energies are high and cross sections of (γ, charged particle) reactions are low for heavy nuclei, the reactions are analytically relevant only for light and medium Z elements (Z ≤ 50).

Table 1: Reactions detected by instrumental photoactivation analysis of dental composites.

Element	Detected reaction	Radionuclide	$T_{1/2}$	E_γ (keV)	I_γ (%)
Strontium	^{88}Sr(γ,n)^{87m}Sr	^{87m}Sr	2.815 h	388.5	82.19
	^{87}Sr(γ,γ′)^{87m}Sr				
	84Sr(γ,n)83Sr	^{83}Sr	32.41 h	762.6	26.7
Chromium	^{52}Cr(γ,n)^{51}Cr	^{51}Cr	27.70 day	320.1	9.91
Manganese	^{55}Mn(γ,n)^{54}Mn	^{54}Mn	312.20 day	834.8	99.98
Arsenic	^{75}As(γ,n)^{74}As	^{74}As	17.77 day	595.8	59
Zirconium	^{90}Zr(γ,n)^{89}Zr	^{89}Zr	78.41 h	909.2	99.04
Niobium	^{93}Nb(γ,n)^{92m}Nb	^{92m}Nb	10.15 day	934.4	99.15
Barium	^{136}Ba(γ,n)^{135m}Ba	^{135m}Ba	28.7 h	268.2	16
	^{135}Ba(γ,γ)^{135m}Ba				
Cerium	^{140}Ce(γ,n)^{139}Ce	^{139}Ce	137.64 day	165.8	80
	^{123}Sb(γ,n)^{122}Sb	^{122}Sb	2.72 day	564.2	70.67
Antimony	^{123}Sb(n,γ)^{124}Sb	^{124}Sb		602.7	97.8
			60.20 day	645.8	7.42
				722.8	10.76
				1690.9	47.57
Nickel	^{58}Ni(γ,n)^{57}Ni	^{57}Ni	35.60 h	1377.6	81.7
Bromine	^{79}Br(γ,2n)^{77}Br	^{77}Br	57.04 h	238.9	23.1
Magnesium	^{25}Mg(γ,p)^{24}Na	^{24}Na	14. 99 h	1368.6	99.99

The γ-ray energies, intensities and half-lives were taken from literature [21].

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Table 2: Analytical results obtained by PAA.

Element	Concentration (in µg/g or as indicated)				
	Sample-1	Sample-2	Sample-3	Sample-4	Sample-5
Sr	671±43	77223±8742	2165±119	3023±170	1287±87
Cr %	0.67±0.12	n.d.	n.d.	n.d.	n.d.
Mn	163±23	152±15	157±28	94±13	93±10
As	84±5	n.d.	31±3	n.d.	n.d.
Zr	4.29±1.16	287±22	387±30	494±37	30±3
Nb	3±1	n.d.	n.d.	n.d	n.d.
Ba %	16±1	0.38±0.01	15±1	21±1	16±1
Ce	87±10	n.d.	n.d.	n.d.	n.d.
Sb	n.d.	114±7	120±8	81±5	47±3
Ni	n.d.	17±3	n.d.	19±2	n.d.
Br	n.d.	n.d.	181±38	82±11	n.d.
Mg	n.d.	n.d.	1422±118	2625±202	1115±127

n.d., Not detected.

One (n,γ) reaction was detected namely $^{123}Sb(n,\gamma)^{124}Sb$. The (n,γ) reaction is quite likely because the cLINAC also is a potent neutron source. The neutrons are produced predominantly by (γ,n) reactions in the bremsstrahlung converter. However, the photoreaction $^{123}Sb(\gamma,n)^{122}Sb$ yields much higher product activity than the aforementioned neutron reaction; it is analytically much more appropriate, accordingly.

Analytical results of the different brands of dental composites are shown in Table 2. The contents of the elemental components can be classified as major, minor and trace; see Table 3. Generally, most of these elements are not defined by the producers. As pointed out by Preoteasa et. al. [4] these elements give information about classification of dental composites; Ba, Yb, Hf enhance the radiological opacity, the hydroxides and fluorides of Ba and Sr are soluble and their intake in hydroxyapatite may retard the enamel and dentine demineralization. Samples 1, 4 and 5 are similar; Ba is the major element in these samples.

Table 3: Classification of detected elements using PAA in dental composites.

Sample	Detected elements		
	Major	Minor	Trace
Sample-1	Ba	Cr	Sr, Mn, As, Zr, Nb, Ce
Sample-2	Sr	Ba	Mn, Zr, Sb, Ni
Sample-3	Sr, Ba	–	Mn, As, Zr, Sb, Br, Mg
Sample-4	Ba	–	Sr, Mn, Zr, Sb, Ni, Br, Mg
Sample-5	Ba	–	Sr, Mn, Zr, Sb, Mg

Some light elements (carbon, oxygen, aluminium and silicon) were detected using energy-dispersive X-ray fluorescence (EDXRF) spectrometry. However, since no respective PAA results could be obtained, these values are irrelevant. Several comparative PAA/EDXRF results of Sr and Ba, respectively are shown in Table 4. SEM micrographs of dental composites and spectra of EDXRF are shown in Figure 4. The elements C, O and Si were detected in all samples. The Sr and Ba results are in agreement only partly (see Table 4). The detection limits of Sr are calculated as 0.02%, 0.09% and 4 µg/g for samples 2, 3 and 5, respectively. Sr is detected only in sample 3 which is important for dentine surface adhesion [22]. Modifications of the surface of dental composites are shown in SEM micrographs and the size and shape of particles of the dental composites were dissimilar (see Figure 4). The particle size in samples 4 and 5 is significantly greater than that of the others. The samples 4 and 5 appear similar because these composites include nanoparticles and some micro particles [23, 24]. The results of Ba obtained by PAA for samples 1 and 4 are

Table 4: Analytical results of strontium and barium using EDXRF.

Element	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Sr % (Uncert. %)	n.d.	n.d.	6.5 (3.3)	n.d.	n.d.
Ba % (Uncert. %)	14.7 (4.9)	20.6 (6.0)	n.d.	18.2 (6.0)	74.9 (5.3)

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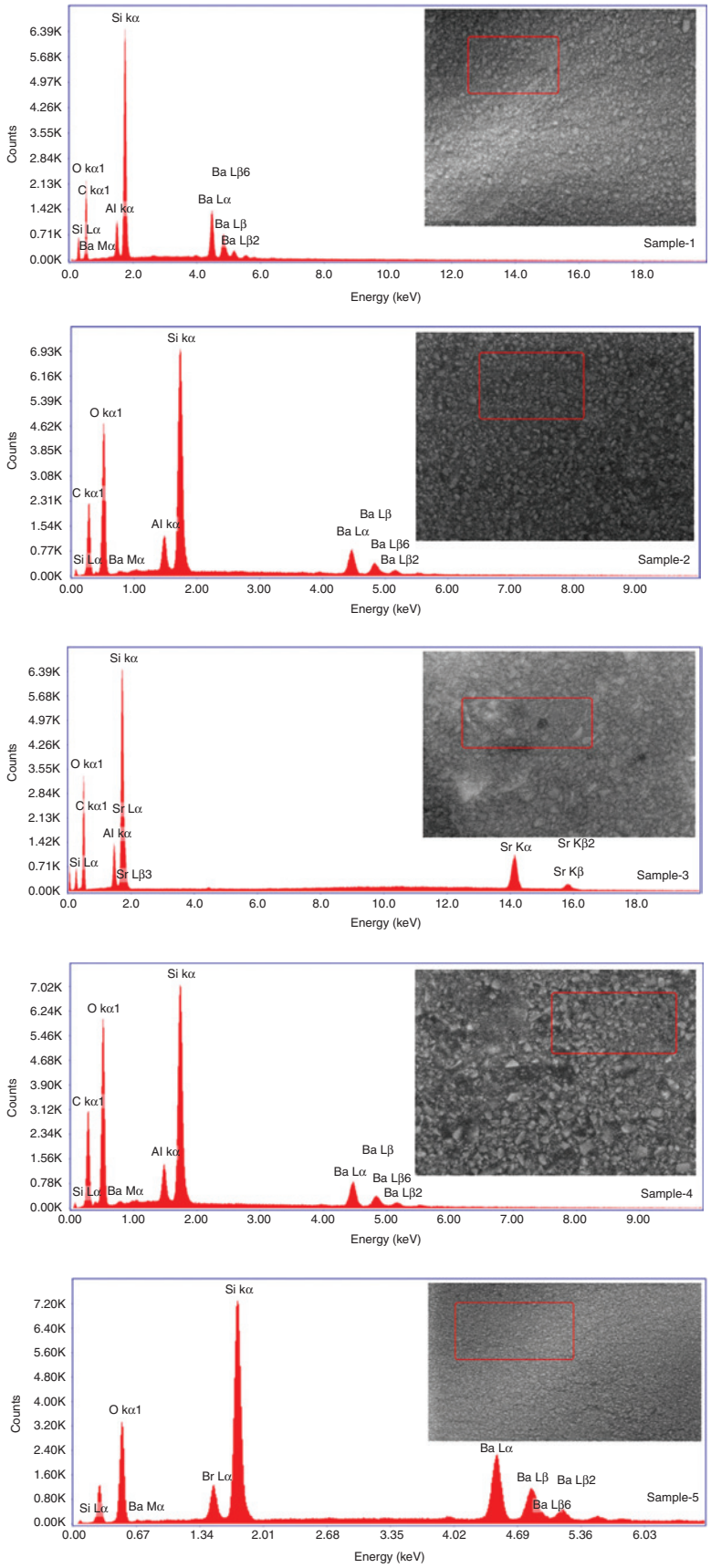


Figure 4: SEM micrographs of dental composites and the corresponding spectra of EDXRF.

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in agreement with those obtained by EDXRF although the results of Ba obtained by both methods are different for samples 2, 3 and 5. This result may be connected with the grain sizes and different mineralogical phases. The detection limits of Ba are calculated as 120 μg/g, 0.02% and 1% for samples 2, 3 and 5, respectively.

Sample 1 and 2 are micro hybrid composites. Elemental content of sample 1 is barium–alumina silicate and content of sample 2 is alumina borosilicate and silicon dioxide which are specified by the producers. As shown in SEM micrographs (see Figure 4) Ba, Al and Si are detected in sample 1 and Al and Si are detected in sample 2. These results are in agreement with contents of the producers. Ba is not defined by the producer but Ba is detected by both EDXRF and PAA for sample 2. Al and Si are not detected by PAA because the half-lives of these radionuclides are too short or too long for our experimental setup. Our experimental setup is off-line system. To determine radionuclides, the half-lives of radionuclides should be higher than about 10 min. Sr, Mn, As, Zr, Nb and Ce are detected as minor and trace elements for sample 1 and Sr is detected as major element, Ba is detected as minor element, Mn, Zr, Sb and Ni are detected as trace elements by PAA for sample 2 (see Table 3). Samples 3 and 4 are nano ceramic composites. Elemental content of sample 3 is defined by glass filling and pyrogenic silica and the elemental content of sample 4 is defined as barium–aluminium–borosilicate glass, silicon dioxide nano filler by the producers. As shown in the SEM micrographs of sample 3, Al, Si and Sr are detected. Only Si is in agreement with content of producer. Sr is detected by both PAA and EDXRF as high concentration, also Ba is detected as major element, and Mn, As, Zr, Sb, Br and Mg are detected as trace elements by PAA for sample 3 (see Table 3). Ba, Al and Si are detected by EDXRF in sample 4. These elements are in agreement with content of producer. Ba is detected by PAA, also Sr, Mn, Zr, Sb, Ni, Br and Mg are detected as trace elements in sample 4 by PAA. Sample 5 is nano quadrant composite which is specified as Ba–Al–F–silicate glass and silicon dioxide by the producer. Si is detected although Al is not detected by EDXRF and Ba is detected both by EDXRF and PAA, however Br is detected by EDXRF. Sr, Mn, Zr, Sb and Mg are detected as trace elements by PAA in sample 5. Ba is detected in all samples by PAA although it is not detected in sample 3 by EDXRF. As a results of PAA, radiological opacity of sample 1, 3, 4 and 5 is high because Ba is the major element for these samples.

Zr is detected in all samples by PAA because generally the filling particles are either barium silicate glass, quartz or zirconium silicate, frequently integrated with very small-sized particles of silica [25]. Elements have their oxide shape because oxygen is detected by EDXRF in all samples.

The colour of dental composites are created by different elements. As pointed out by Asgary et al. [26, 27], the late transition elements (Cr, Mn, Fe and Cu) having free d-electrons which are not required in binding show high colours when their oxide form owing to d-electrons can be easily excited by light in the visual spectrum, although the oxides of the some elements (Mg, Al, Si, P, S, K, Ca and Ti) can not be easily excited and so they are colourless or white. Sample 1 has Cr and Mn. Samples 3, 4 and 5 have Mg. Manganese (Mn) is detected as a trace element in all samples by PAA which is significant due to its structural and enzymatic roles [28]. Concentration of Mn varies from 93 ± 10 μg/g to 163 ± 23 μg/g. Sample 1 has the highest concentration of Mn, however sample 5 has the lowest concentration of Mn. Nickel (Ni) is detected as a trace element in samples 2 and 4 by PAA which constitutes free radicals in humans by oxidation and reduction reactions [28]. Niobium (Nb) is detected as a trace element in sample 1 by PAA. It is present as niobium pentoxide (Nb_2O_5) which enhances microhardness, radiopacity and rate of polymerisation of the dental composite [29]. Apart from sample 1, antimony (Sb) is detected as a trace element in other dental composites. Concentration of Sb varies from 47 ± 3 μg/g to 120 ± 8 μg/g. The oxides of Sb are used as opacifying in enamels [30]. Bromine (Br) is detected as trace element in samples 3 and 4 by PAA; it is also detected in sample-5 by EDXRF. Monomers of iodine or bromine have radiopaque features because electron densities of these elements are high [31]. Cerium (Ce) is detected as trace element only in sample 1 by PAA. Ce is presented as cerium oxide (CeO_2) in enamel and shows natural fluorescence; it is used to remove the colour in glass industry also it considerably reduces the silver staining [32]. Arsenic (As) is detected as trace element by PAA in samples 1 and 3. Concentrations of As are 84 ± 5 μg/g and 31 ± 3 μg/g in sample 1 and sample 3, respectively. The toxic effect of the arsenic may be attributed to its composition with the lethal dose (LD50) applied verbally changing from 2 to 3 mg/kg for arsenic trioxide, 20 mg/kg for calcium arsenate, 600 mg/kg for sodium arsenate, 10–50 mg/kg for sodium arsenate, and 100 mg/kg for Paris green and in food, the presence of arsenic is permitted up to 3.5 μg/g [33, 34]. To evaluate concentration of As level, detailed investigation should be done by other atomic and nuclear techniques and obtained results should be compared.

As shown in results, many elements were detected by PAA although these elements were not shown in

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composites by the producers. Producers do not give information on other elements about their microstructure due to industry privacy [30].

4 Conclusions and outlook

The dental composites are classified by contents of elemental components obtained by PAA and EDXRF. Mostly reactions of medium Z elements were detected using PAA while light elements were detected using EDXRF. The size and shape of the dental composite components were examined using SEM micrographs. The result of this study is multifold, e.g. (a) The applicability of PAA to the investigation of the aforementioned materials; (b) obtaining results of a quality that allows meaningful interpretation and conclusions; (c) recognizing significant differences of element contents in materials from different producers. However, the difference between the PAA and EDXRF values of Sr and Ba is considerable, thus further experimental work is required. Nonetheless, after refinement of the analytical procedures, this method may be well be applied for forensic studies, e.g. victim identification in murder cases.

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