



First detection of lead in black paper from intraoral film An environmental concern

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ABSTRACT

Lead (Pb) contamination in the black paper that recovers intraoral films (BKP) has been investigated. BKP samples were collected from the Radiology Clinics of the Dental School of Ribeirão Preto, University of São Paulo, Brazil. For sake of comparison, four different methods were used. The results revealed the presence of high lead levels, well above the maximum limit allowed by the legislation. Pb contamination levels achieved after the following treatments: paper digestion in nitric acid, microwave treatment, DIN38414-54 method and TCLP method were $997 \mu\text{g g}^{-1}$, $189 \mu\text{g g}^{-1}$, $20.8 \mu\text{g g}^{-1}$, and $54.0 \mu\text{g g}^{-1}$, respectively. Flame atomic absorption spectrometry (FAAS) and inductively coupled plasma mass spectrometry (ICP-MS) were employed for lead determination according to the protocols of the applied methods. Lead contamination in used BKP was confirmed by scanning electron microscopy coupled with energy dispersive X-ray microanalysis (SEM-EDS). All the SEM imaging was carried out in the secondary electron mode (SE) and backscattered-electron mode (QBSD) following punctual X-ray fluorescence spectra. Soil contamination derived from this product revealed the urgent need of addressing this problem. These elevated Pb levels, show that a preliminary treatment of BKP is mandatory before it is disposed into the common trash. The high lead content of this material makes its direct dumping into the environment unwise.

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1. Introduction

Hazardous waste management has recently received considerable attention worldwide. Many governmental legislations have been adapted, in order to force both governmental and private organizations to take measures that shall improve waste handling. Healthcare waste is an extremely hazardous category since it poses both health and environmental hazards because they contain infectious agents; they are sharp, hazardous chemicals or pharmaceuticals; and they may be genotoxic or radioactive [1].

Dentistry is part of the healthcare services, and dental waste management is a sector that needs to be organized virtually from scratch around the world. Dental associations have long been requesting the handling of dental waste for various reasons. Firstly, dentistry involves a variety of materials that are infectious. Furthermore, these materials partially resemble some medical materials due to their use in patients' therapy and their contact with biological fluids. However, dentistry also involves certain compounds that

are not used in general medicine, some of which are extremely toxic, since they consist of heavy metals and other chemical combinations. Therefore, if not carefully handled, dental waste can introduce acute health hazards to citizens and dentistry personnel, as well as serious environmental impacts [2].

Intraoral dental film packaging and film packet components are a type of solid waste that is wrapped with a sheet of lead foil, which protects the film from backscattering and secondary irradiation [3]. There are also outer vinyl covers, paper packet covers, and interior black paper stiffeners. Recyclers may object to receiving such waste if they are combined with regular business paper. Around all the world dentists usually discard lead foil and other intraoral dental film components with together regular refuse, which is typically deposited in landfills [3,4].

Film packaging and film packet components of intraoral dental films should be segregated (Fig. 1). According to the manufacturer's instructions, the plastic end boards that are packaged with the intraoral packets should be discarded into the regular trash. The outermost layer of individual film packets is either vinyl or paper; the film contained inside rests between layers of black paper for added stiffness. Manufacturer's guidelines advise that outer vinyl covers, paper packet covers, and interior black paper stiffeners should be discarded with the regular trash [4].

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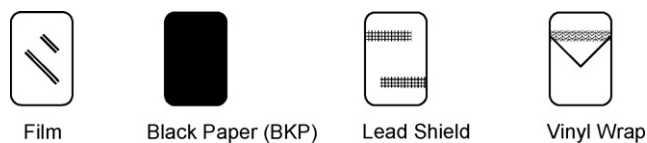


Fig. 1. Intraoral dental film components.

Intraoral films are applied in X-ray for complete examination of the dental structure, so that conditions not viewable upon clinical examination can be seen. This material is frequently used in dentistry, and the correct management and/or recycling of intraoral films is mandatory since its constituents may be damaging to the environment [5,6].

Lead is a heavy, bluish-gray metal with a low melting point. It occurs naturally in the Earth's crust, but it is rarely found in the metal form. Lead usually combines with two or more other elements, to form lead compounds. The main target of lead toxicity is the nervous system, both in adults and children. Long-term exposure of adults to lead at work has resulted in decreased performance in some tests that measure nervous system functions, apart from causing weakness in the fingers, wrists, and ankles. Lead exposure results in slight increases in the blood pressure, as well, particularly in middle-aged and older people, not to mention that it may also cause anemia. At high exposure levels, lead can severely damage the brain and kidneys of adults and children, ultimately causing death. In pregnant women, high lead exposure levels may result in miscarriage, while in men it can harm the organs responsible for sperm production [7].

The present scenario is the disposing of the waste generated from dental products like intraoral film residues. The increasing load of toxic metals causes a potential threat in terms of soil and groundwater contamination [8,9]. The current work investigates lead contamination generated from black paper recovering from intraoral films.

2. Experimental

2.1. Standards and reagents

All chemicals were analytical-reagent grade. Water purified in a milli-Q system was used throughout the entire analytical work. During the digestion and leaching procedures, acetic acid (J.T. Baker, USA), nitric acid (Synth, Brazil), and hydrogen peroxide (Fluka, Sweden) were employed. A stock standard Pb solution at 1000 mg L⁻¹ was prepared from high-purity Spex reagent (Edison, NJ, USA) PLK10-Pb [Pb(NO₃)₂] in 2% (v/v) nitric acid.

2.2. Sampling

The interior black paper stiffeners from new and used films (nBKP and uBKP, respectively) were obtained from the Radiology Clinics of the Dental School of Ribeirão Preto, University of São Paulo–FORP/USP. The size of the intraoral dental film used was Kodak Insight, size 2 (Eastman Kodak Co., Rochester, NY). Each studied sample consisted in three interior black paper stiffeners from films.

2.3. Acid digestion

For each studied nBKP and uBKP sample, three whole pieces of black paper stiffeners from films were used, corresponding to 1.52 g. Stainless steel scissors were used to cut the samples in order to forward the processing extractions. The samples were transferred into a flask (Pyrex, USA) and digested on a hot-plate at 40 °C by using 100 mL HNO₃ (50%) and 10 mL H₂O₂ (30%), for 24 h. The digested sample was filtered through Celab filters 80 G, and the volume was

made up to 150 mL with deionized water. The digested samples and blanks were diluted three times with deionized water, and the samples were then analyzed against an external calibration curve by flame atomic absorption spectrophotometer (FAAS).

2.4. Metal extraction tests

Three different extraction tests were used to ascertain lead lixiviation from BKP in a simple way. Two official tests were employed, namely, DIN and TCLP, which use inorganic extractants. The other extraction test comprised the submission of the sample to a microwave treatment, in order to mimic the currently employed procedure for nosocomial waste disposal.

2.4.1. Microwave (MW) treatment

To assess loss of the studied metal in the normal disposal procedure, BKP samples (whole piece) were submitted to MW energy with water.

BKP samples (1.52 g) were transferred to flasks (Pyrex), and 10 mL Milli-Q water was added to them. The system was placed inside the microwave oven, and microwave radiation was carried out for 4 min at 450 W. After a 5-min cooling period and addition of 10 mL Milli-Q water, microwave radiation was repeated for another 4 min. After cooling, the leached lead was diluted to 30 mL by adding a 0.1 mol L⁻¹ HNO₃ solution. The final solution was analyzed by FAAS for lead determination without dilution, against an external calibration curve. Blank digests were carried out using the same procedure.

2.4.2. DIN 38414eS4 test

The DIN 38414eS4 method (Official German DIN method, 1984) is a standard German method for the determination of metal leaching from solid wastes [10]. This method gives us the leachate contents of different elements after the waste has been in contact with water for a 24 h period. The method is simple and consists of placing 5 g of the material and 100 mL Milli-Q water into a vessel. A solid/water ratio of 1:20 was used instead of the recommended 1:10 ratio because our waste was completely solid. At a later stage, samples were rotated at 30 ± 2 rpm for 24 h in a rotatory agitator. Following the DIN procedure, pH and conductivity were measured after 15 min and after 24 h of agitation. Finally, the samples were vacuum filtered using a 0.45 mm membrane filter (Millipore), and the filtrate was kept at 4 °C until ICP-MS analysis.

2.4.3. TCLP leaching method

TCLP (US EPA method 1311, Environmental Protection Agency (EPA), 1992) [11] was performed using 3 g of each BKP fraction, which were placed in high density polyethylene (HDPE) extraction vessels. These vessels contained 60 mL (maintaining the 20:1 fluid/waste ratio as specified in the method) of the extractant fluid 2 (composition reported in TCLP 1311). The initial pH of the TCLP extraction fluid was 2.85 ± 0.05. We performed this test with two replicates. Samples were agitated at 30 ± 2 rpm for 18 ± 2 h in a rotatory agitator. After agitation, the final pH was measured. The TCLP leachates were filtered through 0.45 mm pore membrane filters. These final solutions were acidified to pH < 2 and stored at 4 °C. Lead analysis was carried out by ICP-MS.

2.5. Instrumental

2.5.1. Flame atomic absorption spectrometry

A Shimadzu (Japan) AA 680 flame atomic absorption spectrophotometer equipped with a deuterium-arc lamp background corrector was used for absorbance measurements at a wavelength of 217.00 nm for lead. Hollow Cathode Lamps (HCL) from Hamamatsu operating at 5.0 mA for Pb were employed. The operating conditions were those recommended by the manufacturer, unless

Table 1
ICP-MS operating conditions.

Perkin Elmer Elan DRC II	
Spray chamber	Cyclonic
Nebulizer	Meinhard®
RF power	1100 W
Nebulizer gas flow (optimized daily)	0.6–0.9 L min ⁻¹
Scan mode	Peak hopping
Resolution	0.7 a.m.u.
Replicate time	1 s
Dwell time	50 ms
Sweeps/reading	20
Integration time	1000 ms
Replicates	3
Isotope	²⁰⁸ Pb

specified otherwise. Replicate numbers in each analysis were equal to three.

2.5.2. Inductively coupled plasma mass spectrometry

A PE ELAN DRC II ICP-MS instrument (PerkinElmer, Norwalk, CT, USA) was used for Pb determination in the BKP extracts. This technique was employed according to the demands of the DIN and TCLP standard methods. Before any quantification measurements,

Table 2

Measured Pb concentration in uBKP samples by different methods. All measured values are the arithmetic average \pm standard deviation.

Method	Pb concentration ($\mu\text{g g}^{-1}$)	Pb concentration, as leachate (mg L^{-1})
Acid digestion ($n=9$)	997 ± 321	–
MW treatment ($n=9$)	189 ± 128	9.46 ± 6.48
DIN 38414eS4 test ($n=10$)	20.8 ± 0.4	1.04 ± 0.02
TCLP leaching ($n=6$)	54.0 ± 0.4	2.70 ± 0.01

The number in parenthesis is the number of uBKP employed.

instrumental parameters were optimized through daily performance. Typical daily instrumental parameters were RF power, Ar nebulizer gas flow, and lens voltage. The operational conditions are shown in Table 1.

2.5.3. Scanning electron microscopy (SEM)

New and used BKP were mounted on aluminum stubs using carbon double-sided tape, and coated with carbon. Samples were imaged and analyzed by a scanning electron microscope (ZEISS – EVO 50, Carl Zeiss, Cambridge, England) equipped with an EDS system (IXRF Systems 500 Digital Processing Si(Li) diode, Liechtenstein). The detector was used in the secondary electron mode (SE)

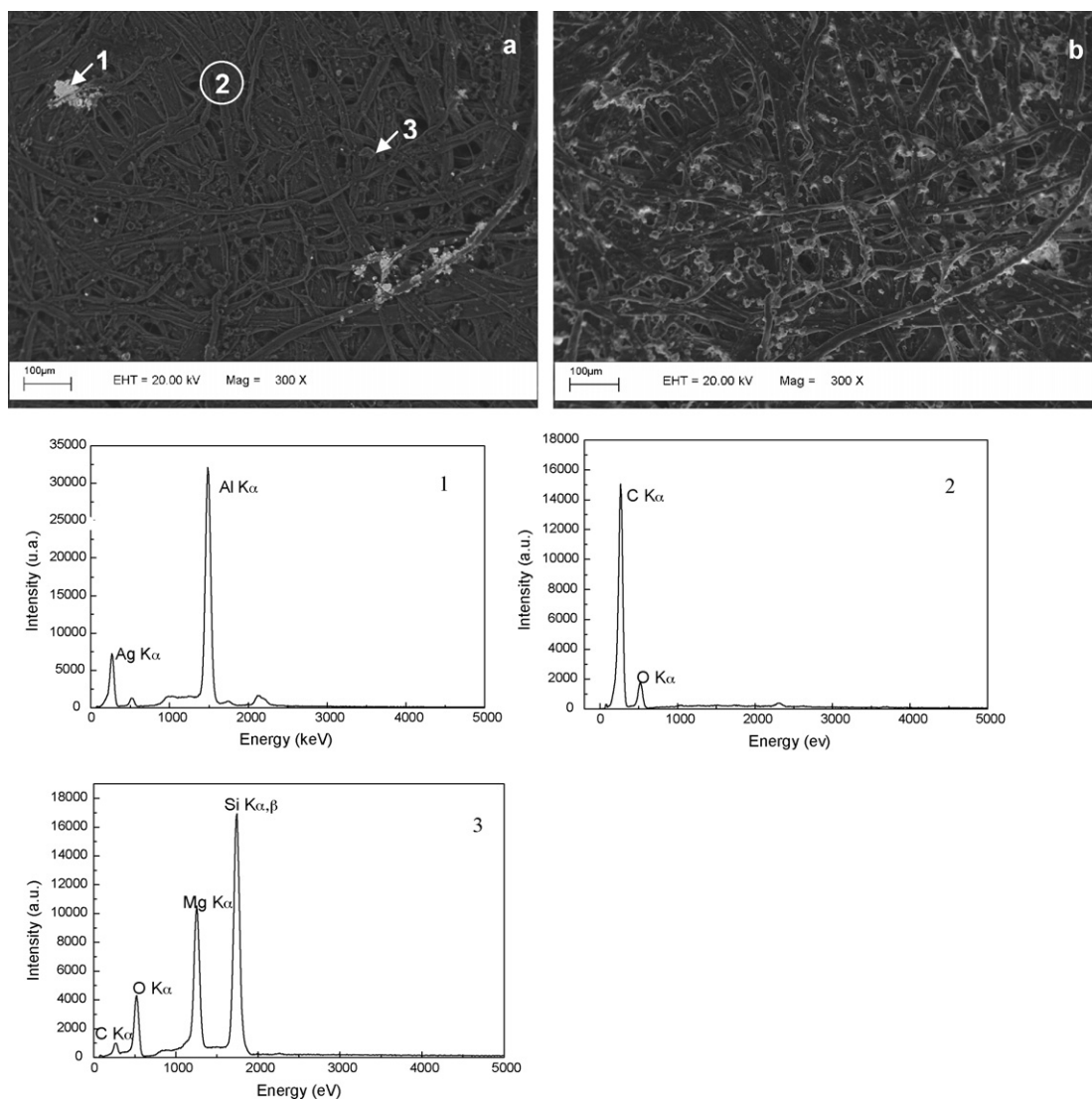


Fig. 2. Image of a new BKP by SEM-EDX in the backscattering electron (a), and secondary electron (b) mode. Punctual X-ray fluorescence spectra for the clear compound (1), dark fiber (2), and gray grain (3).

and backscattered-electron mode (QBSD). The chamber pressure was 10^{-5} Torr and the accelerating voltage was 20 kV.

A household microwave oven (Sharp, Brazil) was used for the secondary digestion of the papers.

A magnetic stirrer (Fisatom, Brazil), a hot-plate (Fisatom), and an orbital stirrer (Fisatom) were used for sample preparation.

3. Results and discussion

Table 2 shown the results for lead measurements in used BKP (used black paper) after acid digestion and the three others leaching methods employed in order to confirm the presence of Pb in uBKP.

3.1. Acid digestion

The first analysis consisted in the digestion of the sample with HNO_3 and H_2O_2 , and Pb determination by FAAS. The results clearly show high Pb values, $997 \pm 321 \mu\text{g g}^{-1}$ (range from 618 to $1404 \mu\text{g g}^{-1}$). A large quantity of this paper is currently disposed together with common waste, so this dangerous material needs to be treated. The Pb concentration was also measured in new black paper (nBKP), and the concentration obtained by FAAS was close to that found for the blank measurements.

3.2. Leaching tests

In a second analysis, uBKP received a combination of water and microwave heat, so as to reproduce the condition of nosocomial waste. The Pb values obtained in this kind of extraction were $189 \pm 128 \mu\text{g g}^{-1}$ (range 69.5 to $366 \mu\text{g g}^{-1}$) and $9.46 \pm 6.48 \text{ mg L}^{-1}$ as effluent. The high lead concentration in this waste makes its environmental risk clear. For this reason, the uBKP needs to be assessed for toxicity and leaching by employing the existing methodologies.

Because of the high Pb values found above, we decided to analyze the lead content in uBKP by means of two standardized labo-

Table 3
Analytical characteristics of the method.

Parameter	ICP-MS	F AAS
LODO	0.02 ng mL^{-1}	$0.2 \mu\text{g mL}^{-1}$
RSD (%)	1.9	1.0
R	0.9997	0.991
Linear range	$0\text{--}50 \mu\text{g L}^{-1}$	$0\text{--}20 \text{ mg L}^{-1}$

ratory protocols: the DIN 38414eS4 test and the TCLP leaching method.

The main objective of this test is to evaluate the environmental risk of the waste. The Pb value found via this test was $20.8 \pm 0.4 \mu\text{g g}^{-1}$ of leachate per dry mass, or 1.04 mg L^{-1} as effluent. The results are well above those of the official Brazilian regulations, CONAMA 357, where the maximum value allowed for lead as effluent is 0.5 mg L^{-1} . This value is also above the one established by different landfill regulations (European Directive 1999/31/EC; CONAMA) [12,13]. Lead concentration is one of the commonest concerns in such kinds of wastes, and the official limit value is commonly overpassed [14,15]. However, the uBKP used in the present work is largely over from the official limit value established for the DIN 38414eS4 test.

The TCLP test results for lead contamination were $54.0 \pm 0.4 \mu\text{g g}^{-1}$ of leachate per dry mass, or 2.70 mg L^{-1} as contaminant in solution. The overall objectives of the TCLP procedures differ from those of the DIN test in that they were designed to check the potential toxicity of wastes. This was evaluated through the use of different extractants to recover leachates from residues or wastes. The TCLP test was created to evaluate the toxicity of 39 compounds, and one of them is Pb. For these 39 compounds, the US EPA established a limit value (called NIPDWS), employed in the evaluation of the toxicity or non-toxicity of our wastes. Our results reveal that the variability of the data is a common aspect of TCLP tests and occurs among the different classes of grain size.

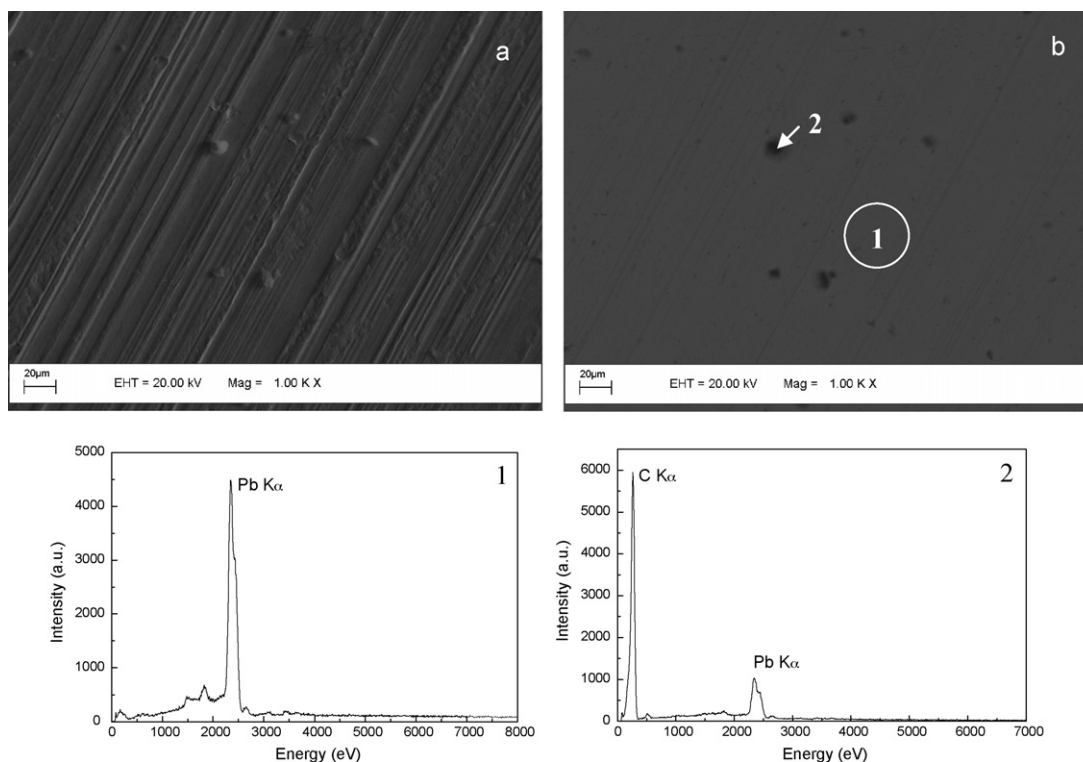


Fig. 3. Image of the lead shield by SEM-EDX in the secondary electron (a), and backscattering electron (b) mode. Punctual X-ray fluorescence spectra in (b) for the metallic surface (1) and dark forms (2).

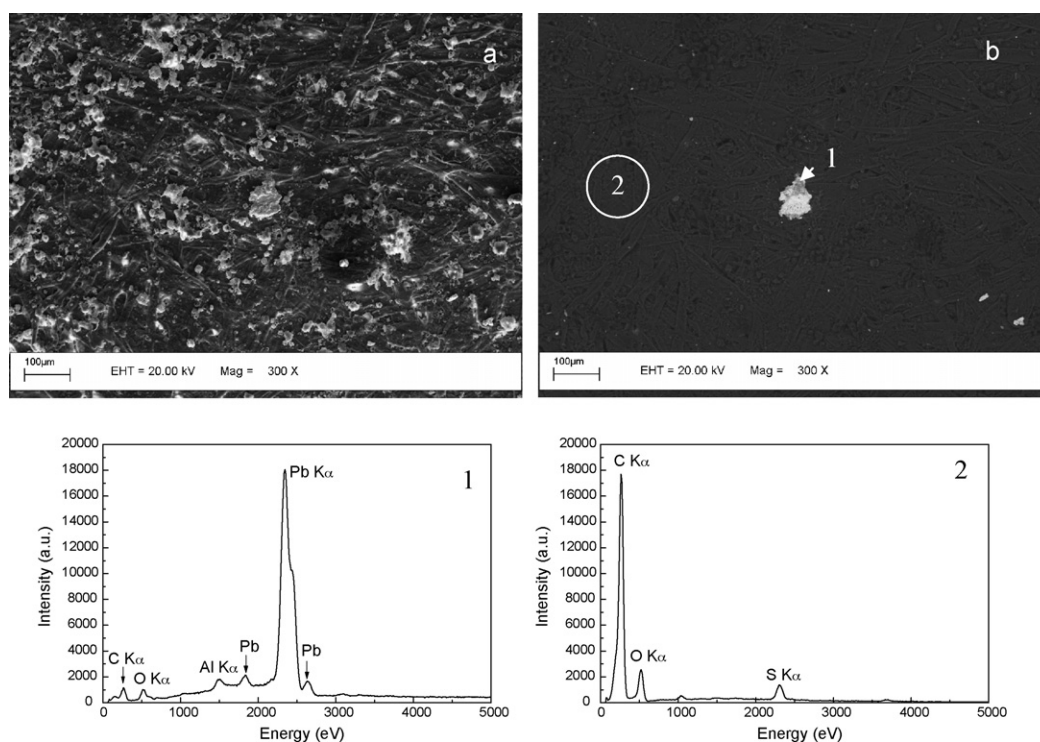


Fig. 4. Image of used BKP by SEM-EDX in the secondary electron (a), and backscattering electron (b) mode. Punctual X-ray fluorescence spectra in (b) for the lead fragment (1) and dark surface (2).

The NIPDWS (National Interim Primary Drinking Water Standards) value for Pb is 0.015 mg L^{-1} . The analyzed fractions gave TCLP data for Pb much higher than the threshold value. From the reported data for TCLP and DIN tests, it is noteworthy that changes in the pH of the solution in contact with uBKP can change the metal release by several orders of magnitude. The values obtained for the TCLP leachate metal content are very different from those reported in the case of the DIN tests.

3.3. Analytical Parameters

The method detection limits (LODs) obtained for Pb were $0.02 \text{ } \mu\text{g L}^{-1}$ for ICP-MS and 0.2 mg L^{-1} for FAAS (Table 3). The LOD was defined as the ratio of the three times the standard deviation of the blank ($n=10$) to the slope of the calibration curve. The correlation coefficients (R) of the calibration curves were better than 0.99. The relative standard deviations, RSDs, obtained

by the consecutive measurement of five sample solutions, were below 1.9%, demonstrating a good precision for such concentrations.

3.4. SEM-EDS analysis

All the SEM imaging was carried out in the secondary electron mode and backscattered-electron mode. In the latter mode, compounds with higher average atomic number appear brighter than those with lower average atomic numbers. Thus, the Pb metal appears brighter than Pb oxide, and heavy-metal compounds appear much brighter than matrix minerals, glasses, and fibers or organic materials. Punctual X-ray fluorescence spectra were performed as indicated in the image. Images in the secondary electron mode give us information about surface and topography, not phases, as in the case of the backscattered-electron mode.

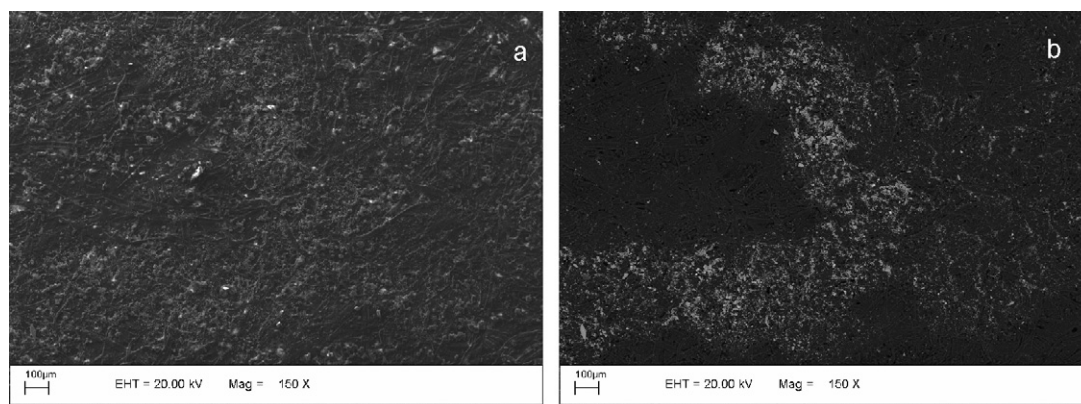


Fig. 5. Image of used BKP by SEM-EDX in the secondary electron (a), and backscattering electron (b) mode, employing a different magnitude (150 \times).

SEM-EDS images of a nBKP (Fig. 2) show that no lead was present in the nBKP sample before X-ray was performed. Only aluminum and silver (spectrum 1 in Fig. 2); carbon from recovery (spectrum 2 in Fig. 2); and silicon magnesium, carbon and oxygen present in the nBKP material (spectrum 3 in Fig. 2) were present.

In Fig. 3, SEM-EDS images show the lead shield in a nBKP. The metallic surface, as expected, contains lead only (spectrum 1 in Fig. 3) and some carbon fragments (spectrum 2 in Fig. 3).

SEM-EDS images obtained for the uBKP show that the integrity of the lead shield was not preserved (Fig. 4). Backscattered-electron images evidence lead contamination in the uBKP, seen as fragments (spectrum 1 in Fig. 4). Fig. 5 has a lower magnification, only 150 \times , and in it we can note lead distribution in the uBKP and confirm lead contamination after the film is used.

4. Conclusions

Used BKP samples were submitted to acid digestion and an elevated Pb concentration was found. For sake of comparison, three leaching tests have been accomplished in order to investigate Pb contamination in uBKP waste: TCLP (Toxicity Characteristic Leaching Procedure), DIN (Deutsches Institut für Normung – DIN 38414-S4), and microwave treatment.

These studies provide valuable information about the metal content in this waste, because all the results from the lixiviation tests indicate that BKP is harmful to the environment, causing contamination if discarded as common waste. The heavy metal concentration in the majority of the analyzed samples was above the prescribed limits set by authorities. SEM-EDS images confirmed lead as contaminant in uBKP, distributed heterogeneously as fragments.

Therefore, the studied wastes could be classified as hazardous according to Brazilian resolutions. For this reason, uBKP should be separated from the common waste and forwarded to appropriate centers for heavy metal recovery.

The findings of the present paper support the current transition from traditional intraoral film packets toward digital technology, which will avoid environment contamination with both lead and processing solutions (with high silver content).

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