Published in final edited form as:
Chem Res Toxicol. 2009 November ; 22(11): 1761–1764. doi:10.1021/tx900309c.

The Chemical Forms of Mercury in Aged and Fresh Dental Amalgam Surfaces

Graham N. George[†], **Satya P. Singh**[†], **Jay Hoover**[‡], and **Ingrid J. Pickering**[†]
Graham N. George: g.george@usask.ca
[†]Department of Geological Sciences, University of Saskatchewan, 114 Science Place, Saskatoon, Saskatchewan S7N 5E2, Canada
[‡]College of Dentistry, University of Saskatchewan, 105 Wiggins Road, Saskatoon, Saskatchewan S7N 5E4, Canada

Abstract

Mercury-containing dental amalgam is known to be a source of human exposure to mercury. We have explored the use of electron-yield Hg L_{III} X-ray absorption spectroscopy to characterize the chemical nature of dental amalgam surfaces. We find that the method is practical, and that it shows extensive mercury depletion in the surface of the aged amalgam with significant differences between old and fresh amalgam surfaces. Whereas the fresh amalgam gives spectra that are typical of metallic mercury, the aged amalgam is predominantly β-mercuric sulfide. The toxicological implications of these results are discussed.

Introduction

The use of mercury-based dental amalgam fillings as a dental restorative is a well established practice that was first introduced in France in 1826 (1). When correctly formulated, and neglecting any concerns related to toxicity, mercury dental amalgams present an almost ideal substance for restorative work, with easy installation, low creep, minimal dimensional change and high compressive strength. Typically amalgam fillings will out-last other restorative materials (2), and it has been estimated that the average American adult has seven mercury amalgam dental fillings, and while formulations vary, most modern amalgams have a typical final composition in the range of 40–50% Hg, 30–40% Ag, 5–15% Sn and smaller amounts of other metals including Cu and Zn or Pd. However, dental amalgam is also one of several sources of human exposure to potentially toxic mercury (3), and its disposal can also be a source of environmental mercury pollution (4). Because of this, in recent decades the use of mercury-containing dental amalgams has become controversial, and several countries including Sweden and Norway have recently banned its use (5). In North America the traditional view is that the advantages of mercury-containing amalgam outweighs any possible health risks (3) and for this reason mercury-containing dental amalgams are still widely used. Nevertheless, the debate continues and dentists are divided about whether the benefits outweigh the risks, or *vice versa*, and more research is needed to quantify and characterize mercury exposure from dental amalgam (6). A number of sources of human exposure are known, and these include evaporation of mercury from the surface of the filling and subsequent inhalation, and leaching of mercury into saliva, in which bacterial action may be involved. Other sources of mercury exposure have also been recently demonstrated, specifically, migration of mercury through the tooth dentinal tubules (6) from where it could enter the blood supply to the pulp.

One source of human exposure to mercury (7) from dental amalgam will be through the surface of the filling, and the chemical composition of the surface is therefore of interest. In this preliminary study we have used a surface sensitive spectroscopic tool – electron yield Hg

L_{III} X-ray absorption spectroscopy – to probe the chemical nature of mercury at the surface of fresh and exposed fillings. Information obtained from this study will assist in understanding released metal toxicological behavior at the molecular scale, and will provide much-needed insights into the potential hazards or otherwise of the use of dental amalgam.

Experimental Procedures

Sample Preparation

Fresh amalgam fillings were prepared using dental amalgam from a commercial capsule (Valliant PhD™ #1, Ivoclar Vivadent Inc., Amherst NY; amalgam of final weight composition Hg 47.9%, Ag 27.3%, Cu 9.1%, Sn 15.5%, Pd 0.2%) into a melamine replacement tooth (Model A5–200 typodont, Kilgore International, Inc. Coldwater MI). Drilling, installation of restorative and burnishing were performed exactly as if for human installation. The filling had a distinctive bright metallic luster. For the aged amalgam extracted molar teeth were obtained from the University of Saskatchewan Dental Clinic's Tooth bank. The tooth examined in this study was a mandibular second molar with a *mesio-occlusal* restoration, and had a discernible dark patina. The exact history and age of the restoration is unknown, but we estimate approximately 2 decades of exposure to normal aural conditions. The tooth was carefully washed with distilled water and allowed to dry in air. Teeth were mounted with conducting aluminum adhesive tape to the backplane of the electron yield detector, taking care to place a slight overlap with the edge of the amalgam filling in order to maintain electrical connectivity and to avoid sample charging artifacts (8). Chemicals were obtained from Sigma-Aldrich and were of the best quality available. Samples of Ag-Hg amalgam and Sn-Hg amalgam were prepared by allowing liquid elemental mercury to come in contact with a small piece of silver or tin metal foil (Goodfellow Metals, Huntingdon, UK) whereupon the mercury was quickly absorbed to form an amalgam containing approximately 50:50 mole-ratios of the two metals (established by weighing the samples). A sample of pure metallic mercury suitable for spectroscopic measurements was precipitated from aqueous $HgCl_2$ solution by reduction with a slight excess of sodium borohydride, which yielded a gray-milky solution which was then frozen prior to spectroscopic examination.

X-ray Absorption Spectroscopy

X-ray Absorption Spectroscopic (XAS) measurements were conducted at the Stanford Synchrotron Radiation Lightsource (SSRL) with the SPEAR storage ring containing between 160 and 200 mA at 3.0 GeV. Mercury L_{III}-edge data were collected on the structural molecular biology XAS beamline 7-3, employing a Si(220) double-crystal monochromator. Beamline 7-3 is equipped with a rhodium-coated vertical collimating mirror upstream of the monochromator, and harmonic rejection was accomplished by setting the cutoff angle of this mirror to 15 keV. Electron yield was detected using a helium-filled gas-amplification detector (EXAFS Co., Pioche Nevada) connected to a SR570 current to voltage amplifier (Stanford Research Systems Inc. Sunnyvale, California). Incident X-ray intensities were measured using a nitrogen-filled ionization chamber. All other spectra were measured by monitoring X-ray transmittance using nitrogen-filled ionization chambers. Spectra were energy-calibrated with reference to L_{III}-edge spectrum of Hg-Sn amalgam foil measured immediately following data collection, the lowest energy inflection of which was assumed to be 12285.0 eV. XAS data were processed using standard techniques and employing the EXAFSPAK program suite (9). Near-edge spectra were fitted to linear combinations of standard spectra using the EXAFSPAK program DATFIT which minimizes the sum of squares difference between the experimental and simulated data, as previously described (10).

Results and Discussion

X-ray absorption spectra (XAS) arise from excitation of a core electron (e.g. a 1s electron for a K-edge, or a $2p_{3/2}$ electron for an L_{III} edge). Such excitation creates a core-hole which relaxes via dipole-allowed decay of an outer electron with either the emission of an X-ray fluorescent photon or the emission of an Auger electron. XAS is commonly detected by one or more of three methods – transmittance, fluorescence yield, electron yield (11). Transmittance is conceptually simplest, and is recorded by monitoring the intensity of a monochromatic X-ray beam before and after the sample. Fluorescence yield detection monitors the X-ray fluorescence which (under ideal circumstances) is proportional to the X-ray absorption, and is the most sensitive method of detection. Electron yield monitors the X-ray induced electron emission, and because of the low electron path-length it is predominantly sensitive to the top 20–30 Å of the sample. It therefore constitutes a surface-sensitive probe, and is well suited to our purposes of characterizing amalgam filling surfaces.

XAS can be arbitrarily divided into two overlapping regions – the near-edge spectrum which is the structured region within approximately 50 eV of the absorption edge, and the extended X-ray absorption fine structure (EXAFS) which is an oscillatory modulation of the absorption on the high-energy side of the absorption edge and which can be interpreted in terms of a local radial structure. Near-edge spectra are comprised of transitions from the core level (1s for a K-edge) to unoccupied molecular orbitals of the system. Intense transitions are dipole-allowed $\Delta l=\pm 1$, and thus for K and L_{III} edges are to levels containing predominantly *p* and *d* orbital character, respectively. Near-edge spectra are therefore sensitive to electronic structure, and give a fingerprint of the chemical species of the metal or metalloid concerned. The advantage of the near-edge region of the spectrum is that it can be collected relatively quickly with good signal to noise. In contrast, EXAFS is more challenging to collect with adequate signal to noise, and may not be practical on dilute samples. A unique benefit of XAS is that it requires no pre-treatment or extraction, and thus provides a tool that can probe chemical species *in situ*, although a disadvantage of electron yield detection is that it cannot be used with wet samples as a film of water would essentially eliminate the electron yield signal.

Figure 1 compares the Hg L_{III} near-edge spectra of a series of solid standard compounds. As we have discussed previously (10), differences between Hg L_{III} spectra are more subtle than other near-edge spectra. With K-edges the valence orbitals have substantial *p*-orbital character, giving rise to intense dipole-allowed transitions and rich chemical variability. In contrast, for Hg L_{III} edges the dipole allowed transitions will be to orbitals with *d*-character transitions and as a result there is a more subtle variability between the spectra. The consequence of this is that data of significantly better signal to noise (when measured relative to the edge jump) are required for Hg than for K-edge spectra, but the spectra can nevertheless give the desired information.

Figure 2 compares the electron yield Hg L_{III} near-edge spectra of fresh and aged amalgam fillings. The quantity of the element of interest (in this case Hg) is, to a first approximation, proportional to the edge-jump which is essentially the difference in signal just below and above absorption edge. The edge-jump is accurately estimated by our background subtraction procedures, and is used for normalization of the data. The electron yield edge-jump of the aged amalgam filling was observed to be only 5% that of the fresh filling, suggesting that the surface material of the aged filling is substantially depleted in mercury, having lost up to 95% of its mercury. We note that part of the reason for the decrease in signal strength may be due to a lowering of the surface conductivity resulting from chemical changes at the surface, or changes in the electron path length (12) and the value of 95% for mercury surface depletion should thus be considered an upper bound. Dental amalgam is known to lose mercury both by evaporation of mercury vapor and by leaching of mercury into saliva (3). Some extent of surface mercury

depletion is therefore expected, although this is normally difficult to quantify. The spectrum of the fresh filling appears metallic in nature, but is distinct from those of elemental Hg, Hg-Ag amalgam, and Hg-Sn amalgam. Examination of the EXAFS data (not illustrated) indicates predominantly metal-metal contacts, consistent with a metallic surface for the freshly prepared filling. Structural examination of the fresh amalgam surface structure by analysis of the EXAFS will be the subject of future investigations. The spectrum of the aged filling (Figure 2) shows subtle but significant differences from that of the fresh filling. A systematic comparison of the aged amalgam spectrum with those of model compounds shows a striking resemblance to the spectrum of β-HgS. Quantitative analysis using linear combination fitting (10) gave excellent fits with 82% β-HgS and 18% fresh amalgam (Figure 3).

β-HgS, otherwise known as metacinnabar, is the common black mercuric sulfide made by precipitation of soluble Hg(II) salts with H_2S. It is one of two common polymorphs of mercuric sulfide, the other being α-HgS, otherwise known as red-HgS or cinnabar (13). The α-HgS polymorph has mercury coordinated by two sulfides in infinite chains, whereas β-HgS adopts the zincblende structure, with the metal bound to four sulfides in a three-dimensional lattice. It is less stable than α-HgS, converting with time into the red polymorph, but trace quantities of other elements such as iron stabilize the black form (14). β-HgS is highly insoluble with a molar solubility product of $10^{-36.4}$ (15). It is also resistant to attack by acids and bases, and compared to other mercury compounds has substantially reduced bio-availability. While β-HgS has not been extensively studied, the other common polymorph α-HgS, has been the subject of a number of studies. The traditional pigment known as vermilion is finely divided α-HgS, and this is commonly found in red tattoo ink which can precipitate severe allergic reaction especially following laser removal of tattoos (16), possibly as a result of photochemical degradation of the α-HgS (16). Moreover, α-HgS in the form of cinnabar is a component of traditional Chinese medicine and is widely used in Asia as a component of infant sedatives (17). Recent work has shown that α-HgS may be absorbed in the gastrointestinal tract and distributed in the tissues (18), and can cause cytotoxic reactions in cell cultures, with DNA fragmentation implying the generation of reactive oxygen species (17). Nevertheless, compared to other mercury species α-HgS is relatively benign, and this is best illustrated by the dose administered in traditional Chinese medical preparations which can be as much as 1.9 grams per person per day (17). While β-HgS has a somewhat different chemistry (13), it is sufficiently similar that we might expect its properties to be similarly benign, at least relative to other more toxic mercury species (7).

The environment to which dental restoratives are exposed is both varied and reasonably extreme. Ingestion of hot drinks such as coffee (19), for example, would cause exposure to sulfur-containing flavor molecules and moderately high temperature (e.g. 70 °C). Ingestion of small quantities of sulfides such as H_2S in food is common (20), and reaction with oxidized Hg(II)-containing amalgam surfaces would directly yield β-HgS. It also seems plausible that organo-sulfur-containing foodstuffs such as coffee (19) or plants such as onion and garlic (21) might react with the surface of mercury-containing dental restoratives yielding complex products that would degrade to eventually yield β-HgS. The mouth contains a rich bacterial flora with hundreds of different species that can associate to form bio-films (22), and a further possibility is that bacterial action could also result in formation of β-HgS from metallic mercury in the amalgam. Conversion from the elemental to mercuric forms, suggested to be mercuric sulfide, has been previously observed by Harris et al. (6) for mercury found in the dentinal tubules adjacent to an amalgam filling, and these workers suggested that reaction of Hg with sulfides present in the organic contents of the tubules might be responsible. It is interesting to note that there is no significant exposure to foods or bacteria in the dentinal tubules, so if HgS is indeed present at this location then neither of these potential sources is likely to play a role. Whatever the origin, due to the bio-unavailability of β-HgS, loss of particulates from the surface

of dental restoratives by teeth grinding, or by polishing during dental cleaning is unlikely to cause any toxic effects.

In summary, the use of electron yield Hg L_{III} XAS reveals the formation of β-HgS on the surface of an aged dental amalgam restorative a chemical form which is bio-unavailable and unlikely to pose a toxic hazard. Of greater concern, perhaps, is the nature of the surface mercury that has been lost from the amalgam, estimated here to be up to 95% of that of a fresh filling. Possibly this missing mercury is in the form of β-HgS abraded from the surface of the filling, or alternatively it predominantly corresponds to mercury lost prior to formation of β-HgS by the established mechanisms discussed above. Whatever the cause, human exposure to mercury lost from fillings is still of concern. While this depletion has been extensively studied with many insightful and elegant studies, none of the previous work uses techniques that can directly address the chemistry or the surface of the system. The feasibility of electron yield Hg L_{III} XAS opens up a number of possible areas for research, including investigation of changes in surface chemistry due to dental hygiene products containing peroxides or other strong oxidizers, the effects of exposure to cigarette smoke, and exposure to various foodstuffs. Such studies combined with the extensive information already available, could shed light on the various chemical mechanisms of mercury loss from dental amalgam fillings.

Acknowledgments

This work was supported by a grant from the Canadian Institutes of Health Research. Research at the University of Saskatchewan was supported by Canada Research Chair awards (to GNG and IJP), the University of Saskatchewan, the Province of Saskatchewan, the National Institutes of Health, and the Natural Sciences and Engineering Research Council (Canada). Portions of this work were also carried out at the Stanford Synchrotron Radiation Lightsource which is funded by the U.S. Department of Energy, Office of Basic Energy Sciences and Office of Biological and Environmental Sciences, and by the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program. We thank members of the George/Pickering research group for contributions to data collection.

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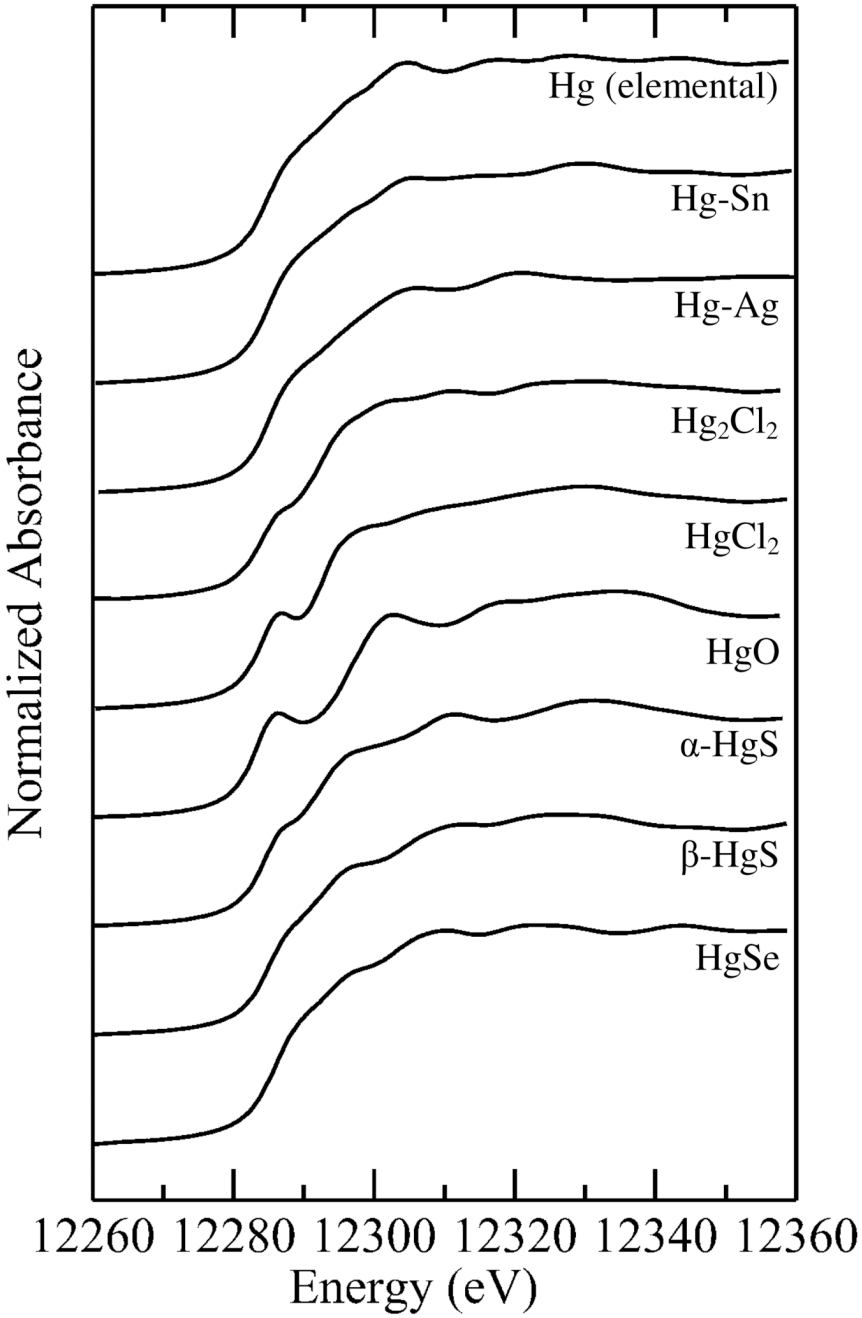

Figure 1.
Comparison of Hg L_{III} near-edge spectra of selected solid standard species. All spectra are normalized with respect to the edge jump.

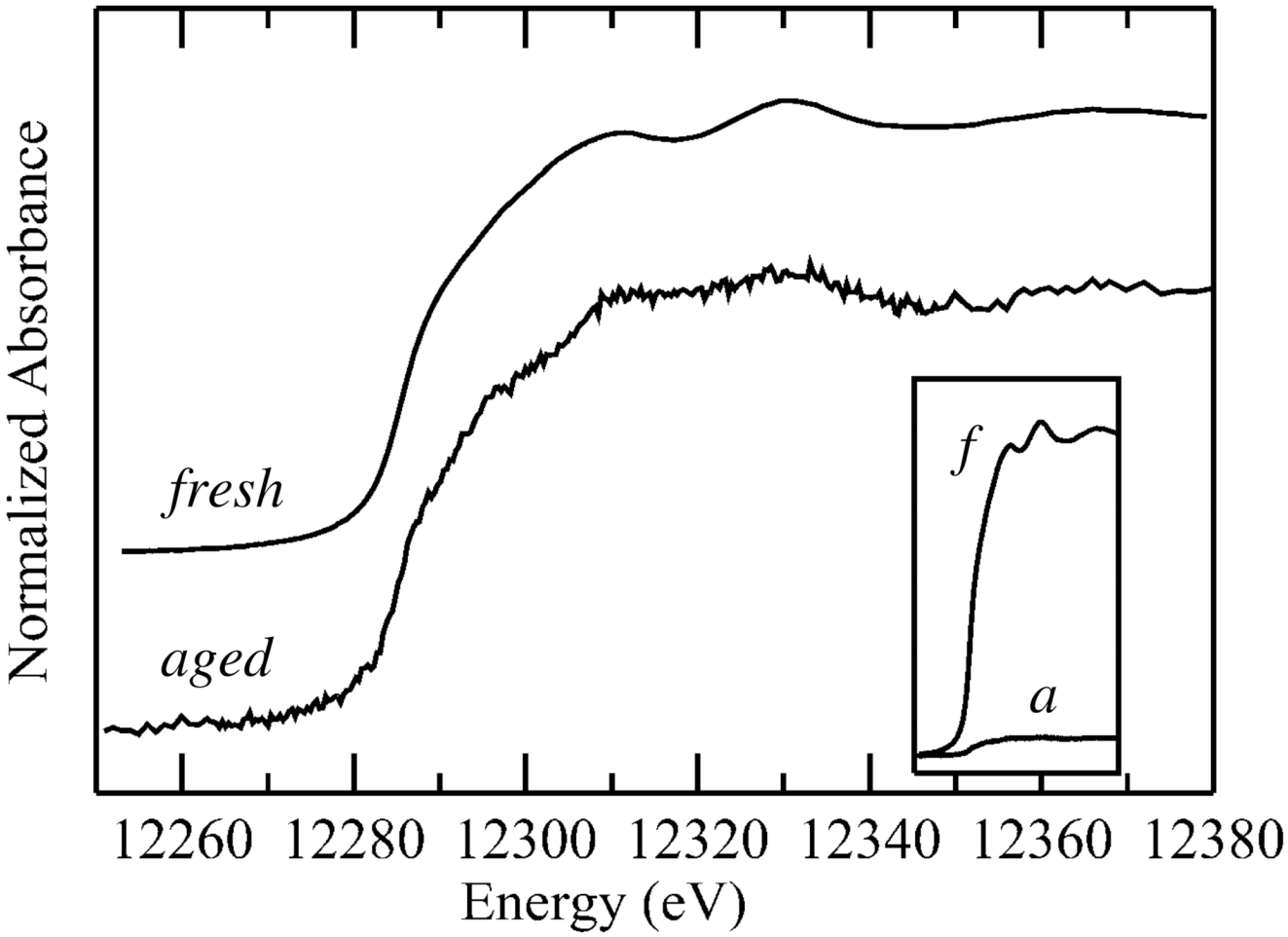

Figure 2.

Mercury L_{III} near-edge spectrum of aged dental amalgam compared with fresh dental amalgam. Spectra are normalized with respect to the edge jump. The inset shows the un-normalized spectra over the same abscissa range, illustrating the significantly smaller signal from the aged dental amalgam (*a*) when compared with the fresh dental amalgam (*f*).

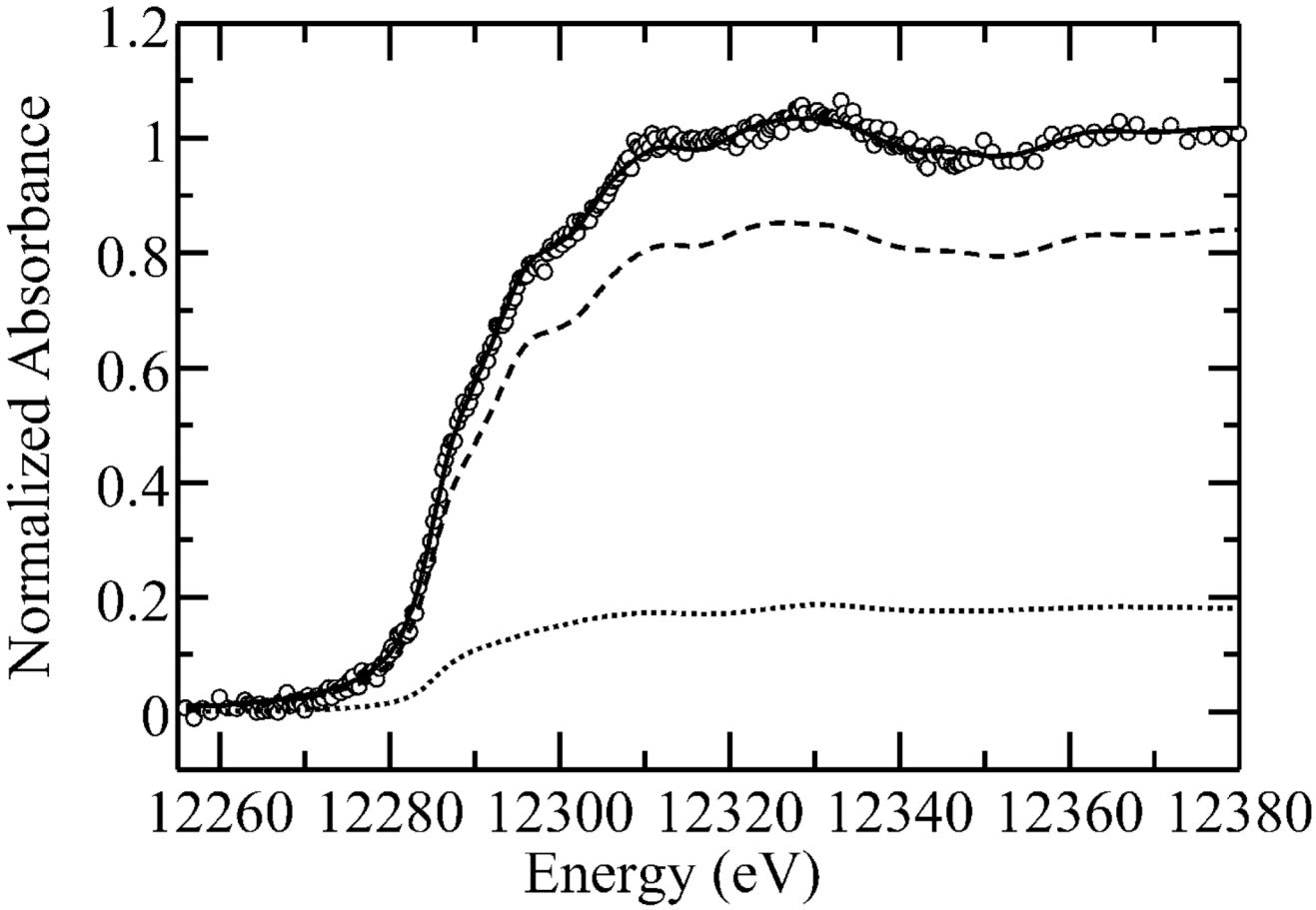

Figure 3.

Mercury L_{III} near-edge spectrum of aged dental amalgam (points) compared with a least squares fit from a linear combination of model compound spectra (———). The two components are plotted below for comparison. The best fit was obtained with 82±4% β-HgS (- - - - - -) and 18±4%, fresh amalgam (.....). The errors are estimated standard deviations obtained from the diagonal elements of the covariance matrix.