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Rapid Analysis of Metallic Dental Restorations using X-ray Scanning Analytical Microscopy

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Abstract

X-ray scanning analytical microscopy (XSAM) makes it possible to analyze small specimens in air without pretreatment. The purpose of this study was to utilize XSAM for rapid analysis of metallic dental restorations by microsampling. Six different dental alloys were scratched with brand-new silicone points to obtain metal on the silicone point for compositional analysis. The major components of the six dental metals, except for palladium, were clearly detected. The identification of palladium was difficult since the fluorescent X-ray of palladium is quite close to that of rhodium, which is the source metal of incident X-rays. But, palladium was also identified with a slight modification of XSAM. The total time required for sampling and analysis with XSAM was less than ten minutes. The amount of attached metal was estimated less than 30μg. This amount of sampling does not damage the metal restorations. Therefore, XSAM analysis with the microsampling technique is useful for the rapid analysis of metallic restorations.

Key words: X-ray scanning analytical microscope, elemental analysis, fluorescent X-ray analysis, dental alloy

Introduction

In recent years, allergies related to dental restorations have been a matter of concern [1 -3]. For the identification of allergens, patch testing using diluted aqueous solutions and petr olatum of metal salts and composition analysis of metallic restorations are employed. In orde r to avoid functional damage to metal restorations set in the oral cavity during the analysis, method for analyzing metal restoration without removal and damaging is required. The micr osampling method uses a silicone point and disk, and compositional analysis using X-ray ph otoelectron spectrometry (XPS) [4-6]. This method makes it possible to analyze metallic rest orations with little damage. The X-ray fluorescence spectrometer is also used for similar met al analysis [7-9].

The recently developed X-ray scanning analytical microscope (XSAM) enables elemen tal mapping analysis for Na to U by energy-dispersed fluorescent X-ray spectra in air without pre-treatment. XSAM makes it possible to obtain elemental mapping images and high-resolu tion X-ray transmission images [10]. The analysis is carried out in air without pretreatment e ven if it contains water, unlike electron probe microanalysis (EPMA) and energy dispersed s pectrometry (EDS) in electron microscopy which require a vacuum and electro-conductive c oating. This feature is appropriate for biological specimens. The authors previously reported the application of elemental mapping analysis by XSAM for unstained soft tissue [11-13]. W ith a XSAM it is also possible to analyze the desired position of the specimen by monitoring with a CCD (charge-coupled device) camera. Using the microsampling technique with the si licone point, elemental analysis of the sampled point was performed simply by setting the sa mple in the appropriate position in a specimen chamber, aiming at the metal-attached point o n the monitor and analyzing it for a few minutes. Since the whole procedure can be finished in a shorter period than for the other methods mentioned above, it is very easy and suitable f or the rapid analysis of the metallic restorations. Watanabe et al. [14] reported that quantitati ve analysis of metallic restorations could be carried from trace sample using XSAM and a sc raping technique.

In this study, the fluorescence X-ray spectra from the dental metals obtained by XSAM were estimated with the aim of applying XSAM for the rapid analysis of metallic restoration s by using microsampling.

Materials and Methods

1. Sample preparation

Six different dental alloys were tested. The compositions of the alloys tested are shown in Table 1. Alloys except for amalgam were used as received. Amalgam was mixed and kept in dry air at room temperature for more than 5 years. Brand-new silicone points (type M, Shofu Inc., Japan) were used for the sampling of metal specimens. Metal specimens were scratched with silicone points for 2, 5 or 10 seconds at low revolution (approximately 1000rpm) and pressure (less than 10gf) for attachment onto the silicone point. One sample was prepared for each metal specimen.

To evaluate the amount of attached metal, pure copper plate (as received) was polished under the same conditions. Silicone points with pure copper were dipped into 2ml of 10% HCl aq. to dissolve the attached copper. The solutions were diluted to 25ml and the concentrations were quantitated with inductively coupled plasma (ICP) analysis (P-4010, Hitachi Co. Ltd., Japan). The amount of attached copper was estimated from the concentration and volume of the solution.

2. XSAM analysis

Both metal attached and brand-new silicone points were analyzed by XSAM (XGT-2000V, Horiba Co. Ltd., Japan). Incident X-rays were generated from a rhodium cathode irradiated by electrons at 50kV, 1mA. The X-ray guide tube (XGT) diameter, which is equal to the X-ray beam size, was 100μmϕ in this experiment. The parts to which metal was attached were a different color from the other parts of the silicone point, therefore it was easy to aim the camera of XSAM at the metal. The fluorescent spectra were measured for 100 seconds for each part and one specimen was analyzed once. In the same position, a silicone point without attached metal was also analyzed to remove the background fluorescent X-rays originating from the silicone point.

Results

Metal particle attachment was easily confirmed by the change in color. The following fluorescence X-ray spectra measurements were made using metal-attached parts. The amounts of attached metal estimated using pure copper were 10, 30 and 90μg for 2, 5 and 10 second sampling, respectively. The reason why pure copper was used for this estimation instead of dental alloys was that pure copper was easily dissolved in acid.

Fig.1 shows the fluorescence X-ray spectra of a silicone point polished for 5 seconds on gold alloy (Protor3) and an unused point. Silicon (Kα=1.74keV) and titanium (Kα=4.51keV) derived from the silicone point were observed with background spectra (Fig.1a and b). In the background, rhodium K and L peaks (Kα=20.15keV and Lα=2.70) from the rhodium cathode of the X-ray tube were clearly observed. To differentiate only the fluorescent X-ray spectrum of the metal, the spectra obtained from the silicone point were subtracted. The silicon Kα, titanium Kα, rhodium Kα and Lα peaks were used as standards for the background subtraction. After background subtraction, gold, silver and copper peaks were clearly observed (Fig.1c). Below, spectra after subtraction treatment are shown.

Fig.2 shows the sampling time of dependence of fluorescent X-ray spectra in gold alloy (Protor 3) . The fluorescent X-ray increased with sampling time from 2 to 5 seconds. However, there was very little change in the increase from 5 to 10 seconds. This meant that a sufficiently thick gold alloy layer was formed on the silicone point with 5-second scratching. Scratching longer than 5 seconds would form a thicker layer. However, the thickness would be larger than the thickness necessary for fluorescence X-ray analysis. Therefore, the following measurements were performed with 5-second scratched specimens.

The spectra of tested base metal alloys are shown in Fig. 3. All components of the silver alloy, Ni-Cr alloy and major components of amalgam (except for Zn) were clearly detected. For the silver alloy, the peak assigned for silver was well separated from the background derived from rhodium. The zinc in amalgam was not identified because of its low concentration (1 atomic percent).

The spectra of tested noble alloys after background subtraction are shown in Fig. 4. The major components, e.g. gold, silver and copper, were clearly observed. In the spectrum of Protor 3, gold, silver, copper and zinc but not palladium, were identified on the spectrum. The platinum was not identified because of its low concentration (1.8 atomic percent). In the spectrum of Au-Ag-Pd alloy (New gold-palladium), the palladium Lα peak (2.84keV) was observed in the low energy side of silver Lα peaks (2.96keV). However, the palladium Lα peak was quite close to the rhodium Lα peak (2.70keV) and the same as the rhodium Lβ peak (2.84keV). Thus, the Lα peak of palladium was strongly affected by that of rhodium. Therefore, differentiation of the palladium peak from the background was difficult. The silver Lα peak was also affected by rhodium, but the peak position was slightly different from that of rhodium. Thus, silver could be identified.

Discussion

Elemental analysis of six dental alloys was successfully performed by XSAM with a sampling technique using a silicone point. As shown in Fig. 1, 5-second scratching was sufficient to obtain samples for analysis. With 5-second polishing we got about 30μg of copper. Scratching more than 5 seconds would result in a thicker layer. However, fluorescence X-rays generated in the deeper part would be absorbed in the specimen itself and could not emerge from the specimen surface. Therefore, a thicker metal layer would not contribute to an increase of the fluorescent X-ray intensity..

The major components of six dental metals, except for palladium, were clearly detected. The fluorescent X-ray of the palladium Lα peak (2.84keV) was quite close to that of the rhodium Lα peak (2.70keV) and the same as that of Lβ (2.84keV). Since the X-ray source in XSAM uses rhodium as the target, the incident X-ray includes the fluorescent X-ray from the rhodium target. Therefore the identification of palladium is difficult. In the ordinary conditions of the XSAM apparatus used (XGT-2000V), the detection limit of fluorescent X-rays is 20keV. Thus, K lines of rhodium and palladium are not detected. But, by changing the internal setting, the measurement range of fluorescent X-rays could be widened from 0-20keV to 0-40keV. Then, the K lines regions of Rh, Pd and Ag could be detected. Fig.5 shows the measured spectra of the background, silver alloy and Au-Ag-Pd alloy in the K and L lines regions of Rh, Pd and Ag. In the L line region, Ag Lα is appeared as a individual peak and easily be identified. However, Pd Lα is slightly appeared nearby Ag Lα peak and acculate differentiation of Pd Lα is difficult. In the K line region, each peaks of Rh, Pd and Ag is identified as a individual peak. Thus, palladium could be identified by measureing the K line region with a slight modification of XSAM.

The minor components of less than few atomic percent could not be identified. This seemed to be the limit of the analysis in the present method. The detection limit of XPS analysis with microsampling was reported to be 1 or 2% [5]. Therefore the sensitivity of the present method is considered to be similar to that of the XPS method. The sample setting and positioning in XSAM could be finished in a few minutes. The total time required for analysis was less than ten minutes. In contrast, the XPS method requires about 30 to 40 minutes from specimen setting to analysis. XSAM analysis can be carried out in atomospheric conditions and specimen setting is quite easy. Therefore, the required analysis time is shorter in the present method. The loss of restorations is estimated to be less than 30μg for pure copper. The Vickers hardness number (VHN) of the tested copper plate was estimated to be 55. The VHNs of typical dental alloys were reported to be 80-270 for noble metals and 175-357 for base metals [15]. Ordinary dental alloys are harder than pure copper, therefore, the amount of sampling was assumed to be lower than 30μg. This amount of sampling would not disturb the normal usage of metal restorations.

In the present study, a silicone point containing silicon and titanium oxide was used for metal sampling. Thus, silicon and titanium in the metallic restorations could not be identified. Using a white point containing potassium, aluminium and silicon, it will be possible to identify the titanium in the metallic restorations. Watanabe et al.[14] was reported the quantitative analysis of metallic restorations using a method and equipment similar to those used in this study. In this study, the fluorescent X-ray spectra from the microsampled metallic restorations were estimated from the spectral study and the possibility of the detection of metallic components was discussed. Most of the major components of six different dental alloys were detected. Palladium was also identified with a slight modification of XSAM. Thus, XSAM anal

ysis using a microsampling method is considered to be very easy and useful for identification of dental alloys.

Acknowledgments

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Table 1 Compositions of alloys tested (atomic per cent)

Product name (Lot number)	System	Au	Pd	Pt	Ag	Cu	Sn	Zn	Ni	Cr	Hg
New gold-palladium* (0802039)	Au-Ag-Pd	6.3	19.6	——	46.2	27.8	——	——	——	——	——
18k Gold*	gold alloy	55.8	——	——	12.2	32.0	——	——	——	——	——
Protor 3¶ (27697)	gold alloy	48.9	5.2	1.8	15.5	23.3	——	5.4	——	——	——
Betalloy§	Ni-Cr alloy	——	——	——	——	16.1	——	——	71.1	12.8	——
Milosilver# (040951)	Silver alloy	——	——	——	60.1	——	16.8	23.1	——	——	——
Dispersalloy & (8I-710)	Amalgam	——	——	——	43.0	12.5	10.1	1.0	——	——	33.4

* Ishifuku Metal Co. (Tokyo, Japan)   ¶ Cendres & Metaux SA (Biel-Bienne, Switzerland)

§ Yata Dental MFG. (Osaka, Japan)   # GC Corporation (Tokyo, Japan)

& Dentsply (Pennsylvania, U.S.A.)

Figure captions

Fig.1   The fluorescence X-ray spectra of a gold alloy-attached silicone point (a), unused silicone point (b) and processed spectrum (c)

Fig.2   The effect of sampling time of gold alloy on fluorescence X-ray spectra.

Fig.3   The fluorescence X-ray spectra of tested base metal alloys.

Fig.4   The fluorescence X-ray spectra of tested noble alloys.

Fig.5   The K and L lines of Rh, Pd and Ag in the fluorescence X-ray spectra of the back ground (a), silver alloy (b) and Au-Ag-Pd alloy (c).
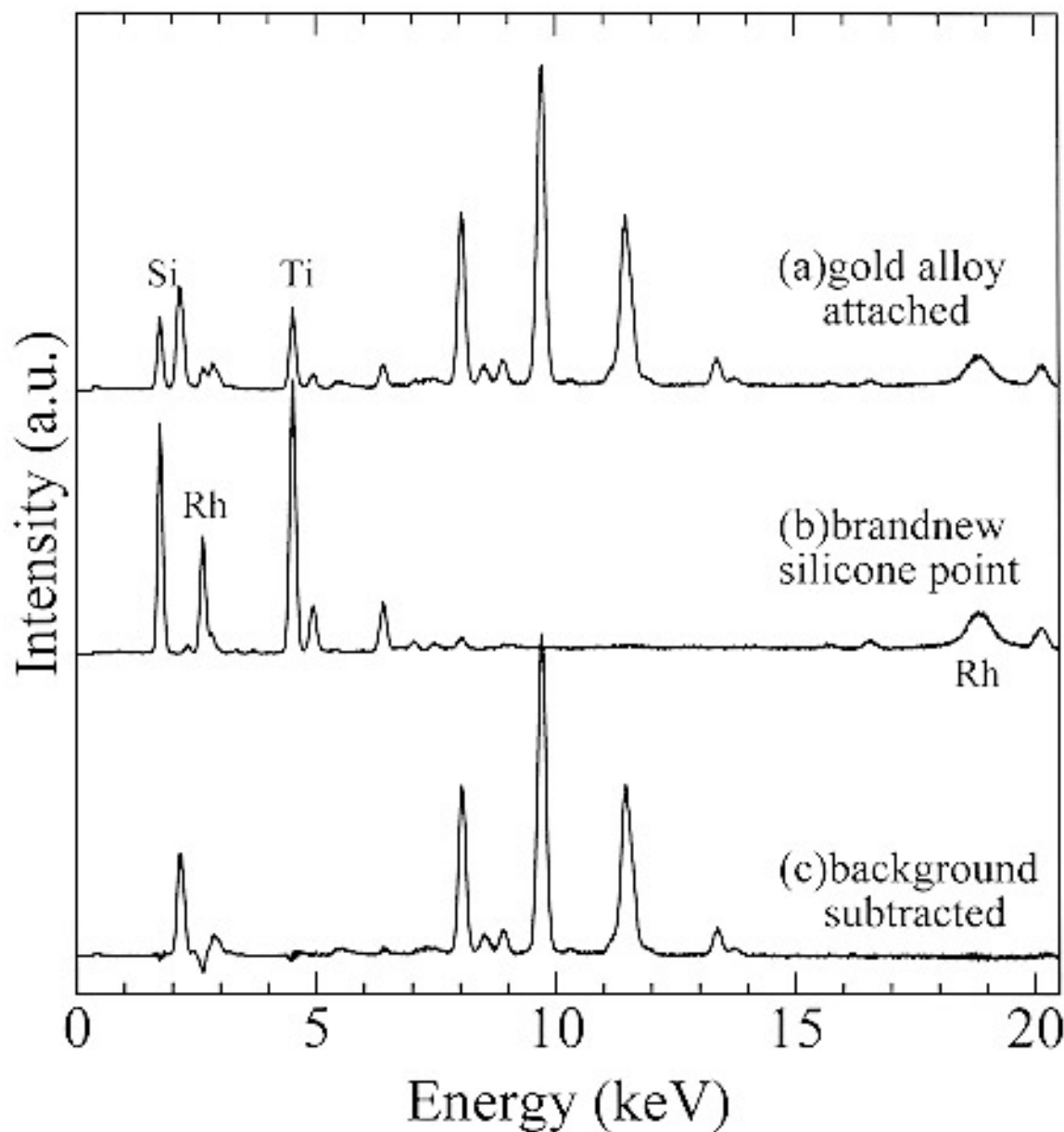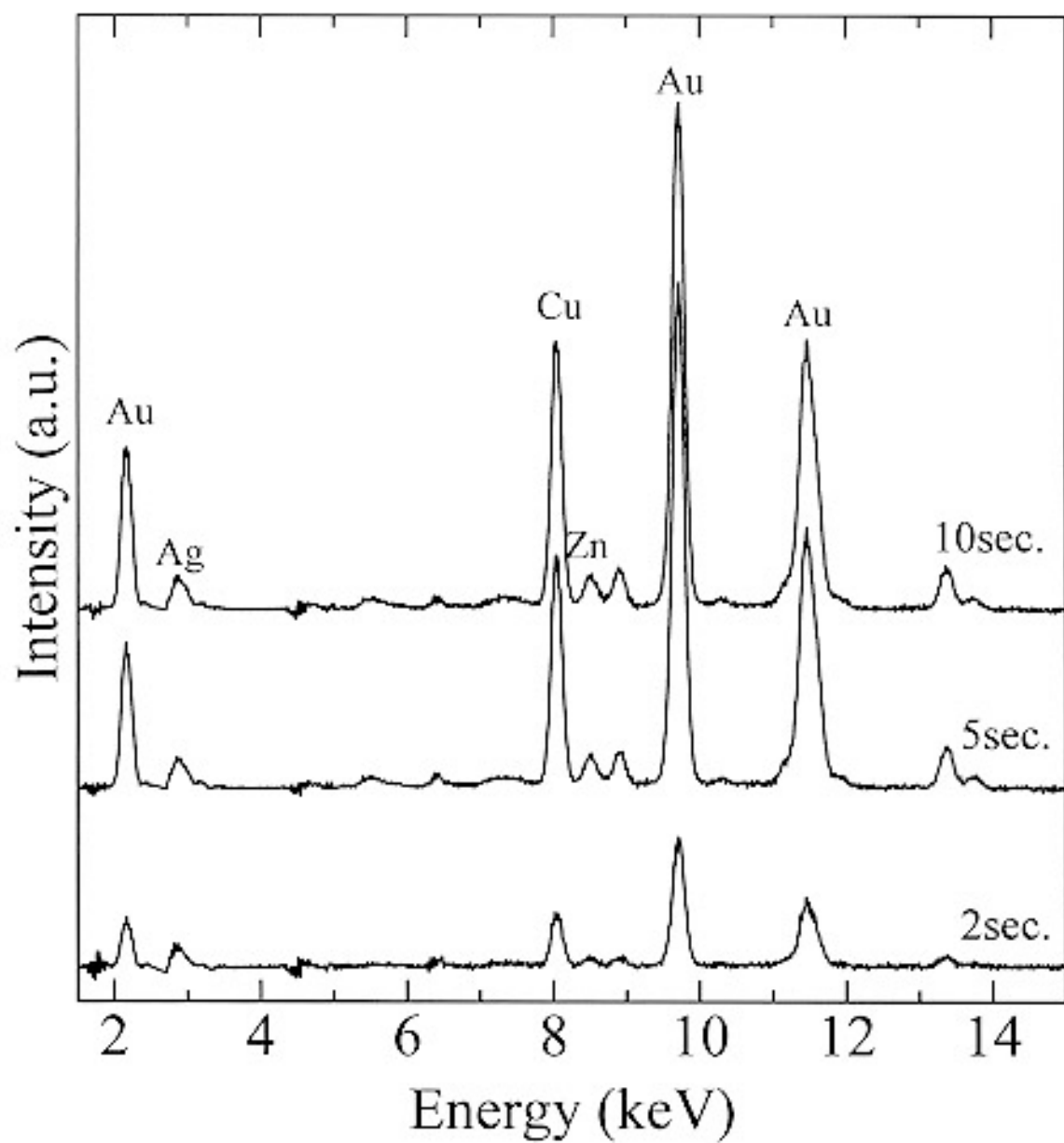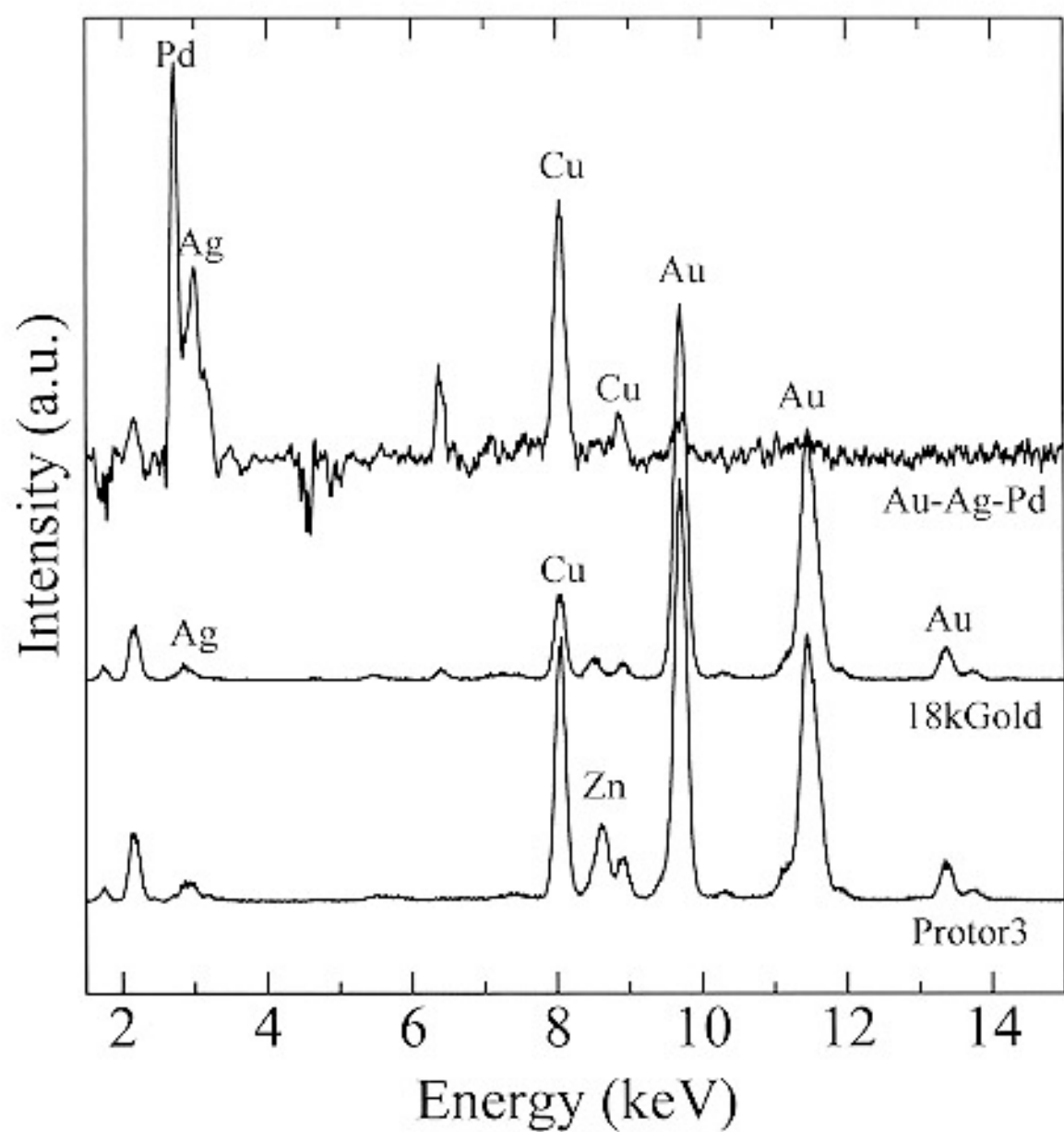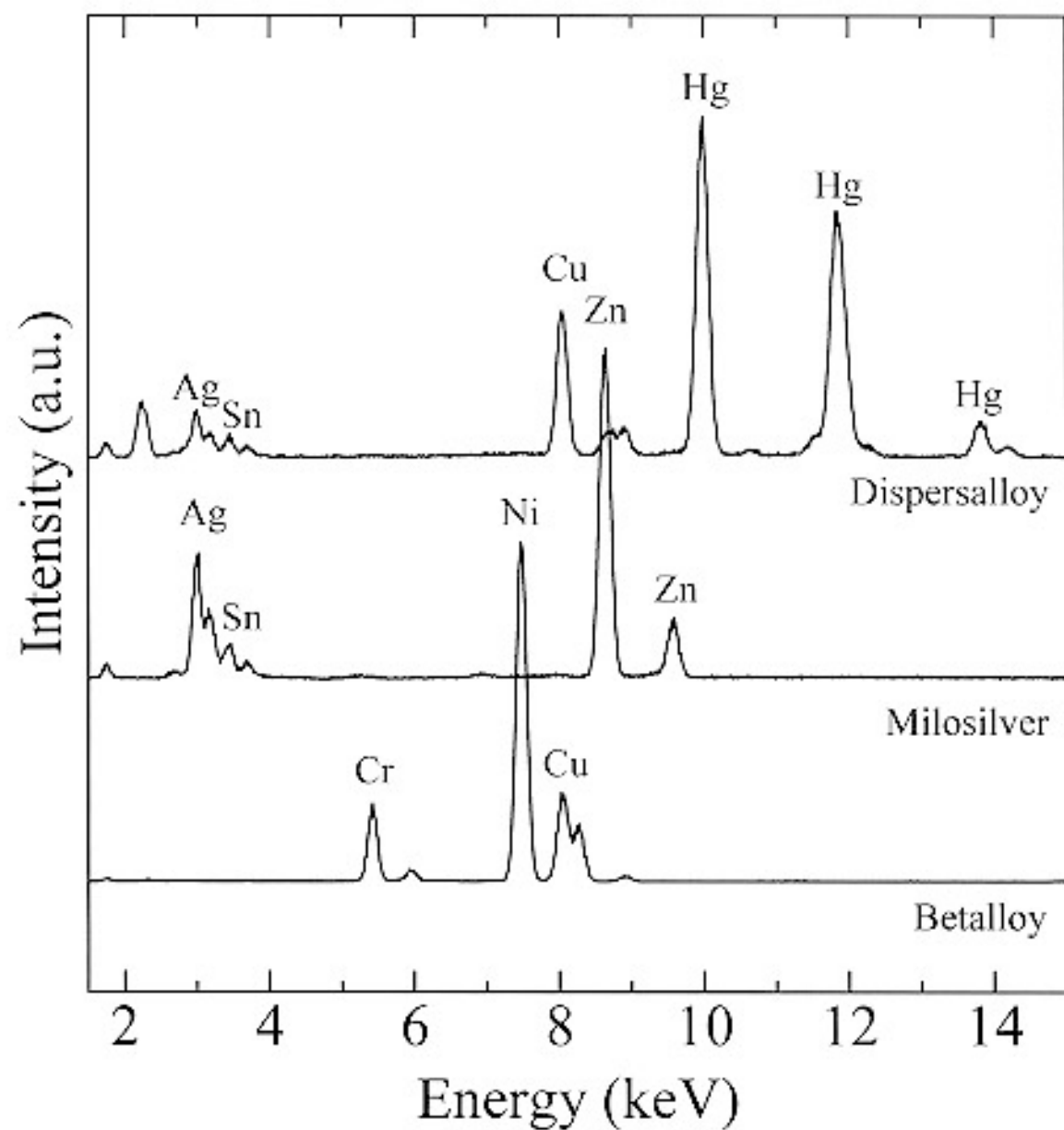
Fig.1

Fig.2

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