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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 30 μ g. 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 petalatum of metal salts and composition analysis of metallic restorations are employed. In order 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 microsampling method uses a silicone point and disk, and compositional analysis using X-ray photoelectron spectrometry (XPS) [4-6]. This method makes it possible to analyze metallic restorations with little damage. The X-ray fluorescence spectrometer is also used for similar metal analysis [7-9].

The recently developed X-ray scanning analytical microscope (XSAM) enables elemental 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-resolution X-ray transmission images [10]. The analysis is carried out in air without pretreatment even if it contains water, unlike electron probe microanalysis (EPMA) and energy dispersed spectrometry (EDS) in electron microscopy which require a vacuum and electro-conductive coating. 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]. With 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 silicone point, elemental analysis of the sampled point was performed simply by setting the sample in the appropriate position in a specimen chamber, aiming at the metal-attached point on 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 for the rapid analysis of the metallic restorations. Watanabe et al. [14] reported that quantitative analysis of metallic restorations could be carried from trace sample using XSAM and a scraping 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 restorations 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 100 μ m ϕ 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 90 μg 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 ($K\alpha=1.74\text{keV}$) and titanium ($K\alpha=4.51\text{keV}$) derived from the silicone point were observed with background spectra (Fig.1a and b). In the background, rhodium K and L peaks ($K\alpha=20.15\text{keV}$ and $L\alpha=2.70$) 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 $K\alpha$, titanium $K\alpha$, rhodium $K\alpha$ and $L\alpha$ 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 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 $L\alpha$ peak (2.84keV) was observed in the low energy side of silver $L\alpha$ peaks (2.96keV). However, the palladium $L\alpha$ peak was quite close to the rhodium $L\alpha$ peak (2.70keV) and the same as the rhodium $L\beta$ peak (2.84keV). Thus, the $L\alpha$ peak of palladium was strongly affected by that of rhodium. Therefore, differentiation of the palladium peak from the background was difficult. The silver $L\alpha$ 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 30 μ g 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 $L\alpha$ peak (2.84keV) was quite close to that of the rhodium $L\alpha$ peak (2.70keV) and the same as that of $L\beta$ (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 $L\alpha$ is appeared as a individual peak and easily be identified. However, Pd $L\alpha$ is slightly appeared nearby Ag $L\alpha$ peak and accurate differentiation of Pd $L\alpha$ 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 measuring 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 atmospheric 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 30 μ g 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 30 μ g. 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.

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References

- [1] Brune D. Metal release from dental biomaterials. *Biomater* 1986; **7**:163-175.
- [2] Hamano H, Uoshima K, Miao W, Masuda T, Matsumura M, Hani H, Kitazaki H, Inoue M. Investigation of metal allergy to constituent elements of intraoral restoration materials (in Japanese). *J Stomatol Soc Jpn* 1998; **65**: 93-99.
- [3] Wataha JC. Biocompatibility of dental casting alloys: A review. *J Prosthet Dent* 2000; **83**: 223-234
- [4] Ohno H, Endo K, Tanabe M. Quantitative analysis of extremely small samples by ESCA (in Japanese). *Shimadzu Hyoron* 1990; **5**: 97-101.
- [5] Yamada K, Ogino S, Gao Y, Endo K, Kawakami T, Ohno H. Intra oral corrosion of metallic restoration and allergic reaction to metals (in Japanese). *Japan J Conserv Dent* 1998; **41**: 821-827
- [6] Hirose Y, Hikage S, Sakaguchi K, Michiya H, Kanazawa M, Endo K, Ohno H. A clinical report of prosthodontic treatment using titanium for a patient with allergic reaction to Sn, Cu, Cr, Au and Pd (in Japanese). *J Jpn Prosthodont Soc* 1998; **42**: 617-624.
- [7] Suzuki N. Metal allergy in dentistry: Detection of allergen metals with X-ray fluorescence spectroscopy and its application toward allergen elimination. *Int J Prosthodont* 1995; **8**: 351-369.
- [8] Fujii H, Nakamura S, Koike M, Terano M, Minami J, Kurogi T, Liu Y. The present state of metal allergy and its countermeasure in dental practice.(in Japanese) *Dental Review* 2000; **689**: 63-73.
- [9] Sawada T, Toyoda M. The metal allergy and the measures against in clinical prosthodontics.(in Japanese) *Dental Review* 2000; **689**: 83-92
- [10] Hosokawa Y, Ozawa S, Nakazawa H, Nakayama Y. An x-ray guide tube and a desk-top scanning x-ray analytical microscope. *X-Ray Spectrom.* 1997; **26**: 380-387.

- [11] Uo M, Watari F, Yokoyama A, Matsuno H, Kawasaki T. Dissolution of nickel and tissue response observed by X-ray scanning analytical microscope. *Biomater* 1999; **20**: 747-755.
- [12] Uo M, Watari F, Yokoyama A, Matsuno H, Kawasaki T. Tissue reaction around metal implants observed by X-ray scanning analytical microscopy. *Biomater* 2001; **22**: 677-685.
- [13] Uo M, Watari F, Yokoyama A, Matsuno H, Kawasaki T. Comparison of XSAM and EPMA in elemental map imaging of unstained soft tissue and detectability of rare content of dissolved elements. *Biomater* 2001; **22**: 1787-1794
- [14] Watanabe K, Honnma H, Okawa S, Kanatani M, Nakano S, Kobayashi M, Miyakawa O. Quick identification of restoration components causing metal allergy by microscopic X-ray fluorescence analysis. *Transactions of the Fourth International Congress on Dental Metals*, 2002; 290
- [15] Annusavice KJ. Phillips' Science of Dental Materials, 10th ed., W.B. Saunders, Philadelphia 1996 : 430-448

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

GC Corporation (Tokyo, Japan)

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).

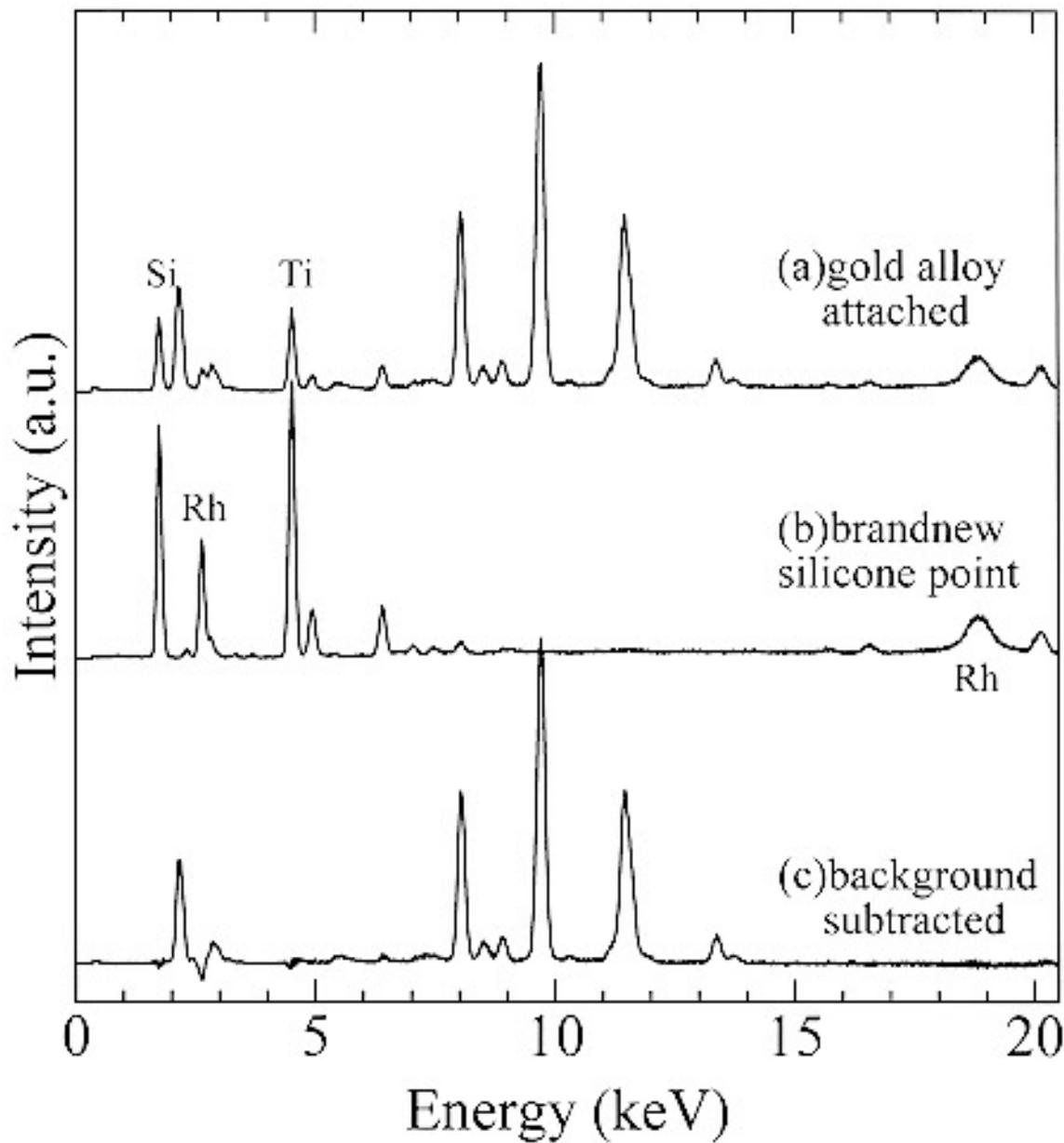


Fig.1

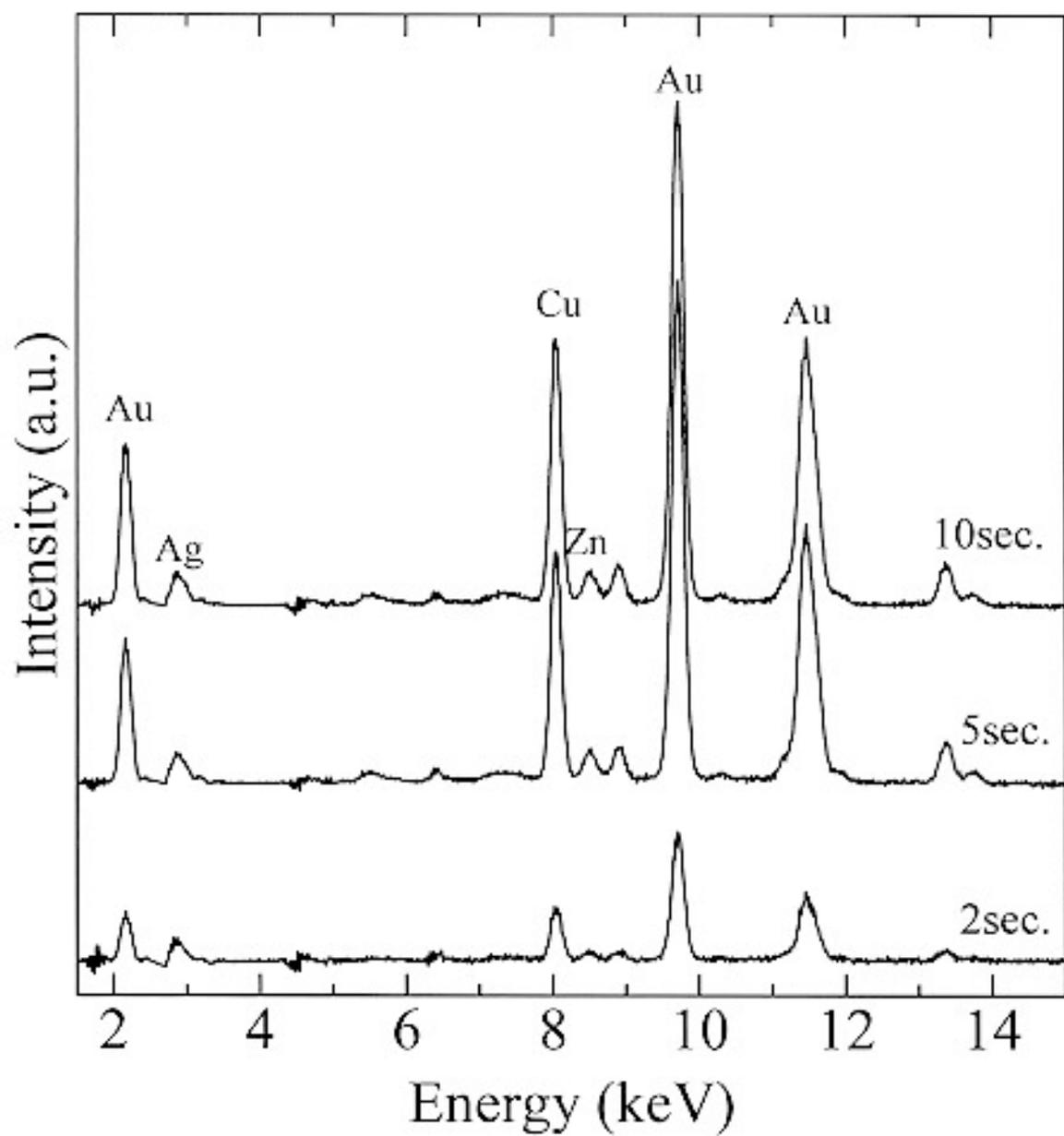


Fig.2

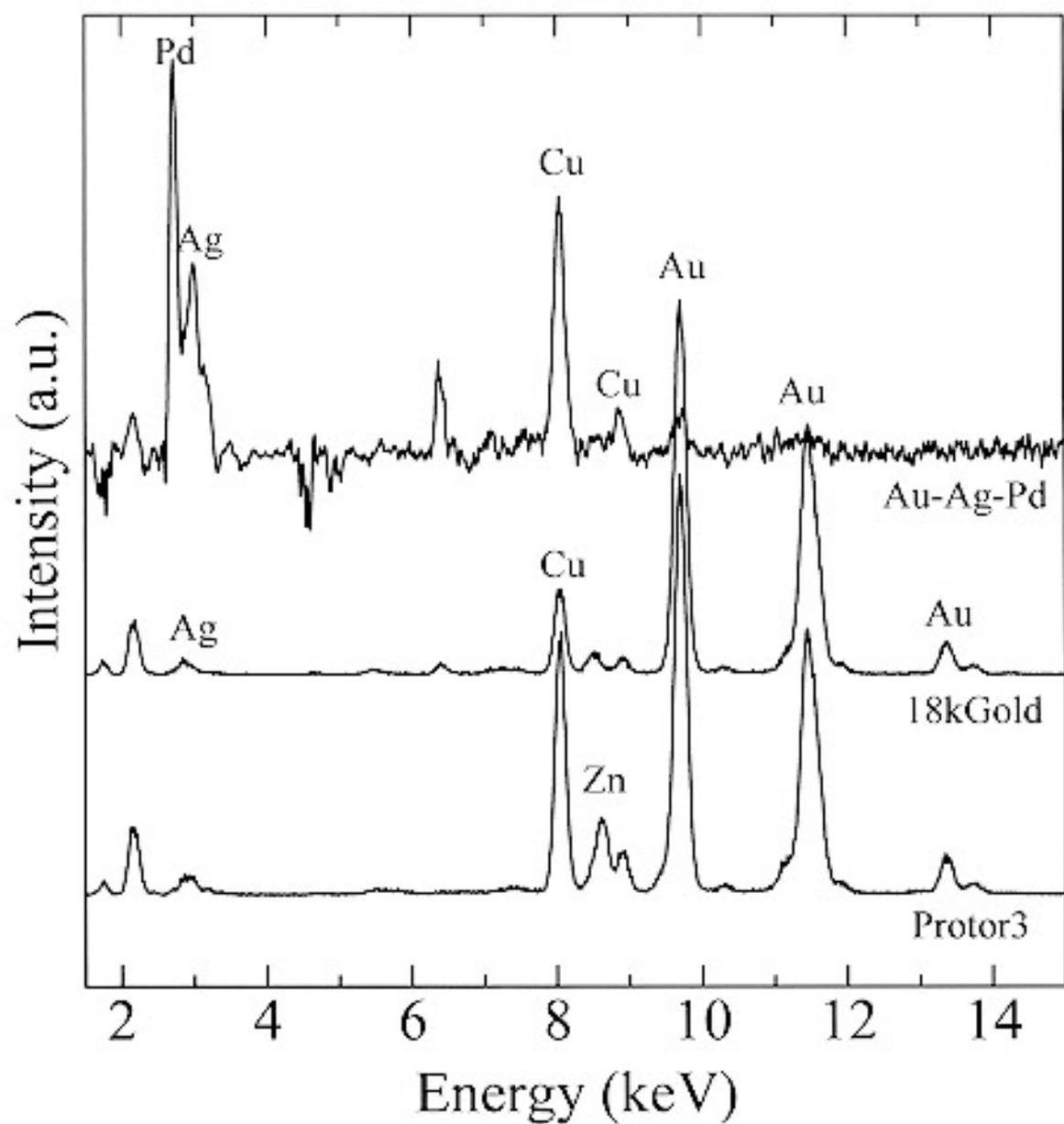


Fig.3

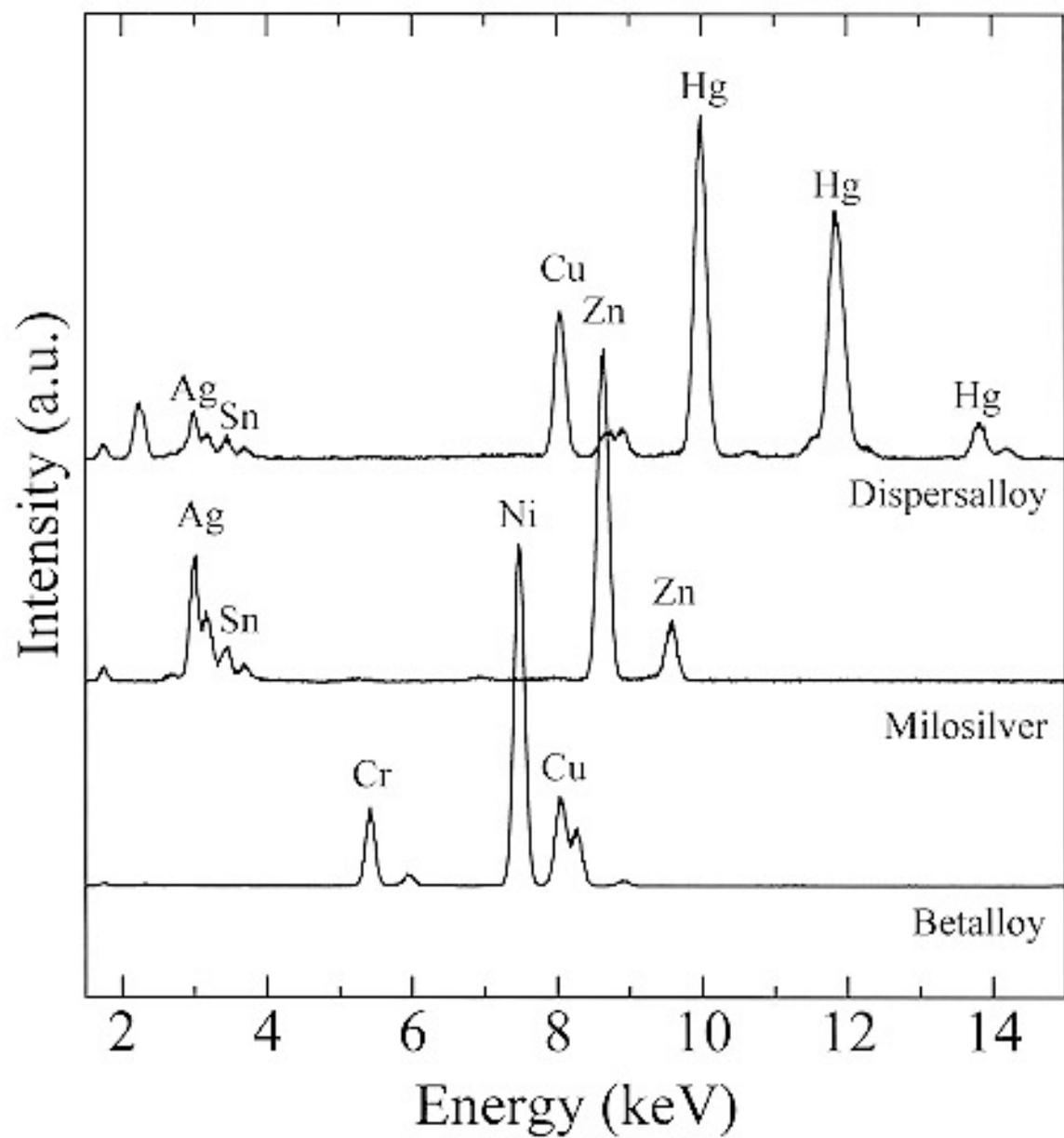


Fig.4