



HOKKAIDO UNIVERSITY

Title	Rapid and non-destructive analysis of metallic dental restorations using X-ray fluorescence spectra and light-element sampling tools
Author(s)	Furuhashi, K.; Uo, M.; Kitagawa, Y. et al.
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•Abstract

1. Introduction

Recently, allergic diseases caused by dental metals have been increasing. Therefore, rapid and accurate analytical methods for the metal restorations in the oral cavities of patients are required. The purpose of this study was to develop a non-destructive extraction method for dental alloys, along with a subsequent, rapid and accurate elemental analysis.

2. Materials and Methods

Samples were obtained by polishing the surfaces of metal restorations using a dental rotating tool with disposable buffs and polishing pastes. As materials for the analysis, three dental alloys were used. To compare the sampling and analysis efficiencies, two buffs and seven pastes were used. After polishing the surface of a metal restoration, the buff was analyzed using X-ray scanning analytical microscopy (XSAM).

3. Results

The efficiency of the analysis was judged based on the sampling rate achieved and the absence of disturbing elements in the background in fluorescence X-ray spectra. The best results were obtained for the combination of TexMet as a buff with diamond as a paste. This combination produced a good collection efficiency and a plain background in the fluorescence X-ray spectra, resulting in a high precision of the analysis.

•Keywords

X-ray scanning analytical microscope; Elemental analysis; light-element sampling tools; Fluorescent X-ray analysis; metal restoration; allergic diseases

1. Introduction

In dentistry, more than 20 metallic elements are processed into various dental metal alloys. These alloys are then cast and processed for use as metal restorations.

Fleischmann [1] first reported stomatitis from an amalgam restoration in the oral cavity in 1928. Various allergic diseases caused by intraoral metal restorations have since been reported [2-9]. Recently, an increase in allergic diseases has been reported in Japan, and metal allergies have attracted attention in dentistry [10]. The removal of metal restorations in the oral cavities of patients has become widespread in Japan, and an improvement in allergic diseases has been reported [11].

Patients with allergic diseases must be examined to determine whether a metal restoration contains the allergenic substance. The sampling method should be a non-destructive extraction from the metal restorations in the oral cavity along with a subsequent rapid and accurate elemental analysis.

The conventional extraction method has been to scrape powder from a metal restoration using a

carbide bur. This powder is then collected on the tip of a fresh cotton swab and analyzed using an X-ray fluorescence spectrometer. However, this method not only damaged the structure of the metal restoration but also exacerbated the allergic reaction by scattering metal fragments [10].

Uo [12] used fresh silicone points (type M, Shofu) to sample dental metal, after which the metal-attached silicone points were analyzed using X-ray scanning analytical microscopy (XSAM) (XGT-2000V, Horiba). The amount of attached metal was estimated to be less than 30 μg . Although this method did not damage metal restorations, it was observed that Si and Ti were found because of the silicone point used. This is a disturbing factor for the X-ray fluorescence analysis.

The purpose of this study was to develop a non-destructive extraction method for dental metal restorations along with a subsequent rapid and accurate elemental analysis.

2. Materials and Method

2.1. Sampling tool

Fig.1a shows a schematic of a polisher disk with a disposable buff and polishing abrasive paste. After the disk was mounted on a rotating dental tool (contra-angle handpiece), as shown by the arrow in Fig.1b, samples were collected by polishing the surface of the metal restorations.

To compare the sampling and analysis efficiencies, two buffs and seven pastes were used.

2.1.1 Polishing buff disk

Two buffs (SuperSnap, Shofu) and (TexMet, Buehler) were used in this study. SuperSnap is composed of a synthetic velvet cloth, used for the final polish of dental prostheses of resin composites and porcelains. TexMet is non-woven pressed cloth, generally used to polish material object in industrials.

2.1.2 Polishing paste

Table 1 lists the various abrasives that the used pastes were composed of: a) diamond (DiamondPaste, Scandia), b) a mixture of diamond and titanium oxide (DirectDiaPaste, Shofu) used as received, c,d) boron nitride (BN-B and BN-T, Showa Denko), and e) alumina (Metapolish, Fujimi), as prepared in this study.

To make the pastes composed of powders of boron nitrides BN-B and BN-T, with META POLISH ($\alpha\text{-Al}_2\text{O}_3$), as abrasives, Vaseline (white petrolatum) and glycerin were used as bonding solvents. BN-B and BN-T are highly crystalline cubic boron nitride super abrasives with a hardness close to that of diamond. The particle size distribution of BN-B was 0~1 μm (mostly about 1 μm from field emission scanning electron microscope observation as shown in the result) with an angular shape, while that of BN-T was 0~2 μm (mostly about 2 μm in a similar way) with a block-like shape. This data provided by supplier.

The solvent/powder volume ratio was set to 50/50.

2.1.3 Dental alloys for sampling

Three dental alloys were used as analysis materials: Au-Ag-Pd (Castwell, GC), Ni-Cr (Betallloy, Yada Kagaku Kougyo), and silver alloy (Milosiver, GC). The commercial names and compositions of these alloys were Castwell (12Au-46Ag-20Pd-20Cu-2(Zn, In, Ir)), Betallloy (62Ni-12Cr-15Cu-8Mo-3others), and Milosiver (65Ag-15Zn-20Sn). To ensure the same surface states for all of the dental alloys, the surfaces were polished using a silicone point set on a dental rotating tool before sampling.

2.2. Sampling Method

Sampling was performed directly with each dental alloy by simulating the method used for a patient's oral cavity in a clinic. The sampling time was 30 s, and the imposed pressure was about 10 gf.

2.3. Observation and analysis

After polishing the surfaces of the metal restorations, the X-ray fluorescence spectra of the buffs were analyzed using XSAM. X-rays were generated from a rhodium (Rh) cathode irradiated by electrons at 50 kV and 1 mA. The spatial resolution of the analysis was 100 $\mu\text{m}\phi$, which was equal to the X-ray beam size formed by the 100 $\mu\text{m}\phi$ X-ray guide tube (XGT) of the XSAM, and the measurement time was 120 s.

The collected amount of dental alloy was determined from weight difference of the buff before and after sampling. Randomly-extracted five samples were measured by Micro Balance (AEM-5200, Shimadzu).

The buffs and pastes were also analyzed, prior to their use, with the help of XSAM and X-ray diffraction (XRD) (Multi Flex, rigaku) and observed by field emission scanning electron microscope (FE-SEM) (S-4000, Hitachi high technologies).

3. Results

3.1. Sampling method

The total time required for the entire analysis and sampling process was under 10 min. The collected amount of dental alloys was less than 30 μg .

3.2. Buff

Fig.2 shows the SEM images of the buffs: (a) TexMet (TM) and (b) SuperSnap (SS). The TM buff was made from numerous fibers bound with adhesives. Titanium dioxide particles adhered to the surface of these fibers. The SS buff was composed of nearly uni-directional fibers with a diameter of 30 μm .

Fig.3 shows the X-ray fluorescence spectra for the SS and TM buffs (used as received). Ti peaks ($\text{K}\alpha = 4.51 \text{ keV}$ and $\text{K}\beta = 4.93 \text{ keV}$) were observed for both buffs. A much larger intensity was

observed for the SS buff. From the XRD results, the titanium dioxide contained in the SS buff was found to be rutile.

3.3. Paste

Fig.4 shows SEM images of the pastes. Fig.4a shows the Diamond Paste. The particle size is about 8 μm , and its shape is granular. Fig.4b shows the SEM image of DirectDiaPaste. Rutile-type titanium dioxide particles of about 120 nm exist around the diamond particles, with a particle size of about 3 μm and an angular shape. Fig.4c shows the SEM image of BN-B. The particle size was about 1 μm , and the shape was angular. Fig.4d shows the SEM image of BN-T. The particle size was about 2 μm , and shape was block-like. Fig.4e shows the SEM image of METAPOLISH ($\alpha\text{-Al}_2\text{O}_3$), which had a particle size of about 3 μm and an angular shape.

Fig.5 shows the X-ray fluorescence spectra of the various pastes (used as received).

A very strong peak for Ti was detected in the case of DirectDiaPaste. The XRD analysis, for which the results are not shown here, also revealed that DirectDiaPaste contained titanium dioxide of the anatase type with a crystal structure.

3.4. Effect of solvent

The paste was composed of abrasive powders with bonding solvents. Fig.6 shows the dependence of the sampling efficiency on the bonding solvent from the X-ray fluorescence spectra. Figs.6a and b are the results for the Au-Ag-Pd alloy obtained by using Vaseline (a) and glycerin (b) as the bonding solvents. In most cases, the paste that used Vaseline as a solvent provided better sampling efficiency than the paste that used glycerin.

In the following sections, only the results for samples using the Vaseline paste are described.

3.5. Analysis of samples

Fig.7 shows the X-ray fluorescence spectra for the Au-Ag-Pd alloy when the TM buff with various pastes and SS with DirectDiaPaste are used.

The analysis efficiency was evaluated based on the sampling rate achieved and the absence of disturbing elements in the background in the X-ray fluorescence spectra. The diamond paste, which was a mixture of diamond and titanium oxide (DirectDiaPaste), and the boron nitride paste, both showed good efficiencies. The samples obtained using these polishing pastes indicated the presence of all the major elements of the alloy. On the other hand, a strong X-ray fluorescence peak for Ti observed in the case of DirectDiaPaste. When DirectDiaPaste was used with the SS buff, the X-ray fluorescence of Ti was further enhanced. Of the two different types of boron nitrides (BN-B and BN-T), in most cases, the collection efficiency of the BN-B paste was superior to that of the BN-T paste.

In this study, a clear peak of Pd ($L\alpha = 2.84 \text{ keV}$) could not observe. $L\alpha$ peak of Pd (2.84 keV) is very close to Rh peaks ($L\alpha = 2.70 \text{ keV}$ and $L\beta = 2.83 \text{ keV}$) of incident X-ray beam and mostly overlapped. To determine qualitatively assessment of Pd Uo already showed the method to use $K\alpha$

peak (Pd = 21.2 keV and Rh = 20.2 keV) in the higher energy region [12].

Fig.8 shows the X-ray fluorescence spectra for the Ni-Cr alloy when the TM buff with diamond paste (a) and alumina (b) was used. The TM buff with diamond paste showed good collection efficiency and clearly produced the spectra of the major elements in the alloy. On the other hand, alumina was inferior in terms of sampling. Among major alloying elements, Mo ($K\alpha = 17.48$ keV) could not be detected.

According to the above discussion, the best results were obtained by using a combination of TexMet as a buff with diamond paste. This combination showed good collection efficiency and a plain background in the X-ray fluorescence spectra for the three dental alloys, resulting in a high precision of the analysis (Figs.7 and 8).

There was no obvious difference in the sampling and analysis efficiencies of the two used buffs. The background did not change as a result of the buffs and pastes.

4. Discussion

4.1. Sampling method

The new sampling method employed in this study, using a disposal buff and polishing paste, is simple and quick. In addition, this method is a non-destructive extraction method for dental alloys that is followed by a rapid and accurate elemental analysis.

4.2. Problem with DirectDiaKit (Shofu) (DirectDiaPaste + SuperSnap)

The strong Ti peak was found in the X-ray fluorescence spectra when the SS buff and DirectDiaPaste were used for sampling. Both contain titanium oxide. The strong oxide X-ray fluorescence peak for Ti was a disturbing factor in the X-ray fluorescence analysis. Recently, titanium has been widely used for dental implants. Titanium nitride (TiC) is also used for cutting dental bars. There have also been reports that Ti acts as an allergen in some cases [13]. Therefore, the presence of the Ti peak would be undesirable in a case where the detection of only a small amount of Ti is permissible. An analytical kit free from Ti is preferable.

4.3. Paste

The sampling efficiency was affected by the shape, hardness, and particle size of the abrasives. Therefore, alumina would be insufficiently hard and inferior when sampling high hardness alloys such as the Ni-Cr alloy. Between the two types of BN pastes (BN-B and BN-T), BN-B showed better sampling efficiency. The Knoop hardness was 4700 for both. It could be inferred that the better efficiency of the BN-B abrasive was related to the greater angularity of its particles as compared to BN-T. The difference in the forms of the abrasive particles, i.e., more angularity in BN-B particles than in BN-T particles, possibly contributes to the difference in the observed sampling efficiencies.

4.4. Best combination

In this study, we compared various sampling tools that consisted of light elements, most of which do not disturb the detection of ordinary metallic elements, and investigated optimum combinations of various buffs and pastes. In terms of a high sampling rate and no disturbing elements, the combination of a TM buff and DiamondPaste gave the best result. The method was effective for all the three alloys: Au-Ag-Pd, Ni-Cr, and dental Ag alloys.

Nowadays, more sensitive and accurate elemental analyses are required for use in clinics (e.g., for metallurgical allergy investigations). The present method is useful for analyzing unknown dental metals and has the potential to be widely applied.

5. Conclusions

In this study, the optimum combination of buff and paste was investigated.

A simple and quick sampling method was newly developed.

The collected amount of dental alloy was less than several tens of micrograms, and the total time required for the whole process of sampling and analysis was less than 10 min.

In terms of a high sampling rate and no disturbing elements, the combination of the TM buff and DiamondPaste gave the best result.

The method was effective for all three representative alloys used in dentistry, namely, Au-Ag-Pd, Ni-Cr, and dental Ag alloys, and it was found suitable for use in clinics.

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•Title

Rapid and non-destructive analysis of metallic dental restorations using X-ray fluorescence spectra and light-element sampling tools

• Author names and affiliations.

K. Furuhashi,^{a*} M. Uo,^b Y. Kitagawa,^a F. Watari^c

^a Oral Diagnosis and Medicine, Department of Oral Pathobiological Science, Hokkaido University Graduate School of Dental Medicine, Hokkaido University, North 13, West 7, Kita-ku, Sapporo 060-8586, Japan.

^b Advanced Biomaterials Section, Graduate School of Medical and Dental Sciences, Tokyo Medical and Dental University, 113-8549, Yushima, Bunkyo-ku, Tokyo 113-8549, Japan

^c Dental Materials and Engineering, Department of Oral Health Science, Graduate School of Dental Medicine, Hokkaido University, North 13 West 7, Kita-ku, Sapporo 060-8586, Japan.

• Corresponding author.

Tel.: +81-11-706-4250; fax: +81-11-706-4250; email: fkazunori@den.hokudai.ac.jp

Highlights

- A non-destructive extraction method for dental prostheses was developed.
- A rapid and precise elemental analysis was used after extraction.
- Sample dental prostheses were polished using pastes and disposable buffs.

- We investigated sampling/analysis efficiencies and optimal buff-paste mixtures.
- The method was effective for all three dental alloys and clinical use.

Figure caption

Fig.1 Clinical sampling situation from dental prostheses set in oral cavity of patient.

- a. A schematic of a polisher disk with a disposable buff and polishing abrasive paste.
- b. Sampling method from patient

Fig.2 SEM images of the buffs: (a) TexMet (TM) and (b) SuperSnap (SS).

Fig.3 X-ray fluorescence spectra for the SS and TM buffs (used as received).

Fig.4 SEM image of various pastes (a, b) and abrasives used for preparation of each paste (c, d, e).

- a: Diamond Paste, b: DirectDiaPaste, c: BN-B, d: BN-T, e: alumina(α -Al₂O₃)

Fig.5 X-ray fluorescence spectra of the various pastes (used as received).

Fig.6 Dependence of the sampling efficiency in X-ray fluorescence spectra from Au-Ag-Pd alloy on the bonding solvents of pastes, (a) Vaseline , (b) glycerin.

Fig.7 X-ray fluorescence spectra for the Au-Ag-Pd alloy when the TM buff with various pastes and SS with DirectDiaPaste are used.

- a: DirectDiaPaste+SS buff, b: α -Al₂O₃+TM buff, c: BN-B+TM buff, d: DirectDiaPaste+TM buff, e: Diamod Paste+TM buff

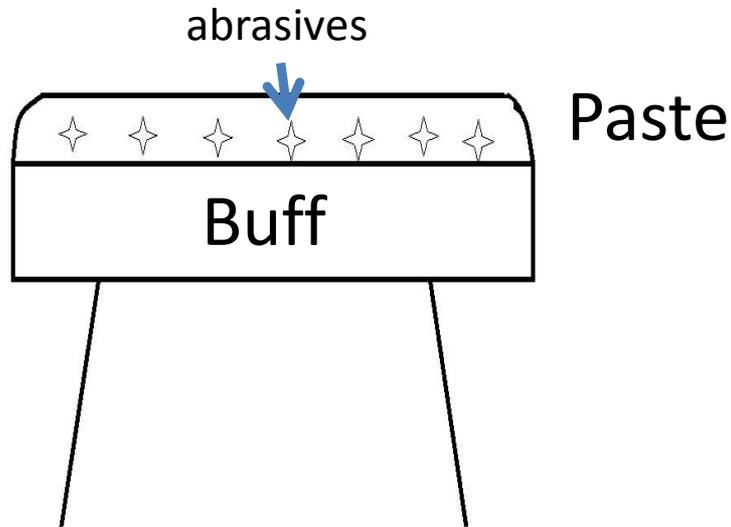
Fig.8 The X-ray fluorescence spectra for the Ni-Cr alloy when the TM buff with diamond paste (a) and alumina (b) was used.

- a: Diamond Paste b: α -Al₂O₃ paste

Sampling Method

a

Schematic Figure of Polisher disk



b

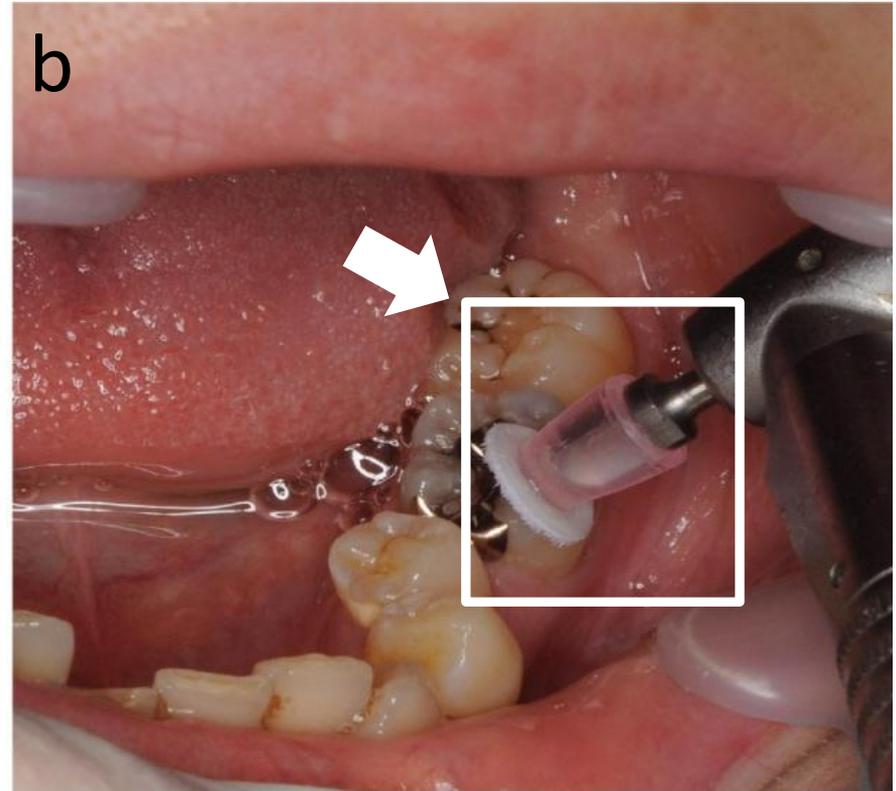


Fig.1 Clinical sampling situation from dental prostheses set in oral cavity of patient.

a. Schematic figure of polisher disk with disposable buff and polishing abrasives in paste

Used Pastes

Table1. Various pastes used for sampling of dental prostheses

* Manufacturer's providing values

Paste name(Product Name)	abrasives	abrasive particle size	solvent
Diamond Paste(SCAN-DIA)	diamond	* 7 μ m	oil
DirectDiaPaste (SHOFU)	diamond +TiO ₂ (anatase)	* diamond 2~4 μ m	-
BN-B(SHOWA DENKO)	BN	* 0~1 μ m	white petrolatum/glycerin
BN-T(SHOWA DENKO)	BN	* 0~2 μ m	white petrolatum/glycerin
META POLISH (FUJIMI)	α -Al ₂ O ₃	* 2 μ m	white petrolatum/glycerin

(1)SEM of Buff

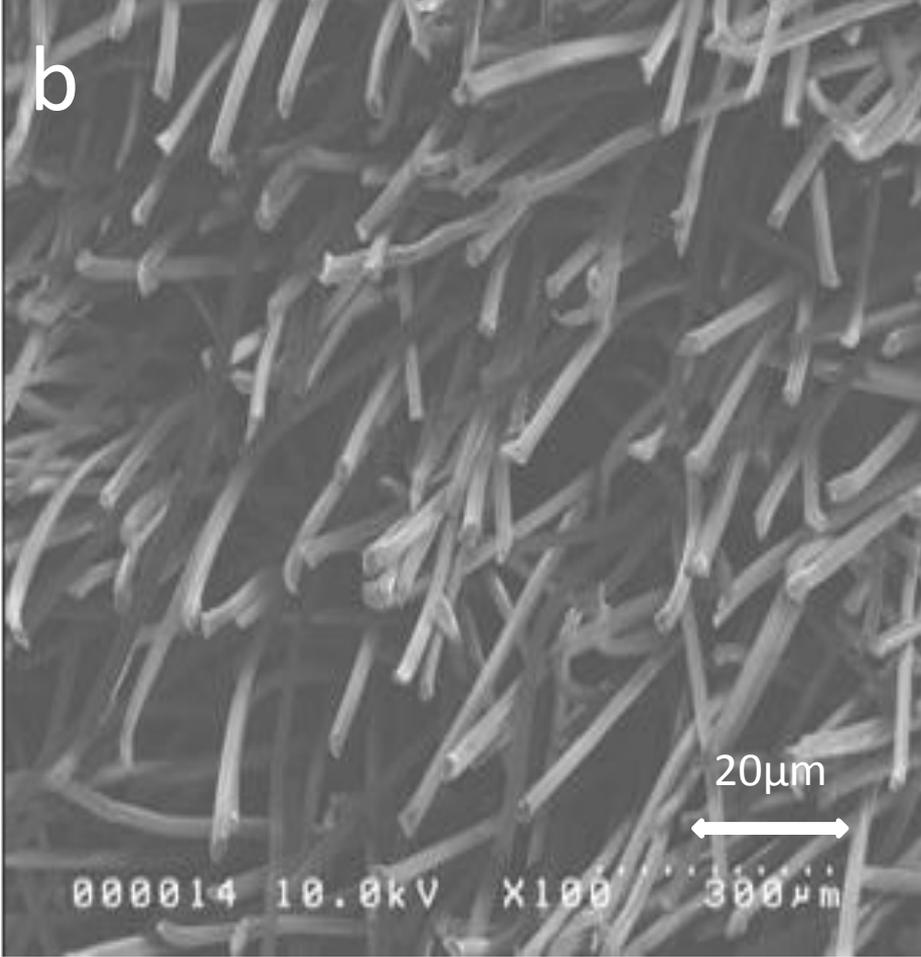
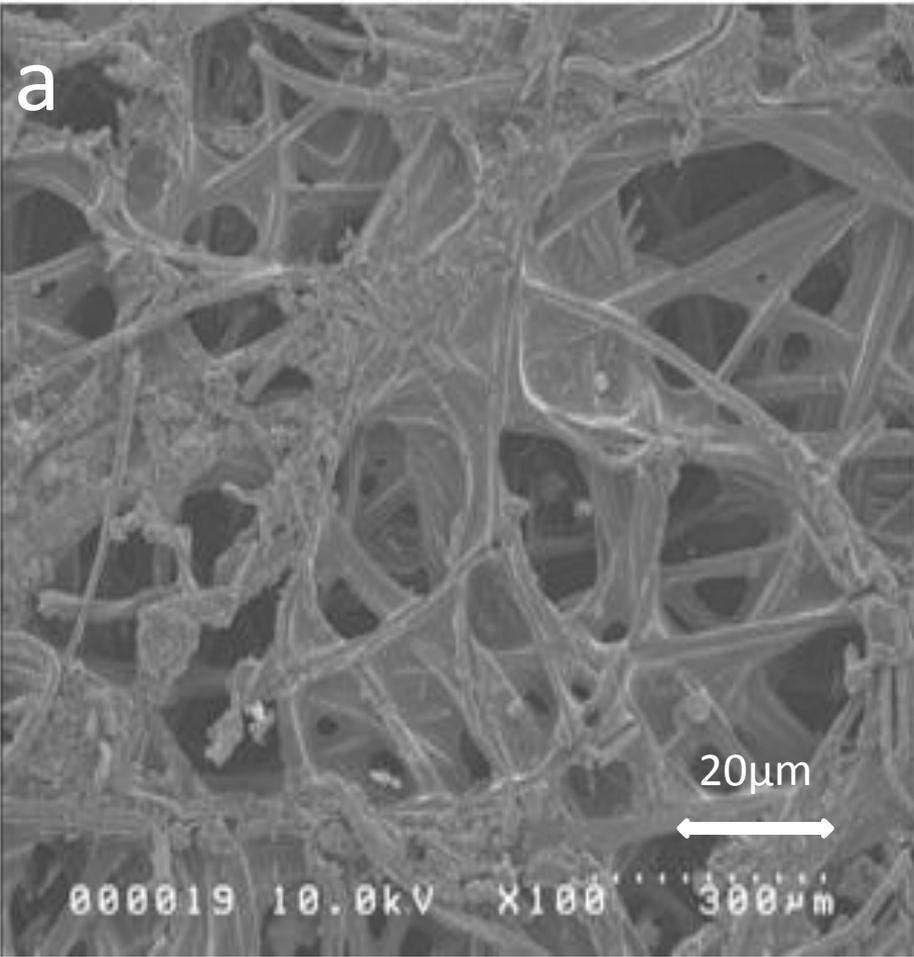


Fig2. SEM images of the buff's a) TexMet TM and b) SuperSnap SS

XRF of Buff

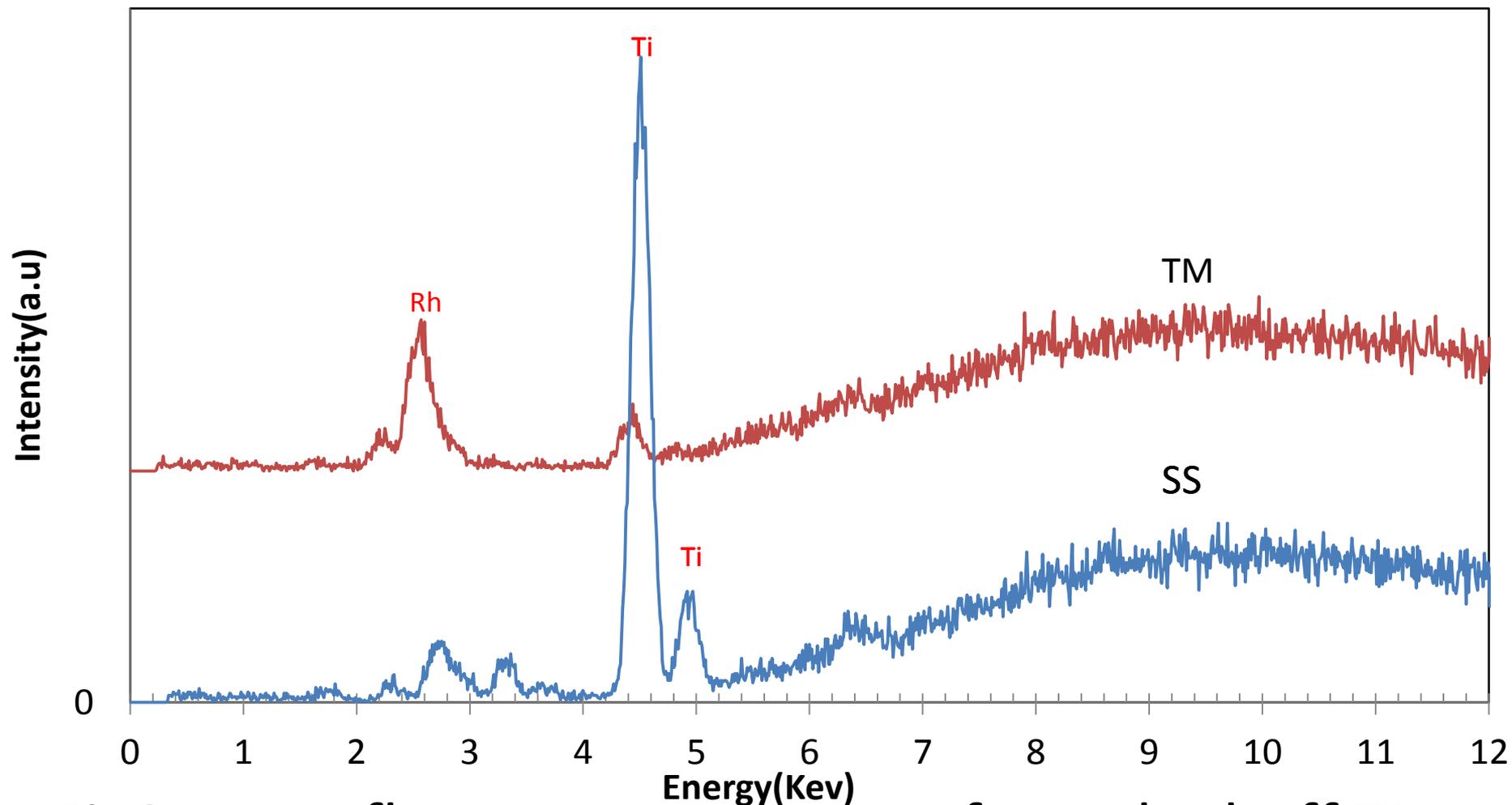


Fig3. X-ray fluorescence spectra from the buff TM and SS (as-made).

SEM of Abrasives

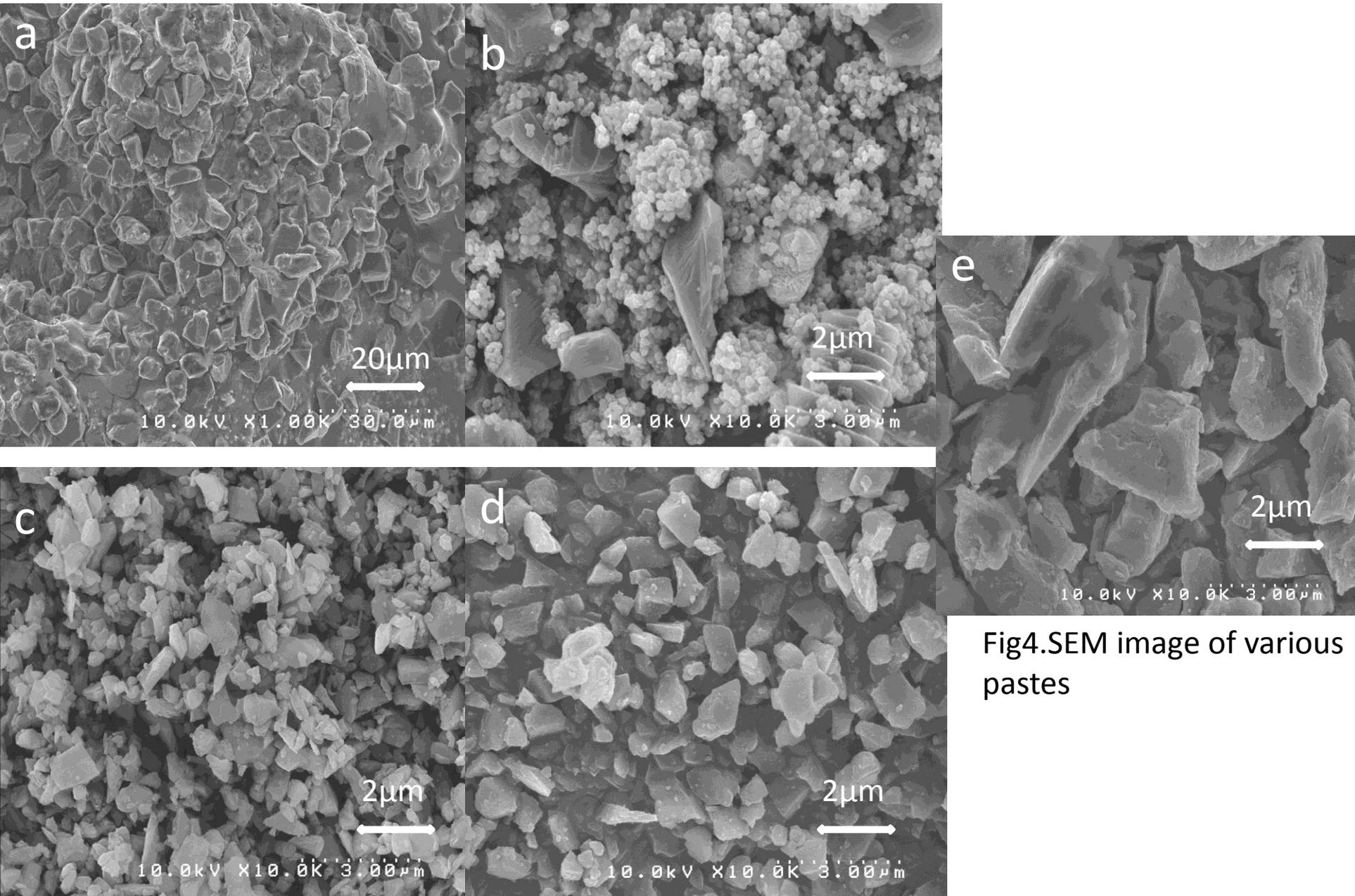


Fig4.SEM image of various pastes

Results XRF of Paste

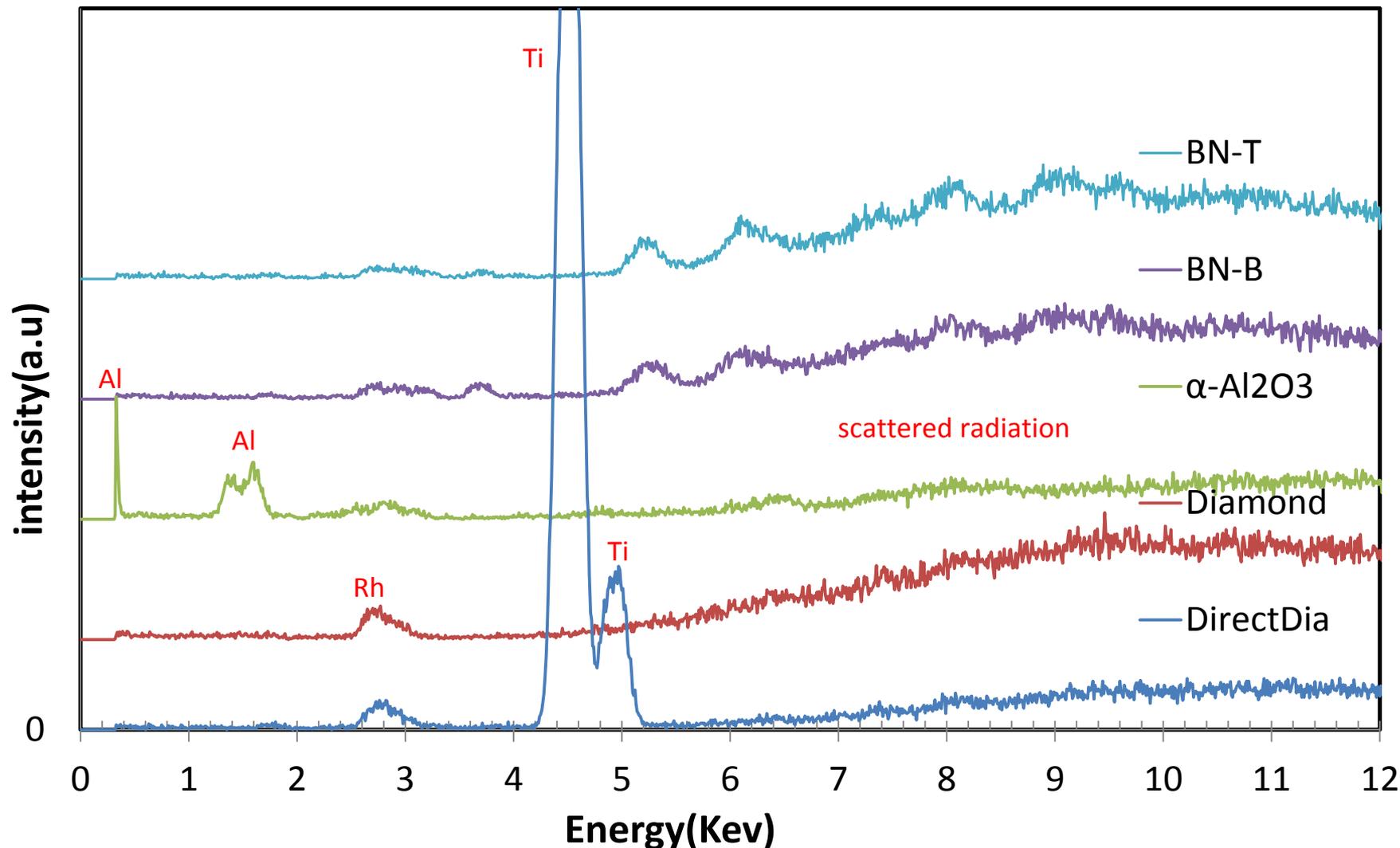


Fig5. X-ray fluorescence spectra from various pastes (as-received).

Effect of solvent

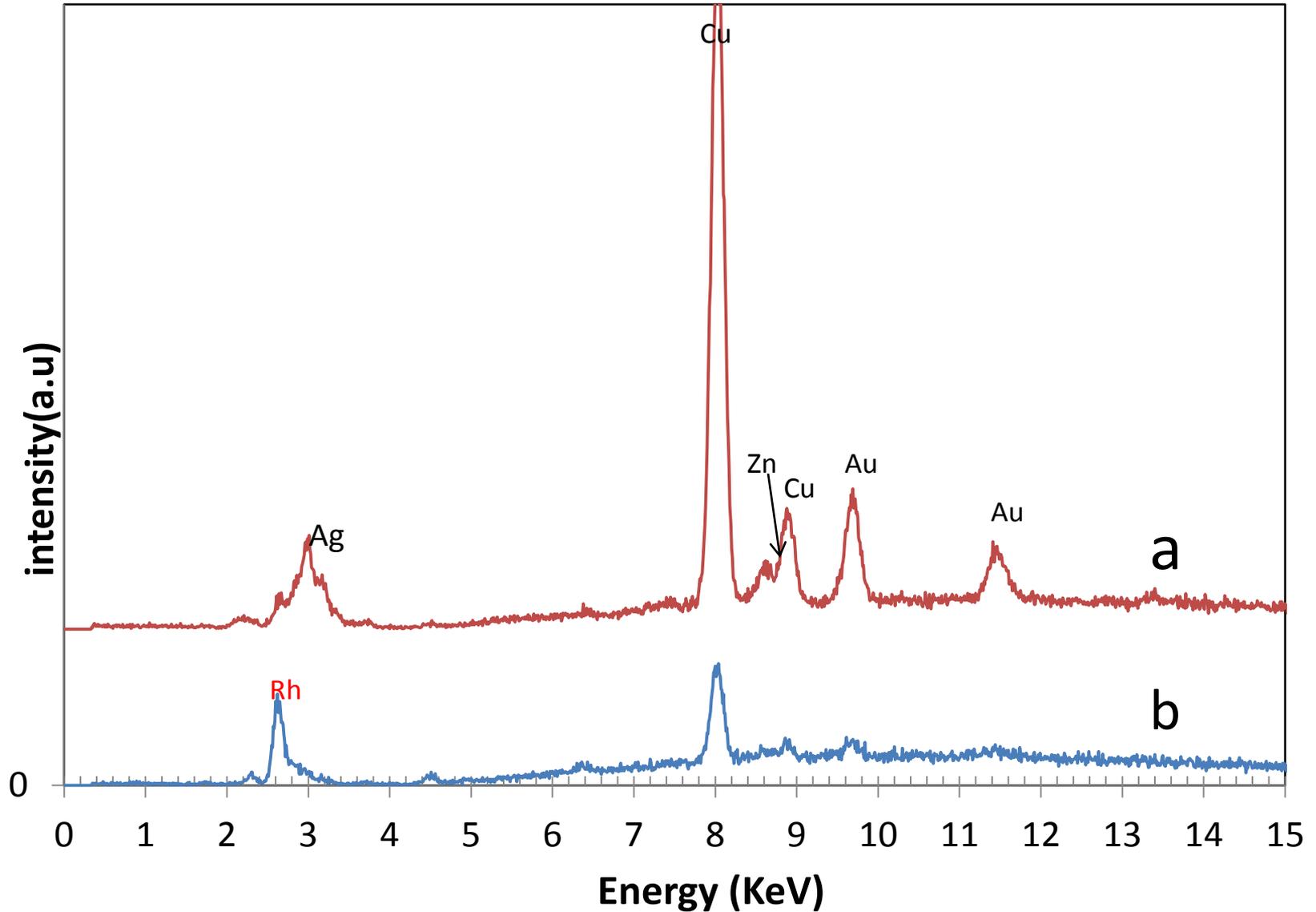


Fig6. Dependence of efficiency of sampling conditions on bonding solvent in X-ray fluorescence spectra from Au-Ag-Pd alloy a) white petrolatum (WP), b)

(2) Analysis of samples

XRF of Au-Ag-Pd alloy

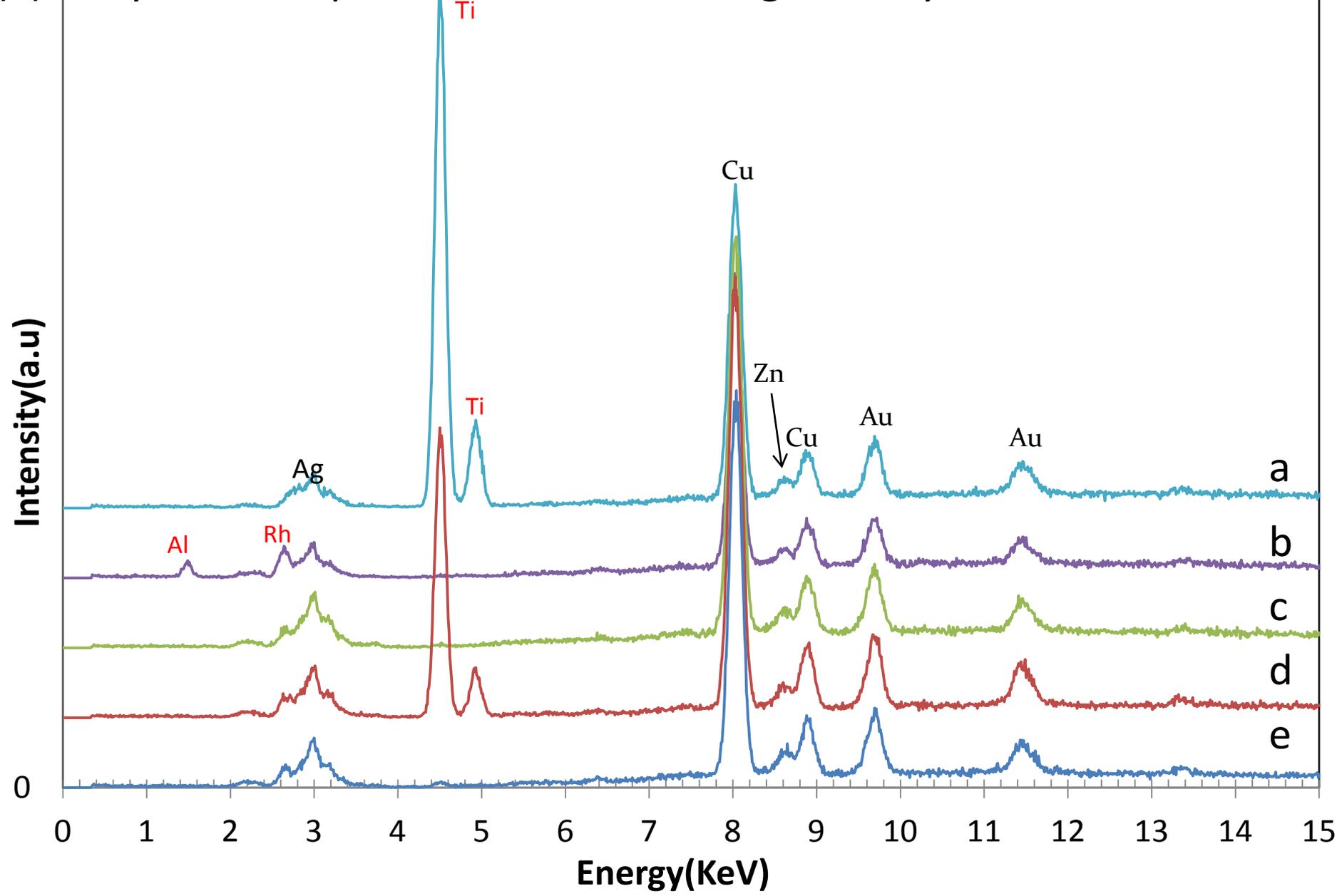


Fig7. X-ray fluorescence spectra from Au-Ag-Pd alloy using buff(TM) with various pastes and Buff(SS) with DirectDiaPaste.

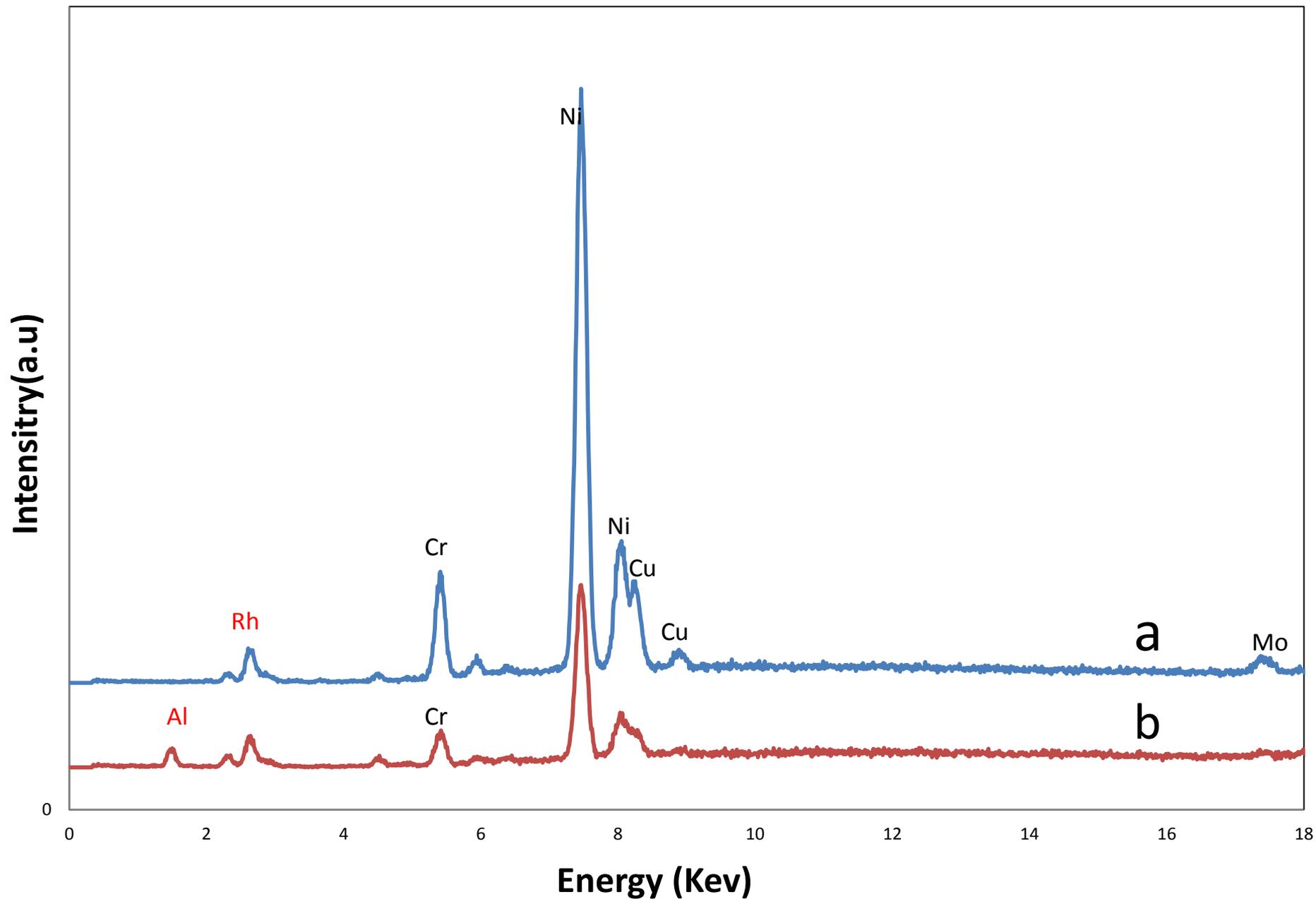


Fig.8 X-ray fluorescence spectra from Ni-Cr alloy using the buff TM with Diamond paste and Al_2O_3 paste