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รายงานวิจัย

เรื่องการออกแบบอุปกรณ์เก็บรักษาตัวอย่างอากาศในสภาวะที่มีออกซิเจนน้อยมากและศึกษาการจำแนกชนิดสารประกอบกำมะถันของPM_{10}ในชั้นบรรยากาศโดยใช้เทคนิค FL-XANES

The Design of Anoxic Air Sample Preservation and Study of Sulfur Speciation of PM10 in the Atmosphere by Using FL-XANES (Fluorescent Mode X-ray Absorption Near Edge Structure)

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FINAL PROJECT REPORT

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Abstract

This paper focuses on providing some innovative perspectives related to the factors affecting the sulfur K-edge XANES spectrum of aerosol samples. Anoxic Preservation Stainless Cylinder (APSC) and Pressure Controlled Glove Box (PCGB) were specially designed for investigating the anoxic preservation effect on variations of sulfur oxidation states in PM_{10}. Further investigation on sulfur K-edge XANES spectra revealed that PM_{10} samples were predominantly dominated by S(VI) even though preserved in anoxic conditions. The "emission source" effect on sulfur oxidation state of PM_{10} was examined by comparing sulfur K-edge XANES spectrum collected from various emission sources in Songkla Province, southern part of Thailand. Additional attempt was conducted on an investigation of "vertical distribution" effects on sulfur oxidation state of PM_{10} collected from three different heights at the highest buildings of three major cities in Thailand. The analytical results have demonstrated that neither "emission sources" nor "vertical distribution" effects appreciably contribute to the variations of sulfur K-edge XANES spectrum in PM_{10}.

Keywords: sulfur K-edge XANES spectrum, aerosols, PM_{10}, vertical distributions, anoxic conditions

INTRODUCTION

Sulfur speciation in aerosol particles play a crucial role in both Earth's energy balance and acid deposition (Kommalapati and Valsaraj 2009; Lauer et al. 2009; Neubauer, Johnson, and Wexler 1995; Righi et al. 2011; Waldman et al. 1991). Numerous efforts have been put to deepen insight and clarify the oxidation pathways of sulfate in aerosol samples (Kerminen et al. 2000; Norman et al. 2006; Vairavamurthy 1998). Over the past decade, several reference publications have been indicating that the most stable oxidation state of sulfur in aerosol is +6 (S(VI)) (Cozzi et al. 2009; Higashi and Takahashi 2009; Takahashi et al. 2006 and 2008). These findings were supported by recent experimental data suggesting that $(NH_4)_2SO_4$ and $CaSO_4$-$2(H_2O)$ are the most dominant sulfur species in aerosols (Takahashi et al. 2009). Regardless of these facts, some ambiguities still remain and need to be clarified. For instances, one may assume that the dominance of S(VI) in air particles is purely based on the lack of proper sample preservation in anoxic condition. Although sulfur possess nine different oxidation states ranging from -2 to +6 in its different compounds, the relatively long oxygen exposure period can noticeably convert all sulfur speciations to a single oxidation form of S(VI).

In other words, the sulfur oxidation state of PM_{10} cannot be accurately identified without an appropriate sample protection in anoxic condition.

Various literature references disclose the limited number of researches related to the investigation of "oxidation" effect on chemical reduction of environmental samples (Prietzel et al. 2011). It is also interesting to note that only one study focused mainly on how "anoxic preservation" enhances the analytical reliability of sulfur K-edge XANES spectra in soil samples (Prietzel et al. 2009). As a consequence, it is extremely crucial to study how "anoxic preservation" can influence the sulfur K-edge XANES spectrum of PM_{10}. Other fundamental questions are how "emission sources" and "vertical distributions" affect sulfur oxidation states in aerosols. Since previous researches focused predominantly on sulfur K-edge XANES spectrum of aerosols in urban monitoring sites and/or remote sampling areas, the comprehension of sulfur oxidation state adjacent to emission sources was insufficient and inevitably neglected. Despite of spatial dynamic movement of aerosols, the majorities of studies so far reported concentrating only in sulfur speciations as a result of particle size segregation at ground level. Additionally, there have been no studies to emphasize the critical analysis of sulfur speciation in PM_{10} as a function of altitude. Thus, the overall aims of this study are:

1. To qualitatively investigate the impact of "anoxic preservation" on diurnal variation of sulfur K-edge XANES spectra of PM_{10} collected at ground level at the main campus of National Institute of Development Administration (NIDA), Bangkapi Campus in Bangkok, Thailand
2. To analyze sulfur K-edge XANES spectra in PM_{10} collected adjacent to various emission sources as representatives of biomass burnings, crude oil combustions, diesel emissions, timber burnings and traffic exhausts in Songkla Province, southern part of Thailand.
3. To conduct the qualitative investigation of "altitude effect" on sulfur K-edge XANES spectra in PM_{10} collected at the urban sampling sites of Bangkok, Chiang-Mai and Hat-Yai, Thailand.

MATERIALS AND METHODS

Sample Collection and Sampling Site Descriptions

Sulfur K-edge XANES Experiment

XANES of the samples and standards were measured at the beamline No.8 at the Siam Photon Laboratory (Klysuban et al. 2007). Photon energy of an X-ray beam transported through the beam-line was scanned by InSb(111) double crystals equipped

in the monochromator (see Fig. 1). The beam size illuminating the sample was 10 mm (w) x 1 mm (h). Figure 2 shows the apparatus setup for measuring fluorescent yield from the sample. A 10-cm-long ion chamber filled with a gas mixture of N_2 (30 mbar) and He (983 mbar) was employed to measure intensity of the X-ray beam before the sample. The ion chamber absorbed only 10 % of the beam intensity for ionization of the filling gas and produced small electrical current signal proportional to the beam intensity.

Fluorescence X-rays were emitted from the sample and collected by either a 13-channel Germanium detector (GeD) or a Lytle detector (LyD). The GeD has advantage over the LyD in discrimination of X-ray fluorescence energy. With the use of a digital window, only K_α photons from sulfur were counted. The Final photon counts were averaged over all the channels. Similar to the ion chamber, the LyD produces small electrical current signal corresponding not only to fluorescence X-rays from sulfur but other elements present in the sample and the scattered photons from the primary beam. The sample chamber was flowed in with He gas to reduce X-ray absorption and scattering by air. A thin polypropylene window was required to protect the GeD from He gas, which can diffuse through thin detector seal of beryllium spoiling cryostat vacuum of the detector. A minimum air gap of 5 mm was introduced for detector clearance. The distances from the sample to detector were 7 mm and 9 mm for GeD and LyD, respectively. XANES spectra were recorded from 2450 eV to 2520 eV with the energy step of 0.2 eV and energy-calibrated using the maximum absorption of iron sulfate at 2481.4 eV (Chauvistre et al. 1997). Absorbance was calculated by the ratio of photon counts from the fluorescent detector to the ion chamber. All QFF samples were applied on adhesive side of the polyimide tape and placed at 45 ^oC to the beam path in the sample chamber. Without dilution, similar approach was used for the preparation of environmental samples. The data processing and quantitative XANES analyses were conducted by ATHENA program in the IFEFFIT computer package (Newville, 2001).

Sampling Equipment

Ambient air samples were collected by using a Graseby-Anderson high volume air sampler with TSP and PM_{10} TE-6001, operating at the flow rate of 1.4 m^3 min^{-1}. TSP and PM_{10} were collected on 47 mm Whatman quartz microfiber filters (QMFs). The filters were pre-heated at 800 ^oC for 12 h prior to sampling. The exposed filters were stored in a refrigerator at about 4 ^oC until sulfur speciation analysis to prevent the evaporation of volatile compounds. All the field sampling and filters weighing were

performed in compliance with the US EPA's guideline of Standard Operating Procedure for sampling and handling of $PM_{2.5}$ filters. It is important to note that all filters were weighed by Mettler Toledo AB204-S Analytical Balance before sending to Synchrotron Light Research Institute (Public Organization), Thailand.

NIDA Bangkapi Campus Monitoring Site

PM_{10} samples were collected every three hours for 27 hours (i.e. n = 9, 18.00-21.00, 21.00-00.00, 00.00-03.00, 03.00-06.00, 06.00-09.00, 09.00-12.00, 12.00-15.00, 15.00-18.00 and 18.00-21.00) at National Institute of Development Administration (NIDA), Thailand's most prestigious graduate university under the Commission on Higher Education, the Ministry of Education in Bangkok. Diurnal variation of urban background samples were taken at an open field located at the south-western side of NIDA Bangkapi campus close to Sereethai Road, one of the most heavily traveled road in this area. Since the monitoring site is only 1 km away from the Mall Shopping Center Bangkapi, Tesco-Lotus Department Stores and Macro Department Stores, it seems reasonable to assume that PM_{10} collected from this site represent aerosols derived from traffic vehicle exhausts. All samples were gathered on QM-A type quartz fiber filters (QFFs) from Whatman, and carefully preserved inside a nitrogen gas purged Pressure Controlled Glove Box (PCGB) to avoid exposure to oxygen. All filters were installed inside Anoxic Preservation Stainless Cylinder (APSC) enclosed with nitrogen gas (see Fig. 3-4) and cautiously delivered to Synchrotron Light Research Institute (SLRI) for sulfur k-edge XANES spectra analysis.

Source Cluster Monitoring Sites

Twenty-four hours sampling was conducted for three consecutive days at PSU (Prince of Songkla University Hat-Yai Campus), TI (Traffic Intersection), CI (Corps Incinerator), CPF (Charoen Phokphand Factory), SL (Songkla Lake), RMF (Rubber Manufacturing Factory), BT (Bus Terminal), WI (Waste Incinerator), BF (Barbeque Festival), PR (Petkrasem Road) and KHH (Kor Hong Hill) stations. The air samples collected at BB and PTB stations represent the most serious period of air quality. Therefore, 3-h samples were collected three times per day in order to avoid any overloading of air particulate matters in these three stations.

It is also worth to mention that all monitoring sites are located in Songkhla province, which is situated 950 km south of Bangkok with the population over 1.32 million people. This province has a complex urban environment, a mix of commercial, residential and industrial estates. Sampling locations were cautiously designated from

this establishment. Sampling locations were carefully selected and 13 monitoring stations were categorized due to the nature of emission sources. The sites descriptions were given as follow (see Table 1):

The site descriptions were given as follow:

Cluster I: The background sampling site cluster was further categorized into three groups.

PSU (*Prince of Songkla University*): The site was situated at about 3 m above ground level in the Faculty of Environmental Management of Prince of Songkla University, and about 550 m away from the main traffic road that leads to the city center of Hat-Yai. It is important to note that PSU represent the sampling period of October (24^{th} -26^{th} October, 2007). This site is considered as an urban residential zone.

SL *(Songkhla Lake Monitoring Station)*: It was situated about 13 km far away from the northern side of Prince of Songkla University at the south of Songkhla Lake and about 14 km away from the western side of the Gulf of Thailand. This sampling station is far away from many industrial and traffic emission sources, including chemical and metallurgy, power plant, and etc in this district. Therefore it is considered as a rural background monitoring stations. SL1 (Songkla 1) and SL2 (Songkla 2) were used to represent the monitoring period of July (27^{th} to 29^{th} July, 2007) and October (20^{th} to 22^{nd} October, 2007) respectively.

KHH (*Korhong Hill Monitoring Stations*): It was located on the top of Kor-Hong hill with the elevation of 356 meters. This site represents as a mixture of all emission sources in urban area. Therefore, the air mass collected from this station considered as urban background. The sampling was conducted on 3^{rd} to 5^{th} November, 2007.

Cluster II: This group is categorized as a source of diesel and benzene emission.

Three sampling stations were classified in this cluster:

BT (*Bus Terminal*): This site was located at the south-western side of PSU and approximately 1.4 km far away from the campus. As the majority of buses, which are diesel-fuelled around this area, we considered this site as a source of diesel emission. The air sample collection was started from $5^{th}$to 7^{th} August 2007.

PR (*Petkrasam Road*): This site was located at the heart of Hat-Yai city. This site faces the heaviest burden from traffic congestions with mixture with the mixture of diesel and gasoline exhaust emissions. Thus, the air mass collected at this area is mainly influenced by diesel and benzene emission. The monitoring was conducted on 27^{th} – 29^{th} August, 2007.

TI (*Traffic Intersection*): This station was located at the traffic intersection in front of the main gate of PSU nearby Tesco supermarket. It is on the eastern side and

approximately 2.5 km far away from the Hat-Yai city center closed to urban residential zone. This station is regarded as traffic area and mainly influenced by diesel and benzene emissions. The air samples were collected from 5th to 7th July, 2007.

Cluster III: This cluster is categorized as a source of industrial emission source. Two sampling stations were classified in this cluster.

CP (*Charoen Phokphand Factory*): This site is located at the fish can-manufacturing factory of CP. This factory is the largest business conglomerate in Thailand. We considered it as an emission source of crude oil-burnings. The monitoring was conducted from 24th to 26th July 2007.

RMF1 & RMF2 (*Rubber Sheet Manufacturing Factory*): This station is located at Tumbol Tungwan, Hat-Yai district. This factory normally used para rubber treatment as fuel for the manufacturing process. The rubber sheet was treated with steam of high temperature and high pressures and then purified with sulfuric acid solution. As para rubber trees were used as fuel for this process, we therefore considered as emission of mixed para rubber tree burning, latex fragments and sulfuric acid aerosols were considered. The air samples were collected from 30th July to 1st August 2007 (RMF1) and from 2nd to 4th August 2007 (RMF2).

Cluster IV: This group is classified as biomass burning sites. We further categorized into two groups, which are

PTB (*Para Rubber Tree Burning*): This station is located at Namom district, Songkhla Province and can be recognized as an emission source of Para rubber tree burning. The air samples were collected on 18th November, 2007.

BB (*Biomass Burning*): This station is situated at the rice filed in Satingpra district, Songkhla Province. By removing rice straw, it can remove the problem of disease organism but leads to the serious air pollution problems in this region. This station was considered as a source of biomass burning. The sampling was conducted on 16th November, 2007.

Cluster V: This cluster is classified as old tire, clinical waste and charcoal burning sites. We further characterized into three groups

CI (*Corpse Incinerator*): This station is a part of Kor-Hong temple, located at the northern side and about 1.5 km far way from TI. Since timbers and tires were generally used as fuel for corpse incineration, this site is considered as an emission source of both timbers and tire-burnings. This site represents the sampling period of 19th - 21st July 2007.

WI (*Waste Incinerator*): This site was situated at the city center and belongs to the municipality of Hat-Yai city. Since the municipal waste incinerated is a heterogeneous

mixture of solid wastes and burning fuels, this site can be recognized as a combination of solid waste burning and diesel exhaust emission. The air samples were collected from 28^{th} – 30^{th} August, 2007.

BF (*Barbeque Festival*): This site was located inside the PSU campus on the top roof of Faculty of Natural Resources. The barbeque festival has become an annual tradition that is held on the second week in August. The 40^{th} Annual Barbecue Festival is set for Wednesday, August 15^{th}, 2007. This site can be considered as an emission of charcoal burning. The air samples were collected from 15^{th} – 18^{th} August, 2007. Additionally, it is also important to emphasize that there were no obstructions in the vicinity of sampling equipment at all sampling sites, which was strategically positioned to be accessible to winds from all directions.

Vertical Sampling Sites

All the three sampling sites are located in the city center of Bangkok, Chiang-Mai and Hat-Yai, representing the capital, the largest city in northern and southern region of Thailand respectively. Air samples were collected at three different heights for three hours (i.e. 9.00 am – 12.00 am) at Bai-Yok Suit Hotel Observatory Site (i.e. Level-1: 38 m; Level-2: 158 m; Level-3: 328 m above the ground level), at Centara Duangtawan Hotel Observatory Site (i.e. Level-1: 12 m; Level-2: 52 m; Level-3: 152 m above the ground level) and at Novotel Centara Hat-Yai Hotel Observatory Site (i.e. Level-1: 30 m; Level-2: 60 m; Level-3: 125 m above the ground level) as monitoring sites for Bangkok, Chiang-Mai and Hat-Yai in that order (see Table 1). It is well known that traffic emissions are considered as main sources of air pollutants in Bangkok atmosphere, whilst agricultural burnings are major air pollution problems in Chiang-Mai. Furthermore, Hat-Yai is located only 30 km at the west of Gulf of Thailand. Thus, one can safely assume that aerosol samples used in this study may consist of traffic aerosols with the mixture of industrial exhausts, biomass burning and sea salt aerosols in the case of Bangkok, Chiang-Mai and Hat-Yai in that order.

RESULTS

Figure 5 illustrates diurnal variation of nine sulfur K-edge XANES spectra of PM_{10} preserved in APSC and PCGB filled with nitrogen gas prior to XANES analysis at SLRI. There are three common features of each sulfur K-edge XANES spectrum: the "pre-edge" (involving the energy of 2450-2465 eV), which signifies to the area at energies lower than the point of the main absorption edge; the "near-edge" region, which refers to the 5 eV wide region instantaneously encompassing the white-line (i.e.

the main peak), which was located at 2482 eV, and the "post-edge" region, which denotes to the region >2490 eV outside the absorption edge. Base on the results of nine sulfur K-edge XANES spectra, one can comprehend that all S compound in PM_{10} shares comparable spectral structures, for instance the relatively flat spectrum of pre-edge region (i.e. 2450-2650 eV) followed by the sharp main peak at 2482 eV and the large post-edge fluctuation that arises in the energy band of 2490-2510 eV (see Fig. 5). These results are in good agreement with previous reports focusing on sulfur K-edge XANES spectra of aerosols with different particle sizes (Takahashi et al. 2006, 2008 and 2009). Since Takahashi et al have concluded that particulate sulfur compounds are predominated by S(VI), it can be deduced that the oxidation number of elemental sulfur collected at NIDA Bangkapi campus is +6 and plausibly occupied by sulfate species.

Figure 6 demonstrates the sulfur K-edge XANES spectra of 15 PM_{10} samples collected from various emission sources in Songkla province. Similar to the previous sulfur K-edge XANES spectra detected at NIDA Bangkapi campus, the spectrum of BT, PR, Tesco, RMF and CPF displays a broad resonance at the pre-edge region, probably due to a superposition of more than one resonance. All 15 spectra demonstrate the maximum peak feature at higher energy of 2482 eV, which is comparable to those of diurnal variation samples. Despite of several deviations in the intensities of the maximum peak features between the different emission source samples, some subtle dissimilarity in post-edge regions are apparent, particularly the subsequent structure in the post-edge region between 2485 and 2510 eV. Previous studies interpreted this phenomenon as a consequence of electron transitions with a d-type shape resonance, which can be influenced by various types of cations binding with sulfates (Myneni, 2002; Sekiyama et al. 1986). These discrepancies among different sulfur K-edge XANES spectra can be applied to characterize the "finger print" of target aerosols associated with various emission backgrounds.

Figure 9 emphasizes the domination of sulfate species in urban aerosols by displaying the relatively similar sulfur K-edge XANES spectra of PM_{10} collected at different heights in comparison with those of "diurnal variation" samples. The analogous spectral features were observed in PM_{10} collected at Chiang-Mai, Bangkok and Hat-Yai, regardless of the different sampling heights. Since the oxidation number of sulfur is positively correlated with photon energy, it appears sensible to consider the uniform of highest peak structures at 2482 eV as an outcome of the majority of S(VI) occupied in urban PM_{10}. It seems also plausible to assume that NH_4HSO_4, $(NH_4)_2SO_4$, $BaSO_4$, $CaSO_4*2H_2O$, K_2SO_4, Na_2SO_4, $Na_2SO_4*10H_2O$ can be regarded as sulfate species contained in PM_{10} due to the similar sulfur K-edge XANES spectra as

mentioned in previous study (Takahashi et al. 2006). In addition, earlier studies revealed that the molecular structure affects little on 1s → 3p transition energy of specific sulfur functional group, thus highlighting the usefulness of XANES to categorize the oxidation number of elemental sulfur in PM_{10} (Huffman et al. 1991; Mitra-Kirtley et al. 1998; Waldo et al. 1992)

DISCUSSIONS

Effect of "Anoxic Preservation" on Sulfur K-edge XANES Spectra of PM_{10}

To investigate the "anoxic preservation" effect on sulfur K-edge XANES spectra of PM_{10}, QFF samples were preserved in APSC enclosed with nitrogen gas immediately after completing sample collection. It is also important to note that all filter-cutting processes were conducted inside PCGB filled with nitrogen gas prior to XANES analysis. The sulfur K-edge XANES spectra of PM_{10} samples collected at different period demonstrated that the position of main peak was relatively stable at 2482 eV without any sign of peak shift within ± 0.5 eV for numerous aerosol samples, indicating that particulate sulfur compositions are not influenced by diurnal variation effect. The moderately uniform sulfur K-edge XANES spectra suggest that the overall sulfate species distribution is constant at the traffic site. This finding is in consistent with the similar works performed by Takahashi et al, indicating that "anoxic preservation" might have minor importance for the oscillation of sulfur K-edge XANES spectra in PM_{10} (Takahashi et al. 2006, 2008 and 2009).

Three interpretations can be considered for this phenomenon. Firstly, all sulfur compounds from emission sources in urban atmospheric environment are composed with S(VI) and conceivably predominated by sulfate species. Secondly, the oxidation rate of aerosol sulfur is too fast to convert all particulate sulfur compounds to the most stable oxidation state of +6 before transporting to the receptor site at NIDA Bangkapi campus. Thirdly, all sulfur compounds were completely oxidized to S(VI) after the deposition of particles on QFFs within three hours of sampling period. Interestingly, this finding is in good agreement with earlier study, which had been applied XANES to the determination and quantification of S(IV) species in aerosol samples collected at Qingdao in northeastern China (Higashi et al. 2009). Higashi et al concluded that sulfite was the only sulfur possessed oxidation number of +4 detected in aerosol, particularly in particles with larger diameters collected in August 2001.

It is also crucial to stress that no S(IV) species, however, were detected at the surface of the aerosols as demonstrated by surface-sensitive conversion electron/He ion

yield XANES (Higashi et al. 2009). In case of PM_{10} collected at NIDA Bangkapi campus, the moderately high reactive trace gaseous (e.g. NO_x, O_3 and OH radical) concentration released from diesel engines and other traffic combustions could oxidize sulfur compounds and conclusively convert all of the sulfur oxidation states to S(VI). In addition, the relatively low absorption intensity of sulfur K-edge XANES spectrum of PM_{10} collected from 12.00 am to 15.00 pm can be described as a consequence of "dilution effect" triggered by the lifting of warm air mass during midday (see Fig. 5).

Effect of "Emission Sources" on Sulfur K-edge XANES Spectra of PM_{10}

Unlike those results of diurnal variation campaign, the comparatively oscillated post-edge regions were discernible and thus highlighting the intricacy of sulfate compositions in PM_{10} collected from various emission sources (Fig. 6). Likewise, the white-line intensity fluctuations are more noticeable for emission source spectra. These unique spectra features can be diagnosed as a divergence in both "amount" and "speciation" of S detected in PM_{10}. Interestingly, the unsmooth pre-edge regions were predominant in sulfur K-edge XANES spectrum of CI, WI, CPF, PSU, BB and PTB (Fig. 6). This can be ascribed to both the mixture of source signals (i.e. more variety of sulfur oxidation states) and the relatively low signal-to-noise ratio of S(VI) particularly in case of PTB and BB (i.e. low white line intensities responsible for high noise backgrounds). It is also worth to mention that different sulfur compounds possess distinctive energy positions of white lines. For example, elemental S, organic polysulfide, thiol, sulfoxide, sulfite, sulfone, sulfonate, ester sulfate and inorganic sulfate display the peak energies of sulfur K-edge white lines (eV) at 2472.5, 2473.0, 2473.4, 2475.8, 2478.7, 2480.2, 2481.3, 2482.5 and 2482.5 respectively (Xia et al. 1998; Prietzel et al. 2007). Therefore, the strong oscillation of pre-edges reveals the crucial information of various sulfur species in target samples (Cozzi et al. 2009).

The second derivative analysis reflects the fact that the pre-edge of Cluster I and Cluster V display relatively oscillated sulfur K-edge XANES spectra in the areas at 2470 eV and 2480 eV as illustrated in Fig. 6 and Fig. 8. The complexity of solid waste types incinerated in CI and WI can be postulated to explain these results, whilst the mixture of PM_{10} from numerous emission sources may accountable for the fluctuations of pre-edge detected in urban background sample of PSU. It is also interesting to note that samples in the same category share similar pre-edges, even in the case of second derivative as illustrated in Fig. 8. For instance, some unique spectral patterns of low background noises at the region of 2470 eV-2478 eV with sharp shoulder peaks from 2478 eV to 2480 eV can be detected at BT, PR and TI (see Fig. 7). Since these three

samples are categorized in Cluster II (i.e. benzene and diesel emissions), it appears reasonable to interpret theses spectral characteristics as a consequence of strong influence from traffic emissions.

A further investigation on sulfur K-edge XANES spectral features was conducted for background samples (i.e. Cluster I). Both SL1 and SL2 showed a considerably high level of reproducibility of pre-edges from 2470 eV to 2480 eV in regardless of different sampling periods (see Fig. 6-7). This pattern of behavior supported the idea that both the anthropogenic emissions and seasonal effects might play a minor role in this monitoring station due to its distance from the urban district of Hat-Yai city combined with "the dilution effect" triggered by clean maritime air mass from the Gulf of Thailand. In contrast, the spectral plateau in the region of 2473 eV – 2476 eV detected in WI illustrates an exceptional feature, which cannot be explained by the differences in climatic conditions due to the relatively similar sampling period and location (see Fig. 7 and Table 1). The most convincing explanation, therefore, was plausibly attributed to the complication of solid waste materials combusted in WI. In addition, the comparatively analogous spectral features of PSU, PTB, RMF1 and RMF2 indicating that para rubber tree combustions might play a major role in governing PM_{10} concentrations in residential zones, and thus raising concerns on the adverse impacts of para rubber industries on air quality of Hat-Yai city.

Effect of "Vertical Distribution" on Sulfur K-edge XANES Spectra of PM_{10}

To the best of our knowledge, this is the first study to examine sulfur K-edge XANES spectra of PM_{10} in different altitudes under the urban atmospheric conditions. All PM_{10} collected from three different cities display moderately similar spectral features in comparison with those of diurnal variation samples monitored at NIDA Bangkapi campus as illustrated in Fig. 5. Further analysis on second derivative confirmed the parallel spectral characteristics of all PM_{10} samples. Surprisingly, this uniform spectral pattern was observed in regardless of different monitoring locations and collecting periods (Fig. 9). The relatively high daytime air temperature may responsible for the upwelling of particles, which can be triggered by the convective heat transfer of air mass from surface boundary layer (SBL) to urban boundary layer (UBL). This phenomenon allows air mass, which is relatively homogeneous vertically, to dominate the urban boundary layer in Bangkok, Chiang-Mai and Hat-Yai during the observations. Despite of differences in either "emission sources" or "climatic conditions" among the three cities, all spectral features were consistently identical with the principal composition of S(VI) as illustrated in Fig. 9.

Conclusions

Several concerns were addressed on factors affecting the sulfur K-edge XANES spectra of PM_{10} collected from various locations with different sampling altitudes. There are three common features of each sulfur K-edge XANES spectrum: the "pre-edge" (involving the energy of 2450-2465 eV), which signifies to the area at energies lower than the point of the main absorption edge; the "near-edge" region, which refers to the 5 eV wide region instantaneously encompassing the white-line (i.e. the main peak), which was located at 2482 eV, and the "post-edge" region, which denotes to the region >2490 eV outside the absorption edge. Neither "anoxic preservation" nor "emission sources" appreciably changed this pattern. Further investigation was conducted to assess the alteration of particulate sulfur K-edge XANES spectra as a function of sampling altitude. Interestingly, the comparatively uniform sulfur K-edge XANES spectra were observed in all PM_{10} collected from different cities and sampling periods. This study has ascertained that the sulfur oxidation state of PM_{10} is predominantly overwhelmed by S(VI).

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TABLE 1

Descriptions of sample types and sampling positions

Site	Source Type	Sampling Period	Latitude				Longitude			
PSU	Urban Residential Zone	24/10/07-26/10/07	7°	00'	21.28"	N	100°	29'	53.27"	E
TI	Traffic	05/07/07-07/07/07	7°	00'	30.81"	N	100°	29'	39.21"	E
CI	Timber	19/07/07-21/07/07	7°	01'	17.55"	N	100°	29'	41.44"	E
CPF	Crude Oil	24/07/07-26/07/07	6°	54'	16.38"	N	100°	28'	05.15"	E
SL1	Rural Background	27/07/07-29/07/07	7°	10'	02.92"	N	100°	35'	11.36"	E
SL2	Rural Background	20/10/07-22/10/07	7°	10'	02.92"	N	100°	35'	11.36"	E
RMF1	Timber	30/07/07-01/08/07	7°	03'	19.97"	N	100°	37'	58.90"	E
RMF2	Timber	02/08/07-04/08/07	7°	03'	06.28"	N	100°	24'	07.77"	E
BT	Diesel Engine	05/08/07-07/08/07	6°	59'	42.78"	N	100°	28'	58.02"	E
WI	Solid Waste + Crude Oil	08/08/07-10/08/08	6°	57'	15.43"	N	100°	24'	00.46"	E
BF	Charcoal	15/08/07-17/08/07	7°	00'	23.09"	N	100°	30'	00.54"	E
PR	Traffic	27/08/07-29/08/07	7°	00'	52.99"	N	100°	28'	20.50"	E
KHH	Urban Background	03/11/07-05/11/07	7°	00'	57.92"	N	100°	31'	12.76"	E
BB	Biomass Burning	17/11/07	6°	57'	40.45"	N	100°	33'	06.68"	E
PTB	Para Rubber Tree Burning	18/11/07	6°	57'	40.45"	N	100°	33'	06.68"	E
BKK-L1	Urban Background	18/02/08	13°	45'	46.30"	N	100°	32'	25.37"	E
BKK-L2	Urban Background	18/02/08	13°	45'	46.30"	N	100°	32'	25.37"	E
BKK-L3	Urban Background	18/02/08	13°	45'	46.30"	N	100°	32'	25.37"	E
CM-L1	Urban Background	25/02/08	18°	47'	02.76"	N	98°	59'	56.40"	E
CM-L2	Urban Background	25/02/08	18°	47'	02.76"	N	98°	59'	56.40"	E
CM-L3	Urban Background	25/02/08	18°	47'	02.76"	N	98°	59'	56.40"	E
HY-L1	Urban Background	17/12/07	7°	00'	20.29"	N	100°	28'	16.44"	E
HY-L2	Urban Background	17/12/07	7°	00'	20.29"	N	100°	28'	16.44"	E
HY-L3	Urban Background	17/12/07	7°	00'	20.29"	N	100°	28'	16.44"	E

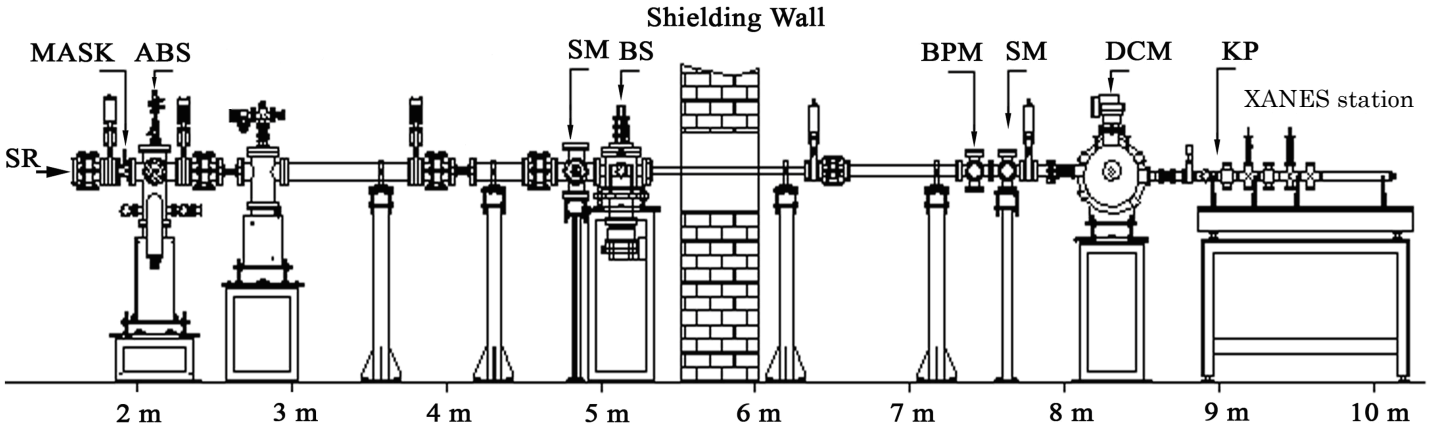


Fig. 1. Schematic view of beamline No.8. Polychromatic Synchrotron X-rays (SR) emitted by a bending magnet (not shown) is transported through the main components of the beamline: mask, heat absorber (ABS), screen monitor (SM), beam shutter (BS), beam position monitor (BPM), double crystal monochromator (DCM), and polyimide window (KP).Distance from the bending magnet source to each component is given at the bottom scale.

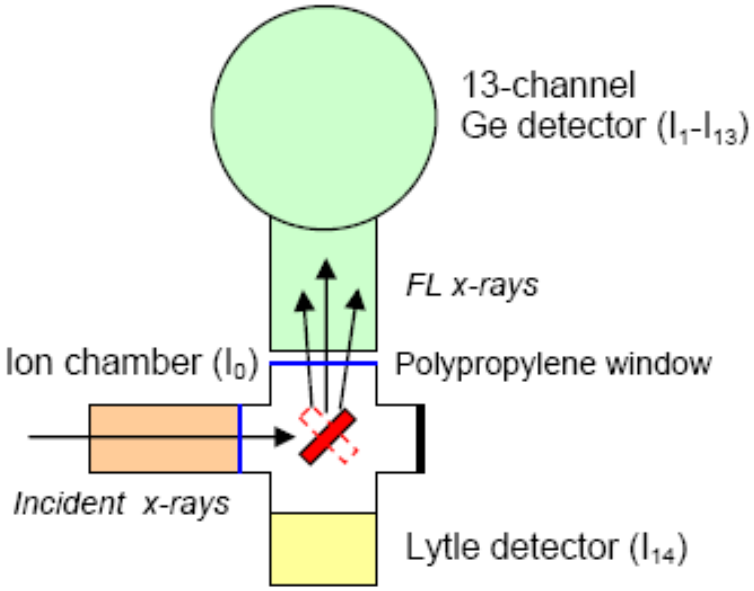
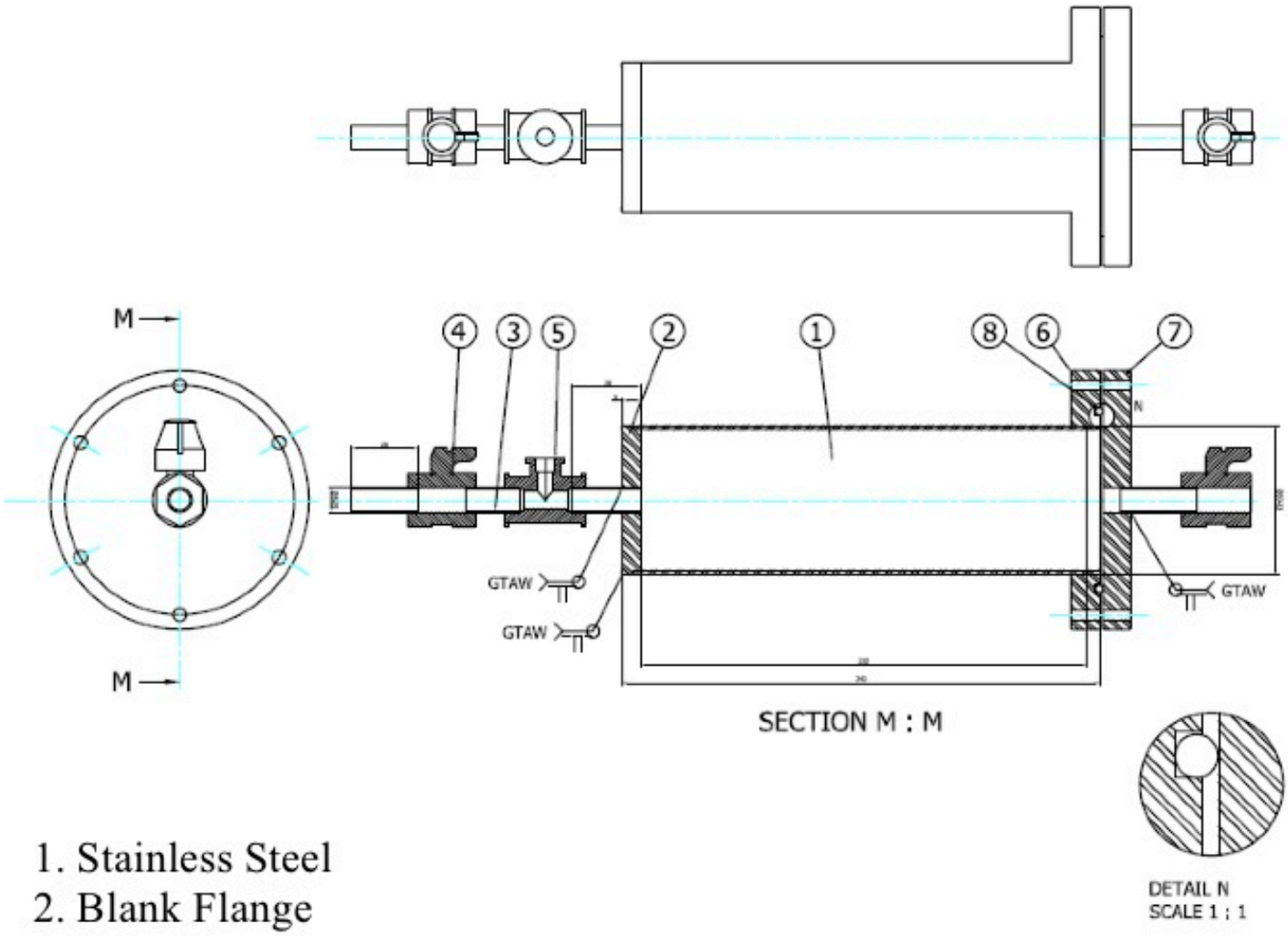


Fig. 2. Apparatus setup for fluorescence-mode XANES. Absorbance in XANES spectra is given by I_n/I_0.



1. Stainless Steel
2. Blank Flange
3. Tube Thread
4. Gas Control Valve
5. Pressure Gauge
6, 7 ISO Flank
8. O-Ring

Fig. 3. Schematic view of Anoxic Preservation Stainless Cylinder (APSC).

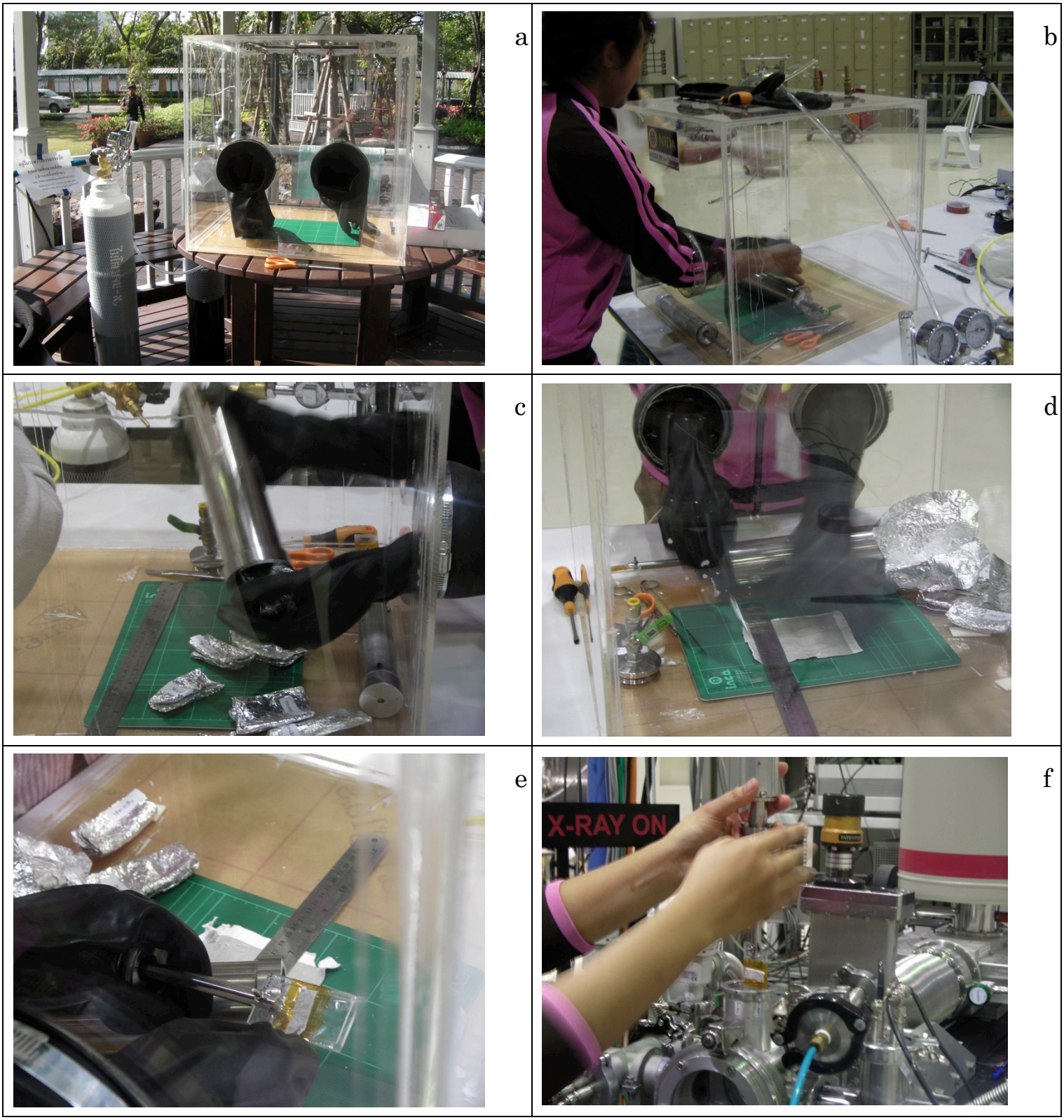


Fig. 4. Anoxic preservation processes; a) Pressure Controlled Glove Box (PCGB) for anoxic preservation at sampling site, b) Installation of APSC inside the PCGB, c) Removal of QFFs from APSC, d) Cutting of QFFs, e) Attachment of QFFs on sample holder, f) Installation of QFFs inside DCM.

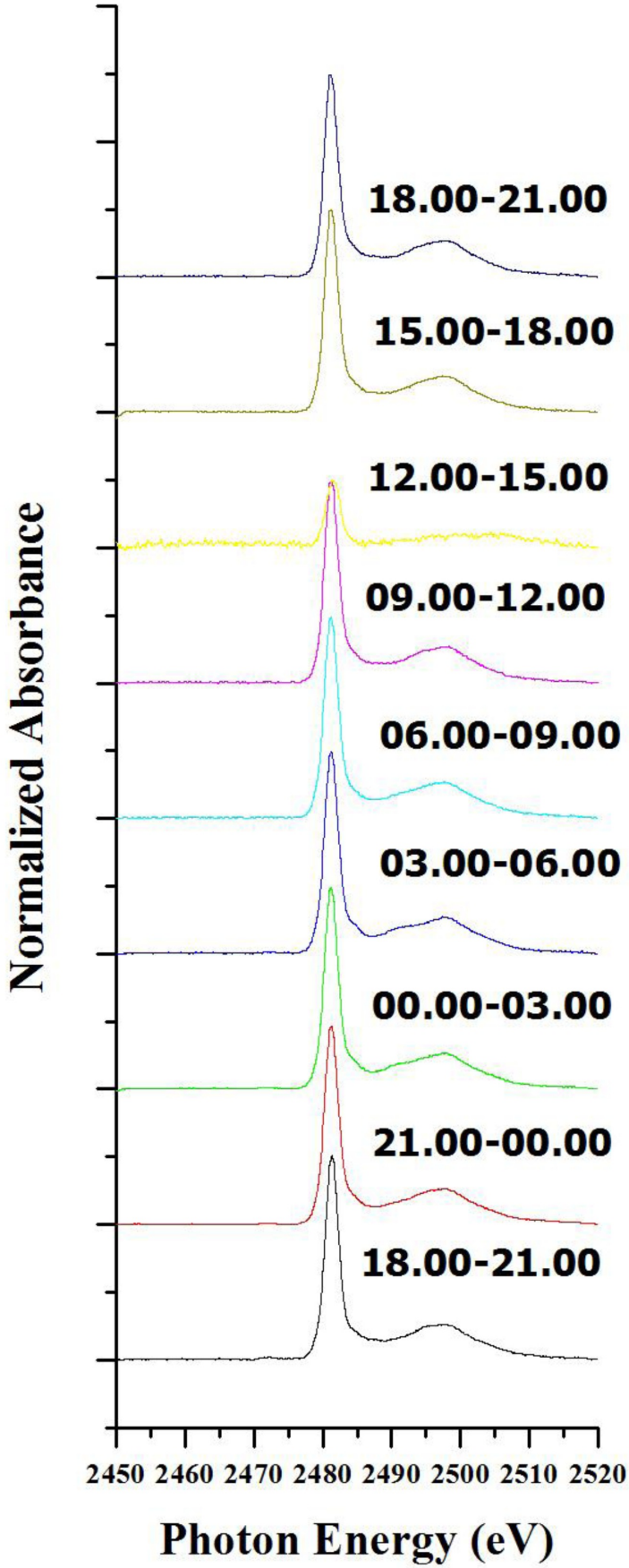


Fig. 5. Sulfur K-edge XANES spectrum of urban PM_{10} collected at NIDA, Bangkok.

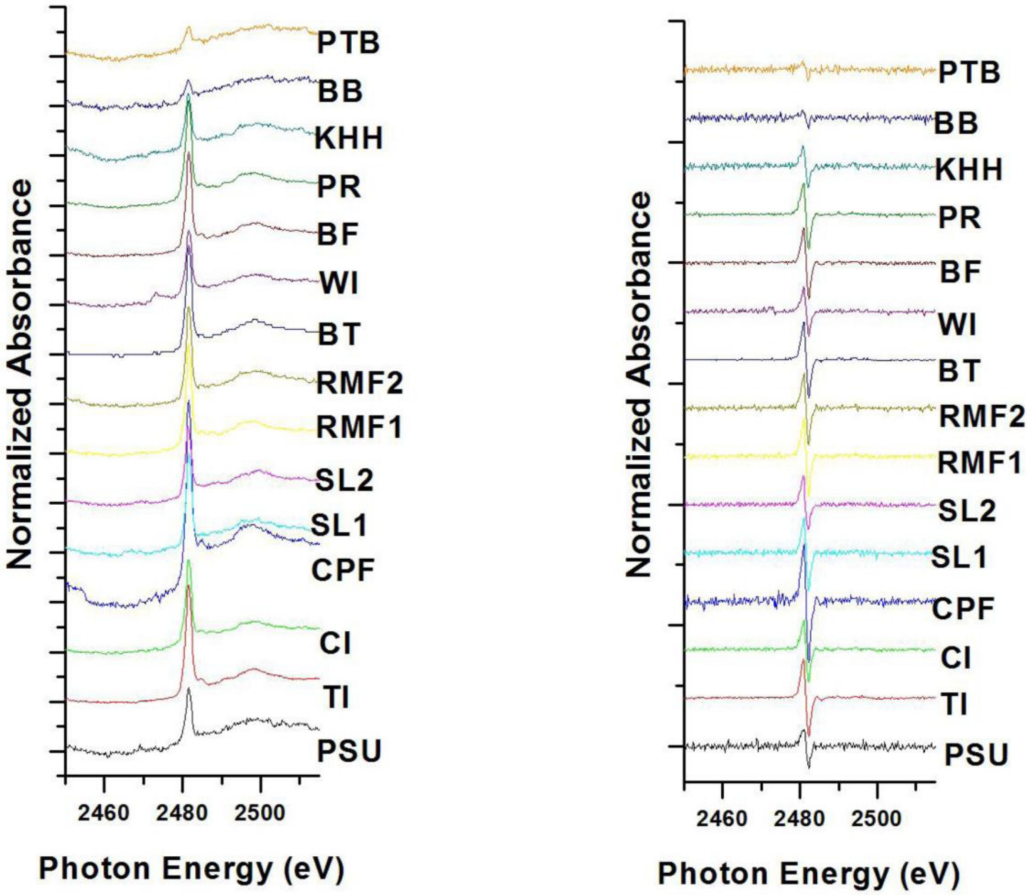


Fig. 6. Comparison of sulfur K-edge XANES and its second derivative spectrum of PM_{10} from various emission sources in Songkla province.

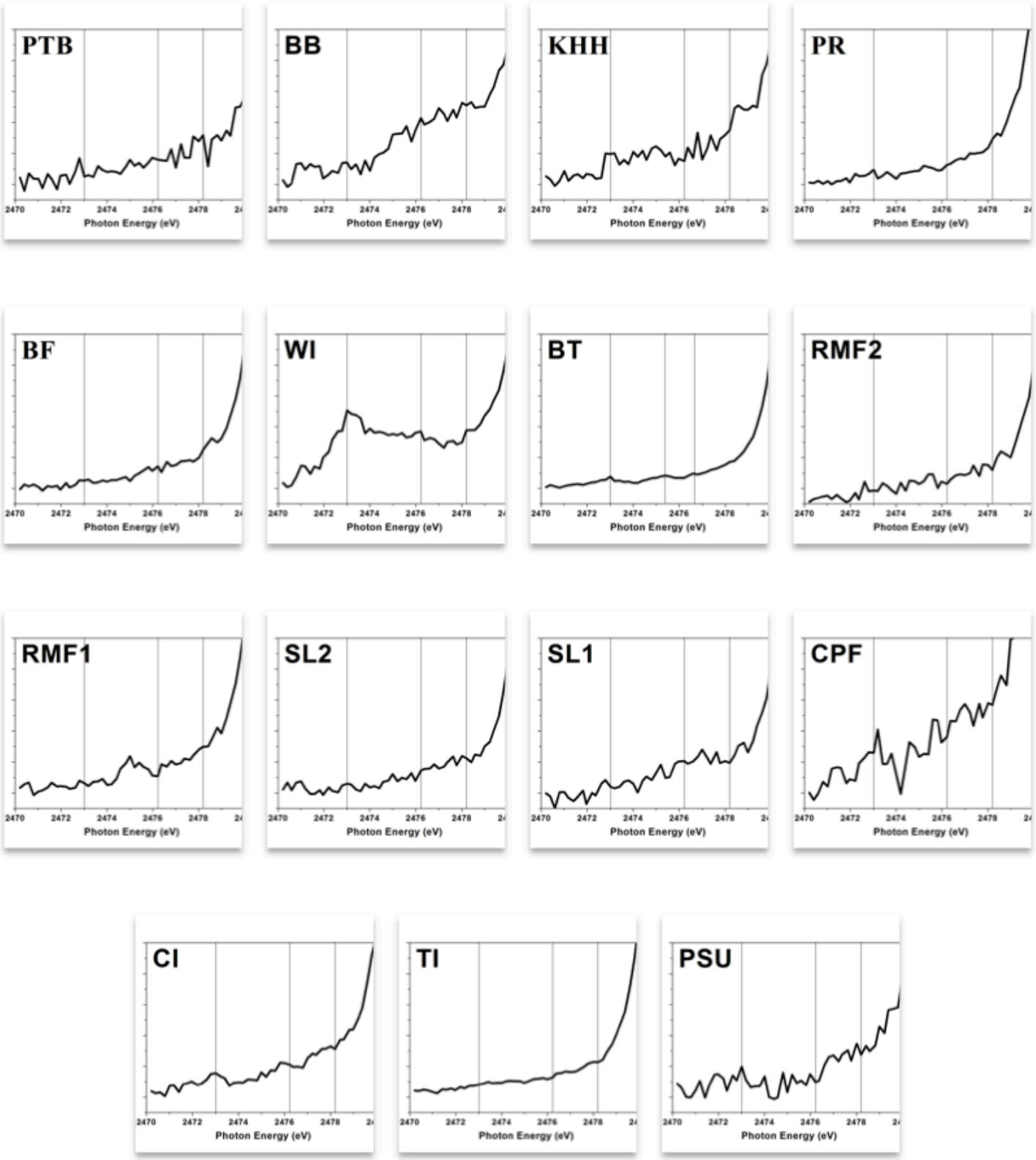


Fig. 7. Comparison of sulfur K-edge XANES of PM_{10} collected at various emission sources from 2,470 – 2,480 eV.

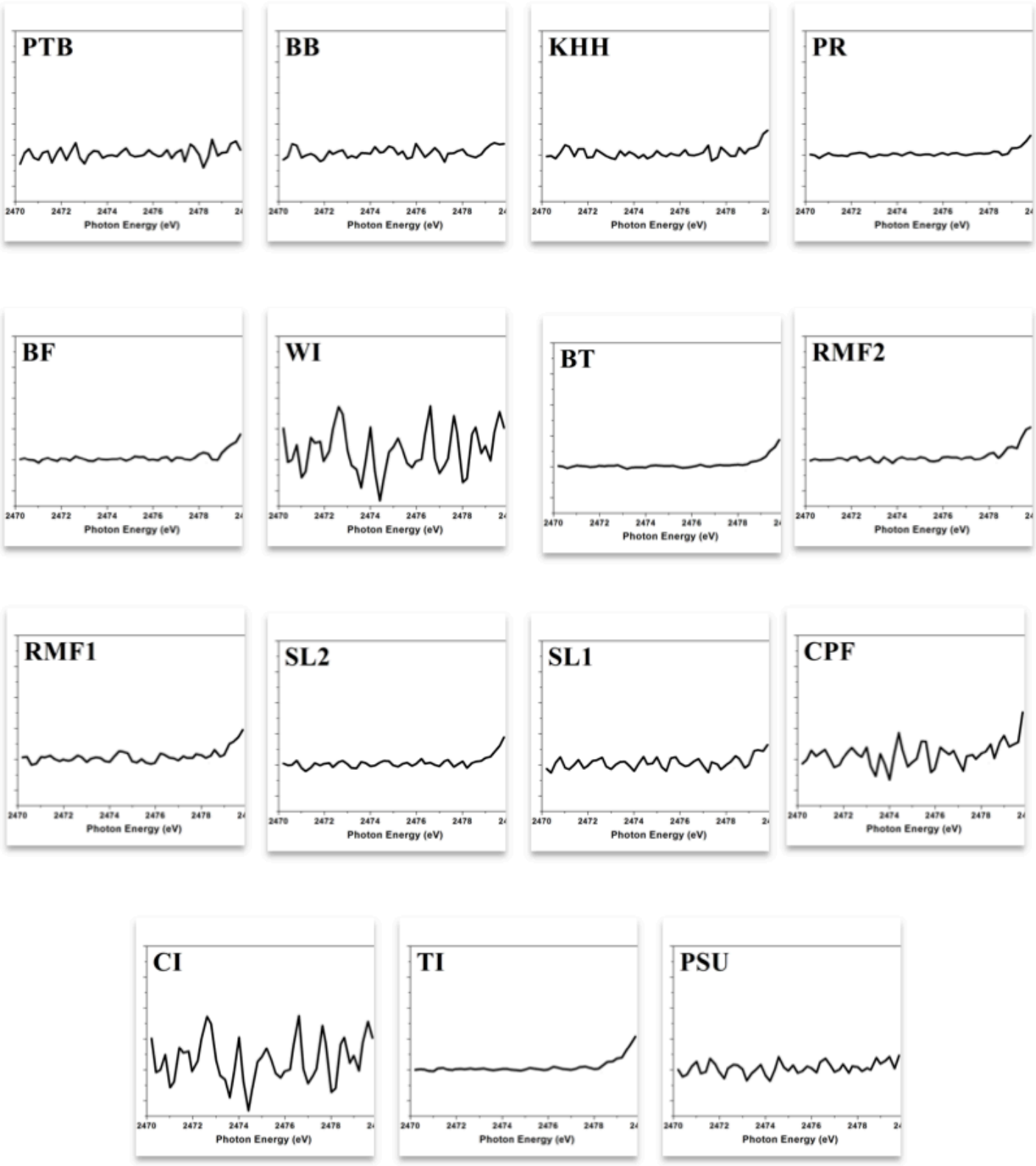


Fig. 8. Comparison of second derivative of sulfur K-edge XANES of PM_{10} collected at various emission sources from 2,470 – 2,480 eV.

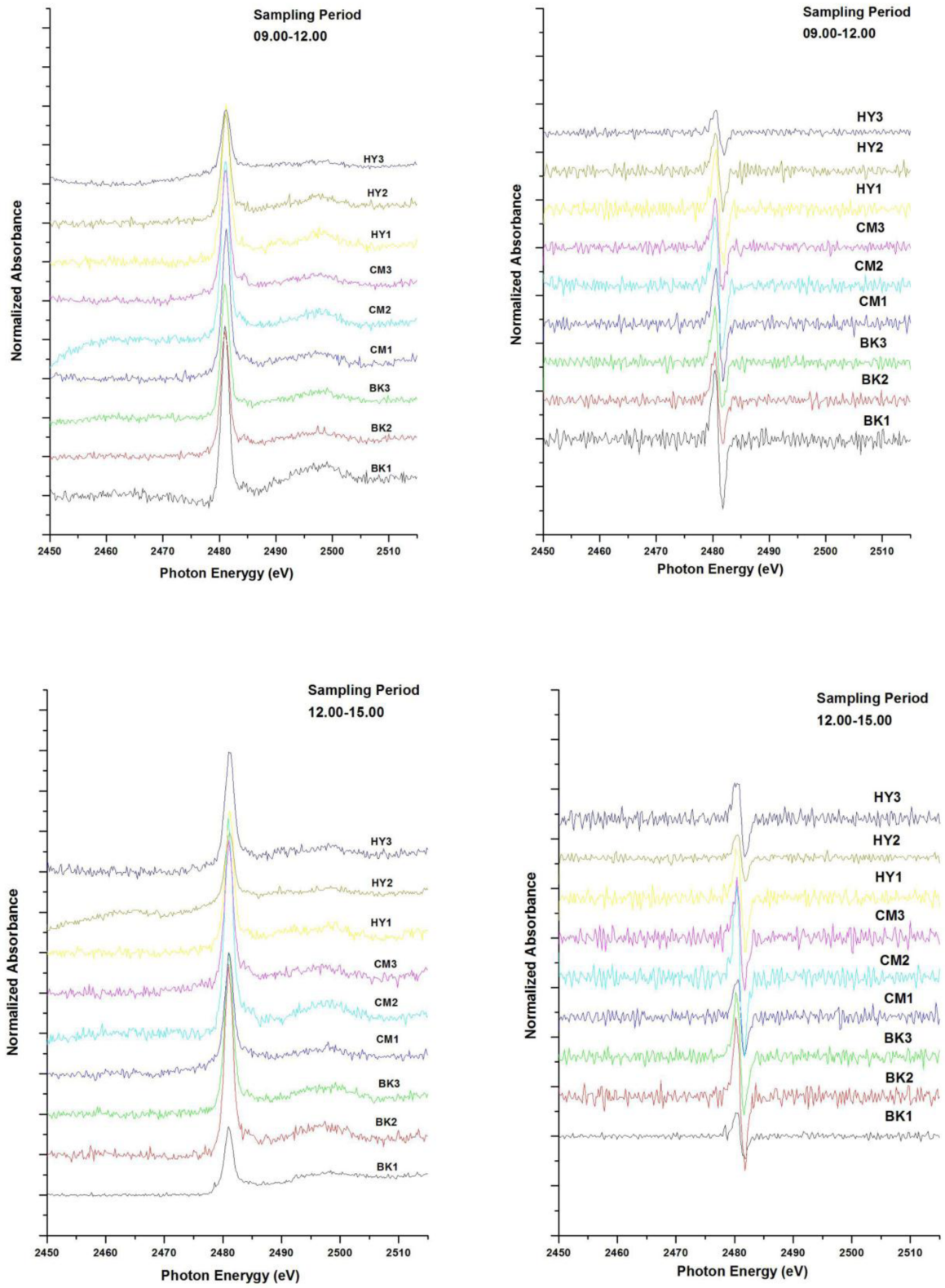


Fig. 9. Sulfur K-edge XANES and its second derivative spectrum of urban PM_{10} collected at three different heights at Bangkok (BK), Chiang-Mai (CM) and Hat-Yai (HY).