Identification of impregnated activated carbon used as adsorbent in protective equipment for chemical warfare agent

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Abstract. It is known that X-rays spectroscopy has been developed to apply to many advantages. In this work, Scanning electron microscope coupled with energy dispersive X-ray spectrometer (SEM-EDS) and synchrotron radiation facilities, such as micro-beam X-ray fluorescent spectroscopy (µ-XRF) and X-ray absorption spectroscopy (XAS) have been carried out to study on impregnated activated carbon samples that have been used as a chemical warfare agent adsorbent in military protective equipment. The elemental composition and distribution of sample surface have been analyzed. Their microstructures were highly porous. The results showed a detection of many kinds of metals, especially chromium (Cr), iron (Fe) and copper (Cu) with different from elemental distribution. It was also detected Cr(VI) which was a carcinogen in some samples. It is proposed that these methods can be used as fingerprint to identify various types of adsorbent.

1. Introduction

It is well known that military conflicts and terrorist incidences in counting from the present highlighted the importance of armed or emergency response operations for dealing with the military and terrorist related events, involving the CBRN (Chemical, Biological, Radiological and Nuclear) agents. It is defined that the chemical warfare is a type of warfare which is operated by using the chemical agents that are incapability, damaging, toxic and lethal components. They are cheap and toxic compounds which are easily made and stored. Meanwhile, the development of chemical industry around the world in nowadays has contributed to a higher risk of exposure to the TICs (Toxic Industrial Chemicals). They are some considered as the CWA (Chemical Warfare Agent) and can be also a consequence of a terrorist attack. The undertaking for the first response remains with individual nations to build on their resources to respond and mitigate the consequence of an emergency, especially to the human being and the environmental contamination. Protective equipment for the chemical warfare is designed to provide protection from serious injuries or illnesses affected from action with the CWA which effect on the respiratory system and parts of the body, such as eyes and skin, etc. The primary protection against the CWA is the respiratory protection by using a protective mask. While the body protection with a protective clothing is also significant. A properly fitted protective mask combined with a protective suit covering the body can offer an excellent protection.

It is also noted that activated carbon is the most common material used to remove toxic gases and vapors from breathable air. It is usually applied as an adsorbent for air filtration both in the military and civilian activities, because of its distinction adsorbing properties, availability durability, lifespan and low cost [1-10]. Activated carbon impregnated with metal salts or metals (such as Fe, Cr, Cu, Ag, and
Ni) is being used in the military filtration system. Cr which contained Cr(VI) which is specifically added to blood agent destruction is toxic as a carcinogen [11-12]. However, it is shown that the granular and powdered activated carbons are less expensive, while the fibrous and fabric forms are very highly expensive.

Figure 1 shows the military gas mask equipped with a canister which separates into internal and external canisters. The internal canister is a slightly curved triangular in shape which composed of light-weight filter material that fits into the cheek pouches of the mask, as shown in figure 2a(3). While the external canister is normally a cylindrical in shape which constituted of a multilayer component of different filters: an aerosol filter which consists of metal grids and fold cellulose sheets or glass fibers and a layer of absorbent, as shown in figure 2b(3). The permeable protective suit as shown in figure 2 is composed of a layer of finely distributed activated carbon, either bound in polyurethane foam or particles, which bound between two layers of textile. The activated carbon consisting layer permits water vapour released from the body to pass through. While, the activated carbon adsorbs the CWA and thereby prevents them from passing through the skin.

**Figure 1.** The military protective mask couple with internal canister (a) and external canister (b)

In this work, the impregnated activated carbon samples which were selected from different sources were aimed to characterize the elemental composition and distribution, structure and oxidation state of chromium by using SEM-EDS, μ-XRF and XAS.
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(a) Types of suit

(b) Multilayer textile

Figure 2. The permeable protective suit

2. Experimental

2.1 Sample
Fourteen impregnated activated carbon samples were selected from different sources, as illustrated in Table 1.

2.2 Methods
2.2.1 SEM-EDS. The samples were gold-coated using SC7620 sputter coater (Quorum, UK). Morphologies and elemental compositions of the samples were analyzed using QUANTA 450 scanning electron microscope (SEM) (FEI Company, USA) coupled with X-Max® 50 energy dispersive X-ray spectrometer (EDS) (Oxford Instruments, UK) at the Synchrotron Light Research Institute, Thailand
(SLRI). The SEM was operated at 20 kV accelerating voltages. Quantitative analysis of XRF spectra was performed using the AZtech program (Oxford Instruments, UK).

**Table 1.** The selected impregnated activated carbon samples

| Sample | Manufactured | Form       |
|--------|--------------|------------|
| A      | WW II era    | Broken GAC |
| C      | Thailand     | Broken GAC |
| D      | Thailand     | Broken GAC |
| E      | USA          | Broken GAC |
| F      | USA          | Broken GAC |
| G      | USA          | Broken GAC |
| H      | USA          | Broken GAC |
| J      | USA          | Broken GAC |
| K      | USA          | Broken GAC |
| L      | UK           | Shaped GAC |
| M      | UK           | Shaped GAC |
| P      | USA          | Broken GAC |
| Q      | USA          | Broken GAC |
| R      | Czech Republic | Broken GAC |

$^a$CWA, TICs and Training denoted to canister used for Chemical warfare agents, Toxic industrial chemicals and Training chemicals, respectively

$^b$broken GAC and shaped GAC denoted to broken and shaped granular activated carbon, respectively

2.2.2 FESEM. The surface topography and porosity of samples were investigated using MIRA3 FE SEM (TESCAN, Czech Republic) at SLRI. FE SEM was operated with 20 kV accelerating voltages.

2.2.3 μ-XRF. SR μ-XRF measurement which was used to analyze elemental composition and distribution were performed at the BL6b of the SLRI, Thailand. Samples were wrapped with PP film, mounted on acrylic plate, and placed on the sample holder. The 2-10 keV white beam with a size of 5 x 2 mm (V x H) was magnetic focused by a polycapillary half lens in order to deliver X-ray beam with a size of 30 µm onto the sample. SR μ-XRF mapping was performed with 30 µm step size in x- and y directions with dwell time of 30 seconds per point. The area of 300 x 300 µm was selected for mapping using a camera with 10X macro lens prior to the SR-beam exposure. The Vortex Si drift detector with resolution of 160 eV was used for fluorescence yield detection. The X-ray fluorescence data were processed by PYMCA software for creation of elemental mapping in the samples.

2.2.4 XAS. For XAS measurements, the samples were sealed in polypropylene bags and measured as received. Due to the expected low concentration of Cr in the samples. All samples were measured in the fluorescence mode using the 19-element Ge detector available at the BL1.1W. Cr foil was used for energy calibration of the Cr K-edge. The XANES spectra of chemical standards Cr2O3, CrO2 and CrO3 were also measured along with the samples as reference for oxidation states 3+, 4+ and 6+. The spectra were processed and normalized using Athena.

3. Results and discussions

Table 2 showed the elemental composition of impregnated activated carbon samples investigated using SEM-EDS and SR μ-XRF. It was evident that the samples were mainly composed of C and O. Minor amounts of Cu and Cr were all present. Amount of C contented for approximately 51.0 and 90.9 wt%, while O was between 7.1 – 34.7 wt%.

The presence of Cl and P was a result of the chemical activation process that used ZnCl₃, and ZnCl₃ and H₃PO₄ as activating agents, respectively [2]. The contents of Al (0.1-1.1 wt%), Si (0.1-1.0 w%), Mg (up to 0.2 wt%), Ca (up to 0.5 wt%), Fe (up to 0.5 wt%), and Ti (up to 0.3 wt%) in the samples corresponded to their contents from the original raw materials which were naturally gas adsorbents for CO and NH₃ [3, 9]. Fe content can be originated from impregnation process. In previous research, activated carbon impregnated with iron salt was utilized as adsorbent for S (II) [3] and As (V).
compounds [13] which were the main compositions of the blister agents that classified as sulfur mustard; 1-chloro-2-[chloroethyl]sulfonyl]ethane, and lewisite; 2-chloroethylarsonous dichloride, respectively [1-10]. The presence of K (up to 2.9 wt%) was caused by impregnation of K in activated carbon, which enhances the specific adsorption and catalyst properties [5].

Table 2. Elemental composition of impregnated activated carbon samples

| Element wt% | Method | Sample | C | D | E | F | G | H | J | K | L | M | P | Q | R |
|-------------|--------|--------|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C           | EDS    | 89.2   | 90.9 | 87.0 | 75.8 | 75.0 | 51.0 | 61.0 | 72.4 | 71.7 | 70.2 | 69.5 | 79.0 | 57.0 | 71.6 |
| O           | µ-XRF  | N/D    | N/D  | N/A  | N/D  | N/D  | N/A  | N/A  | N/D  | N/D  | N/D  | N/D  | N/D  | N/A  | N/A  | N/A  |
| Ar          | µ-XRF  | N/D    | N/D  | N/A  | N/D  | N/D  | N/A  | N/A  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/A  | N/A  |
| Al          | µ-XRF  | 0.3    | 0.1  | 0.1  | 0.8  | 0.8  | 0.6  | 0.5  | 0.6  | 0.6  | 0.4  | 0.4  | 0.2  | 1.1  | 0.6  |       |
| Si          | µ-XRF  | √      | N/A  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/A  |       |
| P           | EDS    | 0.2    | 0.1  | 0.2  | 0.6  | 0.7  | 0.5  | 0.5  | 0.4  | 0.5  | 0.2  | 0.4  | 0.3  | 1.0  | 0.1  |       |
| Cl          | µ-XRF  | √      | N/A  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/A  |       |
| K           | EDS    | 2.2    | 0.7  | 2.9  | N/D  | N/D  | N/D  | N/D  | 0.2  | 0.2  | 1.1  | 0.2  | 0.1  | 0.2  | 1.2  |       |
| Ca          | µ-XRF  | √      | N/A  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/A  |       |
| Ti          | µ-XRF  | √      | N/A  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/A  |       |
| Cr          | EDS    | 0.3    | 0.1  | 0.3  | 0.1  | 0.1  | 0.1  | 0.1  | 0.1  | 0.4  | 0.5  | N/D  | N/D  | N/D  | N/D  |       |
| Fe          | µ-XRF  | √      | N/A  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/D  | N/A  |       |
| Mg          | µ-XRF  | 0.1    | 0.1  | 0.1  | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | N/D  | 0.2  | N/D  | N/D  | N/D  | N/D  | N/A  |
| Cu          | µ-XRF  | 0.1    | 0.1  | 2.8  | 1.8  | 8.9  | 15.2 | 6.7  | 6.3  | 5.0  | 5.9  | 0.1  | 0.1  | 0.1  | 9.1  |       |

N/D denotes to no element detected, √ denotes to element detected, and N/A denotes to no analysis.
By using EDS: Sample D, Na 0.1; Sample G, Zn 12.8, Mo 2.2, Na 1.4; Sample P, Na 0.3; Sample Q, Na 0.6, F 1.6, Sb 0.5 wt%
By using µ-XRF: Sample E, Zn; Sample F, Zn; Sample G, Zn; Sample Q, Sb, Sc, Mn, Zn

Cu and Cr were effective adsorbents of blood agents such as cyanogen chloride, hydrogen chloride, and cyanogen [11, 14-15]. In military application, it was proposed that large amount of Cr (VI) can promote cyanogen chloride destruction [11, 16]. However, the modern filter canisters were stopped in production and replaced with other types of impregnated activated carbon [11-12, 17] due to Cr⁶⁺ compounds were toxic and carcinogenic. Ar was detected in samples J, K, L, M and P by using SR µ-XRF technique. The detectable of Zn (in sample E, F, G and Q), Mn (in sample Q), Sb (in sample Q) and Sc (in sample Q) were also found. While, some elements, such as Na (in sample D, G, P, and Q, up to 1.4 wt%), Zn (in sample G, up to 12.8 wt%), Mo (in sample G, up to 2.2 wt%), F (in sample Q, up to 1.6 wt%) and Sb (in sample Q, up to 2.5 wt%) were also analyzed by using the EDS.

It is proposed that the impregnated element used as adsorbents in sample A which used in the external canister during the World War II was mainly Fe. For other ones (which were newer type canisters), not only Fe but also Cr and Cu were impregnated with activated carbon in order to neutralize the effect of CWAs. Sample C and D which produced from the manufacturing factory in Thailand during 2017 were appropriated for environmental and industrial applications. Sample E and F were used in the internal canister between 1960 -1990. Sample G, H, J, K, L and M were the newer ones made between 2004-2012, which used in the external canister. Sample P and Q were coated on the fabric of textile used in the protective suit that produced in 2000. Sample R was contained with the external canister made in 2018 which was the newest and most safety one.
Ag was not found in both EDS and SR μ-XRF results of any sample. It was suggested that it was due to the accuracy limitation of these techniques for analysis of the investigated samples with the elemental composition below 0.1 wt%. The advanced works by using a transmission electron microscope (TEM), it was shown that Ag was presented in the form of the nanoparticle in some samples. In general, the activated carbon which impregnated with 0.05 wt% Ag was classified as ASC-Whetlerite [17-19]. It revealed inhibitory effects against some bacteria, virus, algae and fungi which were classified as biological warfare agents (BWAs). Heavy metals such as lead or mercury also exhibited these effects, but they originated high toxicity on human [18].

(a) SEM macrographs of impregnated activated carbon samples
By using the SEM (all samples) and FESEM (some samples), the samples possess the highly porous structure of cavities, cracks, and attached fine particles on their surface, as shown in figure 3(b). They showed the macropores, mesopores and micropores with the pore radius (r) of r>50 nm, 50>r>2 nm, and r<2 nm, respectively. It is revealed that these porous structures are used to remove the gases and vaporous components. The macropore and mesopore enable contaminant transportation to the micropore, while the micropore which result in the increasing of the surface energy is able to adsorb a variety of the chemicals [7-9, 20].

SR µ-XRF results provided qualitative information about the elemental compositions of the samples, which were in agreement with the EDS results. However, some elements with low atomic number and/or low concentrations were not detected due to the limit of detection of this technique.

Results using the SR XAS which the spectra were processed using Athena [21] and the normalized spectra were shown in figure 4. The standard spectra in figure 4(a) and (b), showed that at the post edge energy of various compounds were different. Although the Cr$^{6+}$ which was non-oxide compounds, it presented the characteristic pre-peak at the 5993 eV [22]. They were classified into 6 groups. It was analysed that Cr$^{6+}$ with the pre-peak at 5993 eV was found in Group 1, 2 and 3, as shown in figure 4(c), (d) and (e), respectively. While the pre-peak for the Cr$^{3+}$ was not appearing at this energy, as shown in figure 4(f), (g) and (h). Furthermore, it was also found that the concentration of the Cr$^{6+}$ contained in Group 1 > Group 2 > Group 3, as shown in figure 4(i).
(a) Chemical standards with various oxidation states
(b) Chemical standards with various compounds

c) Group 1

(d) Group 2

e) Group 3

(f) Group 4

(g) Group 5

(h) Group 6
Comparison between Group 1, 2 and 3

Figure 4. The XAS spectra of the selected impregnated activated carbon samples

4. Conclusion
The SEM-EDS results provided the information on the elemental composition of impregnated metals in the carbon-based structure. FE SEM results revealed the pore size and morphology. SR μ-XRF results of elemental composition and distribution were in agreement with the EDS results. The use of adsorbents for impregnated activated carbon in Thailand has been developed from solely Fe (in the World War II era) to Cr, Cu, and Fe (at the present time). It was also found that the Cr detected in some samples was presented as Cr$^{6+}$.

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