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# Intercalation of metallic potassium and fullerene $C_{60}$ into natural graphite

**Zemanova Eva[1], Klouda Karel[1, 2], Lach Karel[3], Weisheitelova Marketa[4]**

[1]State Office for Nuclear Safety, Prague, CZ
[2]VŠB-Technical University of Ostrava, Faculty of Safety Engineering, Ostrava, CZ
[3]National Institute of Public Health based in Ostrava, Ostrava, CZ
[4]National Institute for Nuclear, Chemical and Biological Protection, Kamenna, CZ

**Email address:**
Eva.Zemanova@sujb.cz (Z. Eva)

**Abstract:** Graphite was intercalated with potassium to produce $C_8K$ intercalate which was subsequently exposed to suspension of fullerene $C_{60}$ in toluene. The resulting product stabilized potassium against effects of the atmosphere. The prepared product was exposed to tests of thermal stability and other analyses, such as FT-IR, SEM and Energy-dispersive X-ray Spectroscopy (EDAX) with the objective to describe arrangement of potassium in the carbon matrix. The product with stabilized potassium in a carbon skeleton (graphite – fullerite) is partly able to resist the atmosphere, it is relatively thermally stable (up to 150 $^{o}$C) and the energy effects of its decomposition are low up to 600 $^{o}$C. The product may be used in numerous applications – catalysis, hydrogen storage and as an admixture component in aerosol fire suppression systems.

**Keywords:** Graphite, Intercalate, Potassium, Fullerene

## 1. Introduction

Graphite is an allotropic modification of carbon with $sp^2$ bonds and made up of layers of mutually interconnected hexagonal rings. The layers are arranged in parallel planes 335 pm apart. Carbon atoms in the adjoining layers are not chemically bonded to each other and they are attached by weak Van der Waals forces that make it possible for various atoms or molecules in liquid or gaseous form to get in between the carbon layers. The resulting substances are called intercalation compounds of graphite and their characteristic parameter is the so-called "degree of intercalation", which indicates the number of carbon layers between two layers of an intercalated substance (Klouda, 1985).

Depending on a type of the intercalated substance the graphite plane may be either an acceptor or donor of electrons. Another option is the so-called $\pi$–complex created by intercalation of substances of $AX_y$ type, where A is a metal or non-metal with a high valence status, X is an electronegative element and y is a stoichiometric coefficient.

Intercalates of graphite with alkali metals have been known since 1930s. They are called intercalates of the first degree with the formula $C_8M$ (M=K, Rb, Cs), i.e. they are characterized by a stacking sequence of layers of carbon and alkali metal.

Intercalates of graphite with alkali metals or in combination with other metals have been used in a number of applications as catalysts, e.g. for synthesis of ammonia, synthesis of carbohydrates by hydrogenation of carbon oxides, hydrogenation of olefins, they have sorption properties etc. Substituents can be chemically bonded to graphite under certain conditions by fluorination or oxidization (Klouda, 1985).

Fluorination of graphite with elemental fluorine at 400-600°C produces a covalent compound called fluorographite $CF_x$, x = 0.25-1.12, depending on reaction conditions of the fluorination (Klouda, 1985). Oxidization of graphite with strong oxidizing agents produces graphene oxide (GO), which is a precursor for chemical preparation of graphene (Makharza et. al., 2013).

Graphene can be prepared by a chemical method which consists in reduction of oxidized carbon (functional groups) in GO with various reducing agents (hydrazine, metal hydride, hydrogen, hydrogen iodide) or reducing methods, such as reflux in a polar solvent, microwaves irradiation,

electrochemical reduction (Dreyer et. al., 2010).

Another modification of carbon from the realm of nanoparticles are fullerenes: the best known representative is fullerene $C_{60}$ with spherical molecules consisting of 20 hexagonal and 12 pentagonal rings, crystallizing in a cubic system (fullerite). A fullerene molecule may be subject to nucleophilic and radical reactions (Troshin et. al., 2008).

In this work we have prepared graphite-potassium intercalate which was subsequently exposed to suspension of fullerene in toluene in order to intercalate fullerene between the graphite layers.

# 2. Experimental Part

## 2.1. Materials Used

Graphite PM – very fine crystalline powder graphite, mesh 0.025mm, Supplier: Koh-I-Noor Netolice, Czech Republic

Fullerene $C_{60}$, 99.5% purity, SES Research, Houston USA

Toluene, ethanol, metallic potassium – Supplier: Sigma - Aldrich

## 2.2. Measuring Instruments

ATR analysis by means of FTIR spectrometry was performed using the spectrometer Brucker Aplha/FT-IR, ART crystal (identified as Platinum Diamond 1 Ref1), software OPUS 6,5, source j IR SiC Globar. The number of spectrum scans was 24, resolution 4 cm$^{-1}$, spectrum range 375-4000 cm$^{-1}$.

Thermal analyses TGA and DSC were performed on STA 1500, Instrument Specialists Incorporated-THASS, analytical scale SUMMIT, SI 234-4, at flow rate 20 ml/min., heating rate 10°C/min., ceramic crucible, diameter 5 mm and height 8 mm, degradation medium: air.

Morphology was determined with SEM Phenom FEI and SEM FEI Quanta 650 FEG (USA).

## 2.3. Preparation of Intercalate $C_8K$ and its Subsequent Reaction with Fullerene

Potassium (1.07 g) and graphite (2.4 g) were placed into a three-neck glass flask with inert $N_2$-atmosphere inside. The mixture was gradually heated for 30 minutes to reach the temperature ca. 90-100°C in an oil bath in which the flask was immersed. At that temperature the mixture was stirred for 2 hours and subsequently cooled to the laboratory temperature and solution (suspension) of fullerene (0.7 g $C_{60}$) in toluene (35-40 ml) was added, oversaturated at the laboratory temperature. The reaction mixture was stirred for 5 days.

Then the mixture was decomposed by 30 ml of ethanol (no hydrogen was released). After 30 minutes the flask content was placed into a beaker with ethanol (40 ml) and the mixture was filtered by vacuum filtration.

The filtration and drying were performed without any protective atmosphere. Drying was performed for a relatively short period of time at 55°C for safety reasons because the thermal stability was not known and it was followed by FT-IR analysis, TGA and DSC analysis and electron microscope imaging, including Energy-dispersive X-ray Spectroscopy (EDAX).

## 2.4. IR Spectrum of the Product

The obtained IR spectrum is shown in Figure 1. The main absorbance peaks were found in the range 1562-500 cm$^{-1}$. The biggest peak 1562 cm$^{-1}$ has been attributed to the C-C vibration of the circular skeleton. Some frequencies corresponded to the published values (Giannozzi and Andreoni, 1996) for $K_6C_{60}$, e.g. 1476 cm$^{-1}$, 1359 cm$^{-1}$, 656 cm$^{-1}$, 416 cm$^{-1}$. In general, inorganic salts $K^+X^-$ demonstrate vibrations in the range 700-400 cm$^{-1}$. It is not possible to avoid or not to consider potential assignment of $\nu$(O-O) of the superoxide ion $O_2^-$ (Itoh et al., 2006) the formation of which can be expected in contact with atmospheric environment. The vibration at 3230 cm$^{-1}$, which corresponds to the –OH group, can be explained with adsorbed ethanol as a result of the short period of drying.
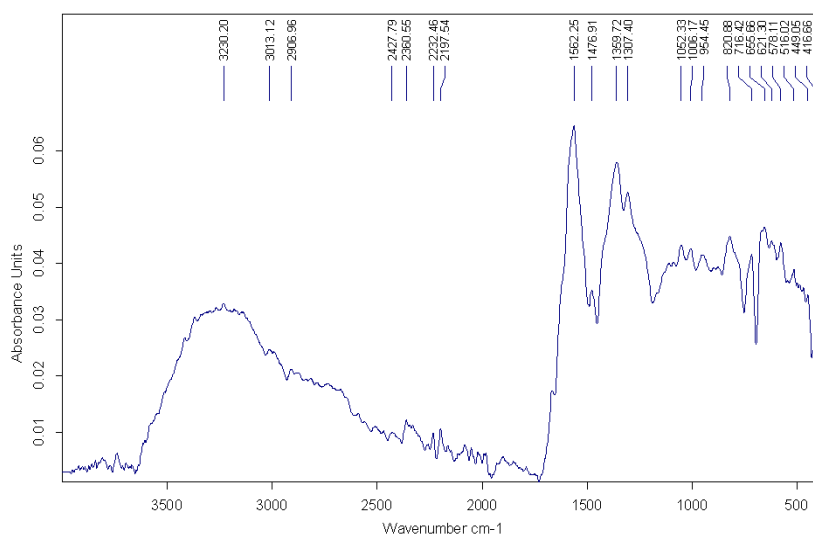


*Fig. 1. IR spectrum of the product of $C_8K$ reaction with fullerene*

## 2.5. Thermal Analysis of the Product

Based on material balance of the individual components of the mutual reaction the summary formula of the product should be $C_{200}K_{27}C_{60}$, i.e. the content of carbon in form of graphite 57.55%, the content of carbon in form of fullerene 16.7% and 25.6% of potassium. The DSC curve (Figure 2) in the measured range featured two peaks corresponding to endothermic reactions with weight loss of 5-6% and we anticipate that this was mainly due to desorption of ethanol. After a further increase of temperature two partly overlapping peaks were identified which corresponded to exothermic thermal processes with heat release as shown in Table 2. The shape of the curve suggests that there is another exothermic process which would have occurred if we had further increased the temperature of the analysis. The weight loss of the samples (see TGA Tab. 1) was essentially linear and it depended on temperature; up to the temperature of 600°C the weight loss was 36%.

We can anticipate that while the sample was heated in the air and before fullerene was added potassium intercalated into graphite to form a pre-defined intercalate $C_8K$. We also anticipate that the added solution (suspension) of fullerene intercalated into graphite (the distance between the layers had expanded) which was probably associated with intercalation of potassium into the crystalline system of $C_{60}$-fullerite molecules to form $K_xC_{60}$, where x=1- 6. The content of potassium in the intercalate graphite is more than four times higher than that corresponding to the maximum stoichiometry of the $K_6C_{60}$ salt. We assume that the excessive potassium is further intercalated between the layers of graphitic carbon. We can only speculate about the position of K-fullerite salts in respect to graphite. The material is non-homogenous which has been also demonstrated by electron microscopy and by EDAX (see Figures 4 and 5 below). EDAX also identified oxygen in a part of the sample while we can assume that a partial oxidation of potassium occurred during the product processing (filtration, drying). In case of thermal exposure we anticipate reaction of potassium with atmospheric oxygen to produce potassium superoxide $KO_2$ (the compound alone is thermally stable up to 550°C) but in presence of an oxidizable substance it may provide oxygen and oxidize carbon, both in the fullerene molecule ( we do not anticipate priority) and also partly in the graphite. A lower weight loss during the TG analysis can be also explained by partial contamination of the sample with potassium carbonate (reaction of $CO_2$ with $KO_2$), which may also operate as a fire retardant.
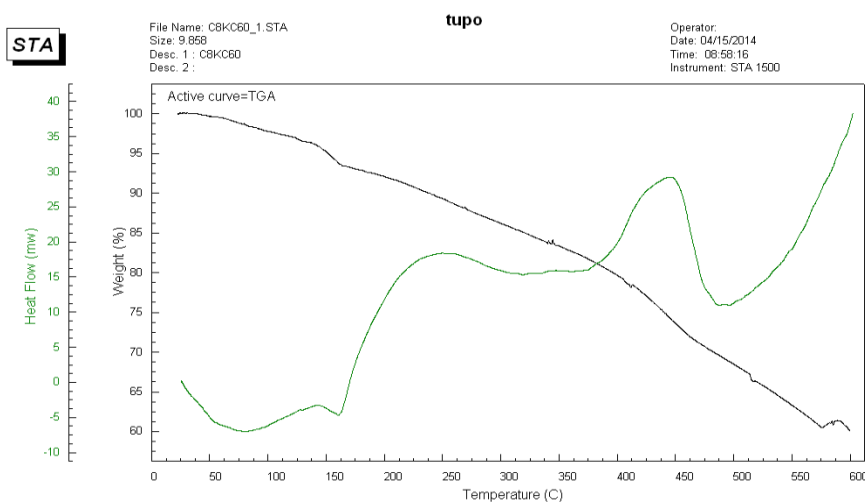


**Fig. 2.** Thermal analysis of the product of $C_8K$ reaction with fullerene

**Tab. 1.** Division of the TGA curve into temperature intervals

| Sample No. | Interval No. | Temperature range (°C) | Weight loss (%) |
|---|---|---|---|
| *) $C_{200}K_{27}C_{60}$ | 1 | 25,0 – 51,3 | 0,3 |
| | 2 | 51,3 – 126,8 | 3,0 |
| | 3 | 126,8 – 161,9 | 3,0 |
| | 4 | 161,9 – 374,1 | 11,9 |
| | 5 | 374,1 – 472,9 | 10,9 |
| | 6 | 472,9 – 576,4 | 10,3 |

*) Theoretical summary formula based on material balance of the individual components
(degradation medium: air , air flow 20 ml/min, temperature regime 25-600°C, heating rate 10°/min, sample weight 8.6 mg)

| Sample No. | Thermal process No. | Temperature range (°C) | ΔH (kJ/kg) ** | $H_{fl}$ (mW) | Σ ΔH (kJ/kg) |
|---|---|---|---|---|---|
| *) $C_{200}K_{27}C_{60}$ | 1 | 25,0 – 104,7 | 182,9 | 1,4 | |
| | 2 | 104,7 – 156,4 | 26,3 | 2,3 | -873,5 |
| | 3 | 156,4 – 302,5 | -572,1 | 23,1 | |
| | 4 | 370,7 – 482,3 | -510,6 | 13,2 | |

** ΔH = thermal energy released /absorbed according to the DSC curves
(ΔH > 0…endothermic process , ΔH < 0…exothermic process )
*) Theoretical summary formula based on material balance of the individual components

## 2.6. Morphology of the Product Prepared by Reaction of $C_8K$ Intercalate with Fullerene – Electron Microscope Images

We investigated the prepared product with a scanning electron microscope with energy-dispersive micro-analyzer and we proved that the ratio of carbon and potassium was non-homogeneous. The lighter parts (see Fig. 3) are always enriched with potassium and, on the contrary, the darker parts are enriched with carbon. Parts with a higher content of potassium have different morphology (crystalline), while parts with dominating carbon have a layered structure. Changes of the mutual ratio of carbon and potassium in a selected crystal are visible in Figure 4.

The elemental analysis of the crystals identified also presence of oxygen and it confirmed non-homogeneity of the material (see the EDS spectrums on Figures 5 a) $C_{10}K_2O$, b) $C_{28}K_{1,6}O$, c) $C_{26}K_{1,33}O$).
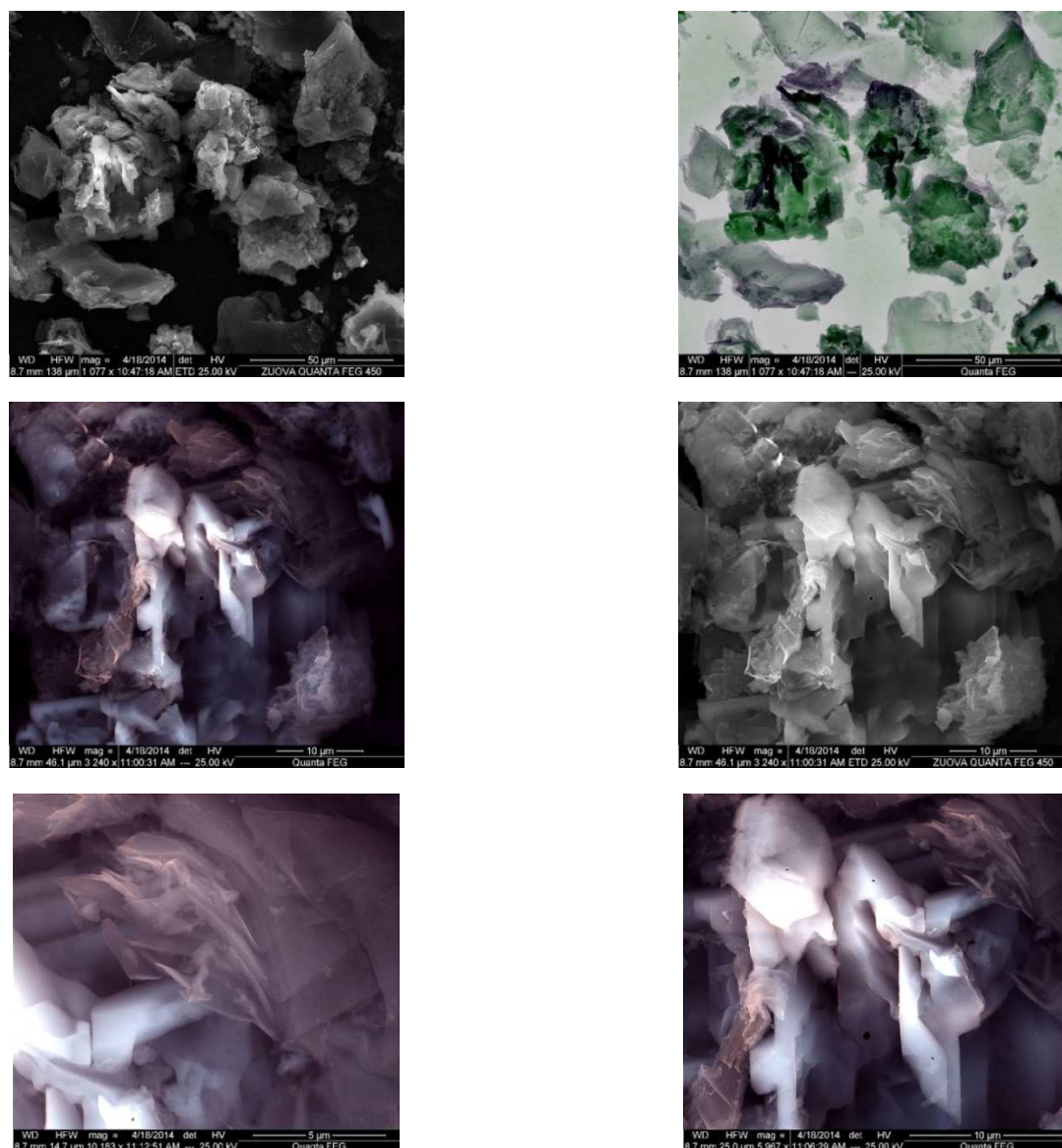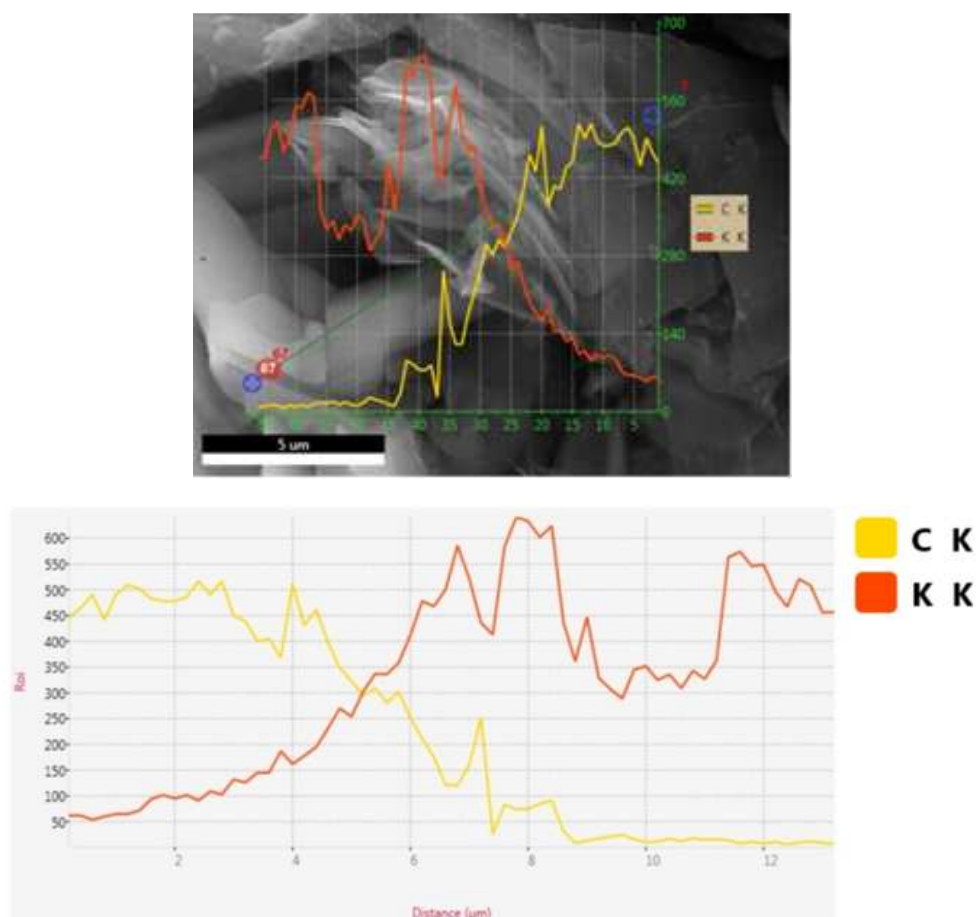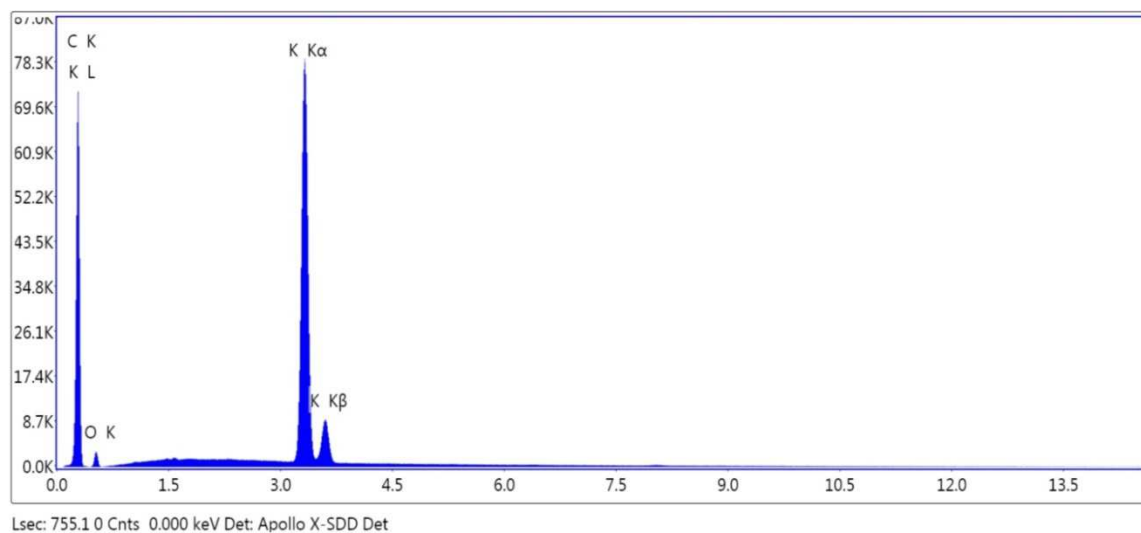


***Fig. 3.** Electron microscope images of the product prepared by reaction of intercalate $C_8K$ with fullerene $C_{60}$, various images*

*Fig. 4. Distribution of carbon and potassium in a crystal*

**Phase: K K/C K**



$C_{10}K_2O$

*eZAF Smart Quant Results*

| Element | Weight % | Atomic % | Net Int. | Error % |
|---------|----------|----------|----------|---------|
| CK | 56.39 | 77.13 | 420.8 | 3.71 |
| OK | 7.49 | 7.69 | 16.4 | 11.42 |
| KK | 36.12 | 15.18 | 1061.6 | 1.39 |

**Phase: Sum Spectrum**



Lsec: 2498.6 0 Cnts  0.000 keV Det: Apollo X-SDD Det

$C_{28}K_{1,6}O$
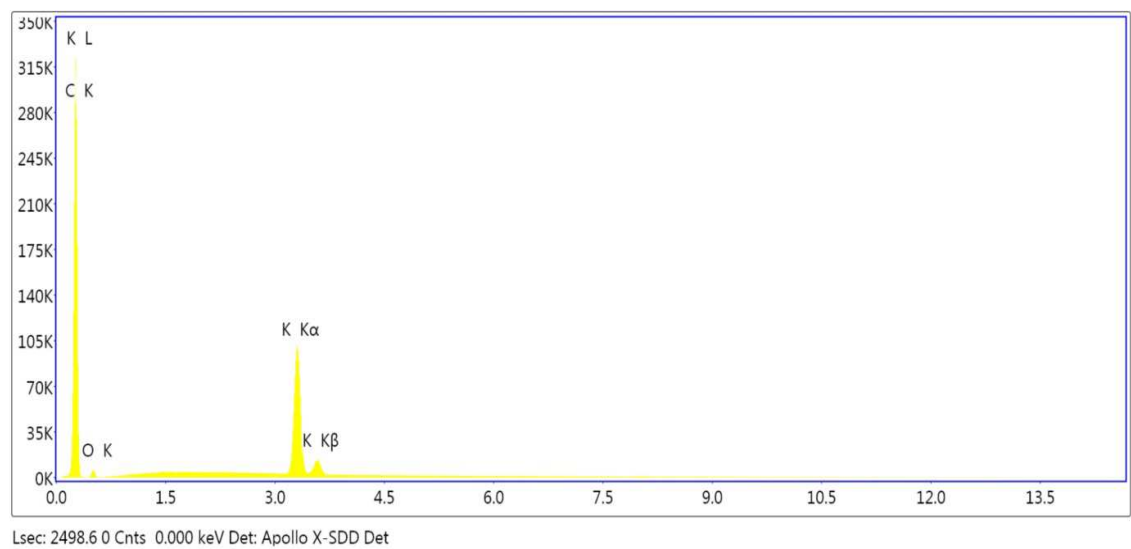
*eZAF Smart Quant Results*

| Element | Weight % | Atomic % | Net Int. | Error % |
|---------|----------|----------|----------|---------|
| CK | 80.69 | 91.33 | 628.6 | 2.39 |
| OK | 3.9 | 3.31 | 8.1 | 11.18 |
| KK | 15.41 | 5.36 | 407.9 | 1.53 |

**Phase: Unallocated**



Lsec: 543.2 0 Cnts  0.000 keV Det: Apollo X-SDD Det

$C_{26}K_{1,33}O$
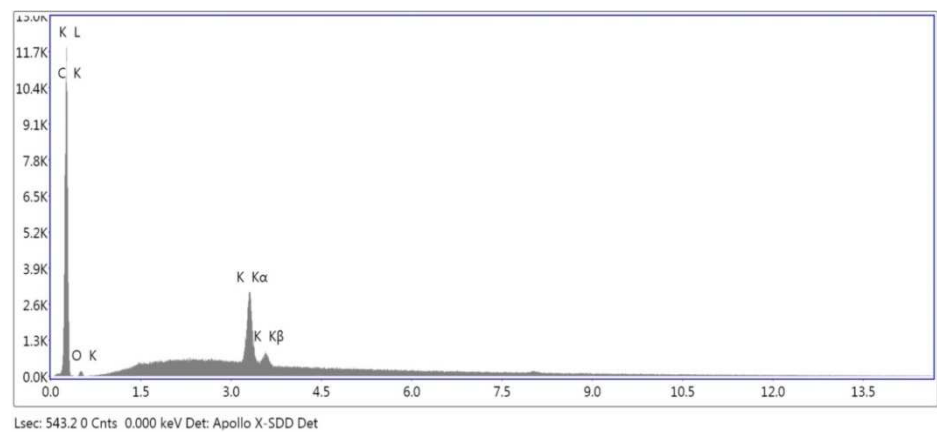
*eZAF Smart Quant Results*

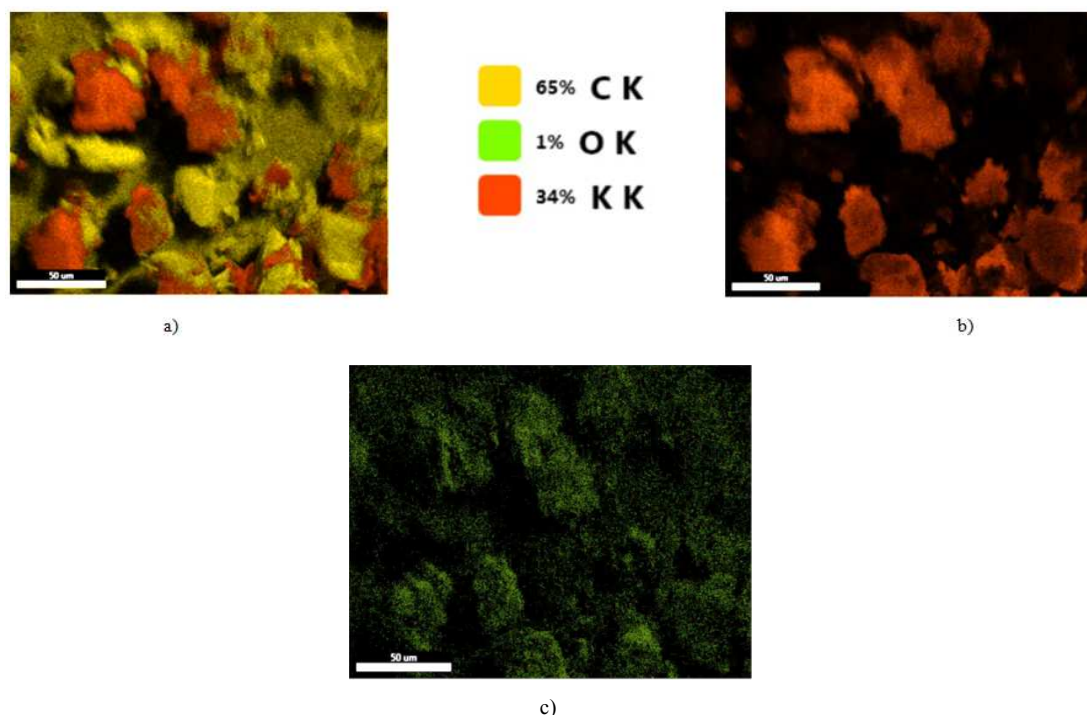| Element | Weight % | Atomic % | Net Int. | Error % |
|---------|----------|----------|----------|---------|
| CK | 82.27 | 91.87 | 118.1 | 2.61 |
| OK | 4.13 | 3.46 | 1.6 | 15.49 |
| KK | 13.61 | 4.67 | 65.8 | 2.25 |

**Fig. 5.** *Elemental analysis in various parts of the product prepared by reaction of intercalate $C_8K$ with fullerene a) $C_{10}K_2O$, b) $C_{28}K_{1,6}O$, c) $C_{26}K_{1,33}O$*

# 3. Results and Discussion

## 3.1. Reaction Product of Intercalate $C_8K$ and Fullerene $C_{60}$ (Fullerite)

In this experiment we wanted to take advantage of our previous experience when we used intercalate $C_8K$ to replace potassium with various other metals (Cu, Co, Cd, Ni, Zn, Al, Ag, Fe, Sb) and thus we produced their intercalates in graphite (Klouda, 1985). We assumed that intercalation of potassium in between the graphite layers will expand the space and that the affinity of $C_{60}$ to the negative charge will facilitate the intercalation. Direct intercalation of $C_{60}$ into graphite requires heating of the mixture to a high temperature (600° C), deep vacuum and long reaction time (15 days). Before the intercalation process graphite must be expanded with sulfuric and nitric acids (Gupta et al., 2004; Miura et al., 2005).

Also intercalation of alkali metals into crystal lattice by means of $C_{60}$ fullerite molecules has been described.

There are three known methods that can be used (Hou et al., 2004; Holczer et al., 1991):

- in vapors of alkali metal in deep vacuum and at the temperature of 200 – 450° C for several days
- decomposition of alkali metal azide in presence of $C_{60}$ in vacuum at ca. 550° C
- at a relatively low temperature in a THF solvent, liquid ammonia, $CS_2$

Apart from mono-intercalation, it is also possible to prepare ternary intercalates by combination with other alkali metals (Hou et al., 2004) or even intercalates which, in addition to potassium, contain also an intercalated organic component (Janiak et al., 1996) e.g. the compound $K_3C_{60}$ $(THF)_{14}$ was prepared in a solution during preparation of potassium intercalate. Intercalation of potassium into the crystal lattice of fullerite produced intercalates $KC_{60}$, $K_3C_{60}$, $K_4C_{60}$ and $K_6C_{60}$. We assume that in these compounds potassium operates as an electron donor and fullerene molecule as an electron acceptor, e.g. $K_3^{3+}C_{30}^{3-}$. Most works (Degiorgi, L., 1998) deal with testing of their superconductivity (Tc in $K_3C_{60}$ ~ 19K), physical properties, such as electric and optical conductivity, analysis of spectrums of electron spin resonance, 13C-NMR spectrums, distribution of electron density in a molecule etc. Compounds $K_xC_{60}$ (x=2,3,4,6) are extremely sensitive to the atmosphere, with the exception of $KC_{60}$, the so-called "rock salt" which decomposes at ca. 100°C into $K_3C_{60}$ and fullerene. $KC_{60}$ is expected to have a chain-like polymer structure (Koller et al., 1995).

Fullerene in the form of the so-called "nanowhiskers", prepared by the LLIP method (Liquid – Liquid Interfacial Precipitation Polymer), was intercalated to produce $K_{3,3}C_{60}$NWS with supraconductive properties (Takeya et al., 2012).

Apart from their atypical physical properties, potassium–fullerene intercalates may be also used to store hydrogen ($K_3C_{60}H_{29}$) (Loutfy and Wexler, 2001).

The method of mutual reaction which we have used to produce potassium fullerene intercalate was described by Fuhrer MS. (Fuhrer et al., 1994). The reaction was performed at 80°C and fullerene was applied in a solution of anhydrous benzene. According to the authors, the formula of the prepared product was $C_{32}K_4C_{60}$. The product prepared by us was a black powder. Its further processing, i.e. filtration and drying, was performed without protective atmosphere.

Drying was performed for a relatively short period of time at 55°C for safety reasons because the thermal stability was

not known and it was followed by FT-IR analysis, TGA and DSC analysis and electron microscope imaging, including Energy-dispersive X-ray Spectroscopy (EDAX).

# 4. Conclusion

The works were performed to obtain experimental information for future routine preparation of the products for their further application. We have prepared and partly described a product with stabilized potassium in a carbon skeleton (graphite – fullerite). It is partly able to resist the atmosphere, it is relatively thermally stable (up to 150 $^{o}$C) and the energy effects of its decomposition are low up to 600 $^{o}$C. The product may be used in numerous applications – catalysis, hydrogen storage and as an admixture component in aerosol fire suppression systems.

It is essential to determine ecotoxicity of the prepared material, including verification of its potential antibacterial properties.

# Acknowledgement

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