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subject: Study of Poly(ether ketone ketone) (PEKK): Outgassing Characteristics and Likely Residual Synthesis Impurities

Executive Summary

In May-June, 2020, a study was conducted to characterize the outgassing properties of a series PEKK (Poly(ether ketone ketone)) samples using cryo-GC/MS headspace analysis. Three sets of samples were interrogated: sample group 1 consisted of 2 additively manufactured PEKK samples (PEKK "Old" and "New") prepared by KCNSC from powder material from Solvay Specialty Polymers USA, LLC. Sample groups 2 and 3 consist of 5 PEKK powder types (used as feedstock for additive manufacturing processes) and 4 additively-manufactured PEKK material lots, respectively. Contrary to expectations, all samples of PEKK material were observed to outgas sulfur-containing compounds. Other analyses (EDS/EMA, GC-TOF/MS of PEKK sample extractions) confirmed the presence of sulfur in the PEKK bulk material. Specifically, Diphenyl sulfone (used as a reagent or high-temperature solvent in the synthesis of Polyaryletherketone or PAEK polymers) was observed in three of the powders and in both the PEKK "Old" and "New" samples, suggesting that the source of the sulfur can be traced to impurities in the material left over from the synthesis process. A summary of the test matrix and results is presented below in Table I.

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National Nuclear Security Administration

Table I. Summary of PEKK sample matrix and results. Note: All samples held in all-metal ampoules at 138 ºC for 1 week for headspace analysis.

Sample	Material Weight (g); Headspace	Sulfur Species Identified in Headspace	Approx. COS in Headspace (ppb)*	Sulfur Species Identified in DCM Extraction
SAMPLE GROUP 1: PEKK "Old" & "New" Material				
Control 1	0	**None**	0	N/A
Control 2	0	**None**	0	N/A
PEKK "old" A	0.9401	COS, CS_2	184	Diphenyl sulfone
PEKK "old" B	0.9399	COS, CS_2	89	Diphenyl sulfone
PEKK "New" A	1.6501	COS, CS_2	1	Diphenyl sulfone
PEKK "New" B	1.4187	COS, CS_2	5	Diphenyl sulfone
SAMPLE GROUP 2: PEKK Powders				
Control C1G	0	**None**	0	N/A
Control C2G	0	**None**	0	N/A
KSNSC Solvay PEKK Powder	1.1788	COS, CS_2	162	Diphenyl sulfone
KSNSC Solvay PEKK Powder	1.0526	COS, CS_2, $(CH_3SO_2)_2O$	175	Diphenyl sulfone
KCNSC Material ALM HT-0 PEKK Powder**	0.9979	COS, CS_2	85	**None**
KCNSC Material ALM HT-0 PEKK Powder**	0.967	COS, CS_2	86	**None**
PXM-17196 Lot 0040	1.049	COS, CS_2	129	Diphenyl sulfone
PXM-17196 Lot 0040 A	0.992	COS, CS_2	100	Diphenyl sulfone
PXM-17196 Lot 00148	1.0396	COS, CS_2	128	Diphenyl sulfone
PXM-17196 Lot 00148	1.0032	COS, CS_2	100	Diphenyl sulfone
Virgin Powder H7-0**	0.9838	COS, CS_2	93	**None**
ALM virgin powder HT-0**	1.0122	COS, CS_2	139	**None**
SAMPLE GROUP 3: PEKK Solid Materials				
Control S1	0	**None**	0	N/A
Control S2	0	**None**	0	N/A
PXM-17196 Lot 0103	1.0385	COS, $(CH_3)_2S_2$	1	N/A
PXM-17196 Lot 0103	1.697	COS, $(CH_3)_2S_2$	3	N/A
PXM-17196 Lot 0148	0.9264	COS	51	N/A
PXM-17196 Lot 0148	0.9624	COS, CS_2	33	N/A
KCNSC Material Solvay PEKK Parts	0.3091	COS, CS_2, $(CH_3SO_2)_2O$	481	N/A
KCNSC Material Solvay PEKK Parts	0.2997	COS, CS_2	547	N/A
KCNSC Material Kerlospire Filament	1.746	COS, $(CH_3SO_2)_2O$	18	N/A
KCNSC Material Kerlospire Filament	1.5904	COS, CS_2	46	N/A

COS = Carbonyl sulfide
CS_2 = Carbon disulfide
$(CH_3)_2S_2$ = Dimethyl disulfide
$(CH_3SO_2)_2O$ = Methanesulfonic anhydride

***Normalized ppb of analyte per gram of sample**
****Repeat extraction with non-aged material**

Background

Recently, there has been increased attention on the outgassing characteristics of high-performance thermoplastics used in hermetically-sealed environments. The observation of various sulfur compounds in the outgassing profiles of these materials has generated concern over their use in the systems, as gas-phase sulfur species (even in very low concentrations) are known to facilitate corrosion reactions in a variety of materials.[1] For example, PPS (polyphenylene sulfide), whose chemical structure consists of two aromatic rings linked by thioether (R-S-R) groups, has been recently conclusively shown to outgas carbonyl sulfide (COS).[2,3,4,5] While the precise source of the COS in the PPS is not known, it was originally assumed to be a biproduct of a degradative reaction of the material generated through the prolonged heating of the samples during the outgassing study.

In an effort to eliminate the risk associated with sulfur outgassing in PPS, focus shifted into identifying a candidate polymer with comparable performance characteristics to PPS but that did not contain sulfur as an inherent part of its chemical structure. PEKK (Poly(ether ketone ketone)) belongs to the PAEK (Poly(aryl ether ketone)) class of thermoplastics whose chemical structure contains ketone (R-CO-R) and ether (R-O-R) groups. Because its chemical backbone does not contain sulfur, it was predicted that PEKK would exhibit an innocuous outgassing profile and was therefore deemed to be a likely safe alternative to PPS for long term applications from an aging and materials compatibility standpoint.

PEKK "Old" & "New" Study

An outgassing study using cryo-GC/MS was conducted on two samples of additively-manufactured PEKK (labeled "Old" and "New") provided by KCNSC. Samples of each material were placed in an all-metal ampoule and held at 138 ºC for one week, after which the gas headspace was analyzed. Contrary to expectations, these PEKK samples were shown to exhibit outgassing of Carbonyl sulfide (COS) to a degree comparable to what had previously been observed in PPS, shown below in Figure 1. (The manner in which the identification of COS was confirmed / concentrations estimated has been discussed in previous reports relating to the aforementioned PPS outgassing studies.[2])

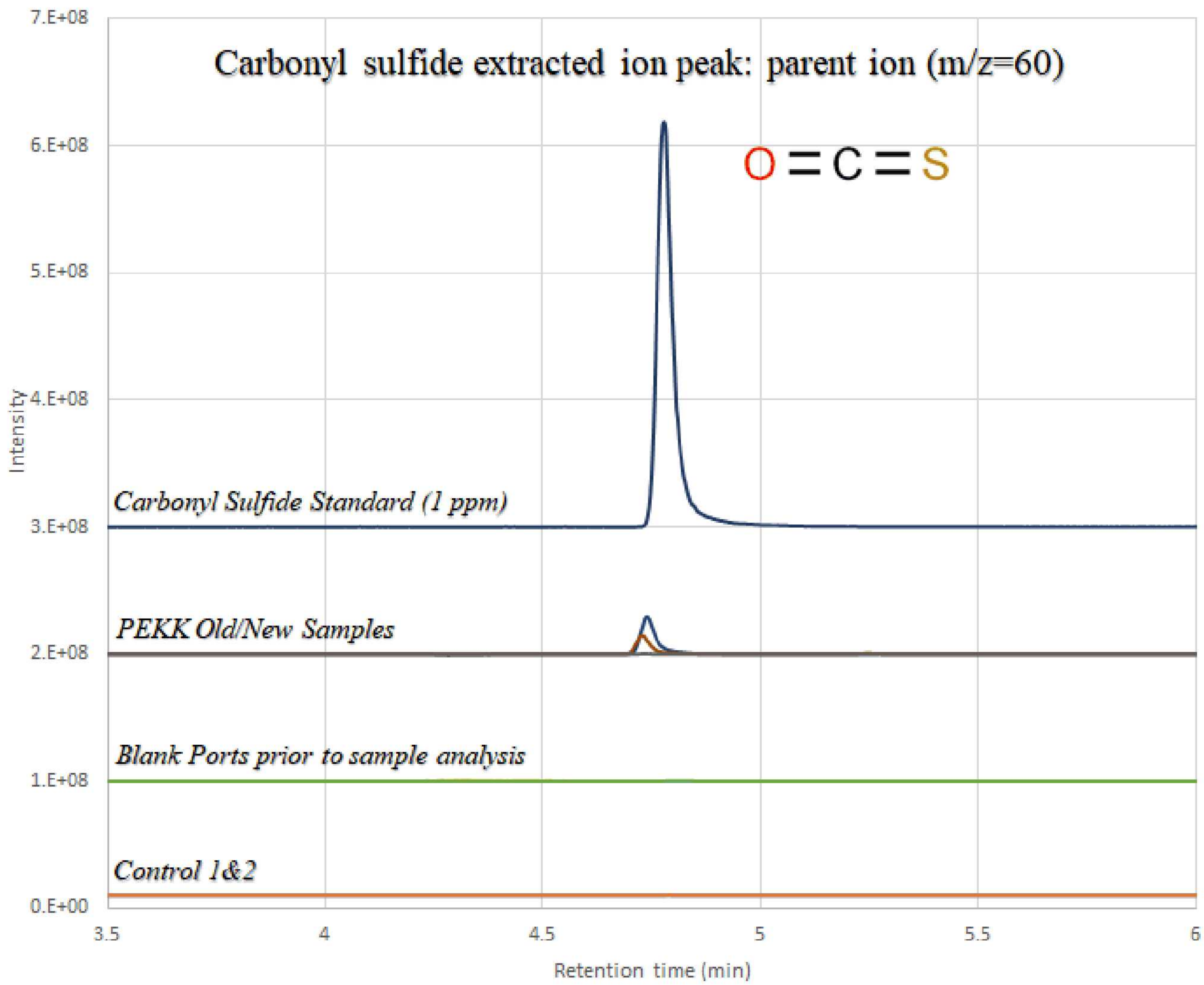

Figure 1. Extracted Ion Chromatograms for m/z=60 (parent ion of Carbonyl sulfide) in PEKK "Old" and "New" outgassing analysis. Note: chromatograms are displayed on the same intensity scale but grouped and offset for clarity.

Direct Material Analysis

Because of these unexpected results, a corroborating analysis was sought to directly confirm the presence of sulfur in the PEKK Old/New samples. Two candidate analyses were identified: EDS (Energy-dispersive X-ray Spectroscopy) and EMA (Electron Microprobe Analysis); these analyses were deemed appropriate because they require minimal time and sample preparation, they have relatively low limits of detection for sulfur, and they directly analyze the composition of the bulk sample material (as opposed to cryo GC/MS used in the outgassing study, which analyzed the gas headspace of the sample materials). Between these two techniques, the presence of sulfur was confirmed in both PEKK samples (analyses performed by Luis Juaregui and Richard Grant, SNL/1819), indicating that the carbonyl sulfide observed in the outgassing study was likely originating from the material itself and not contamination of the system. Unfortunately, these analyses do not provide insight into the specific chemical identity of the sulfur compound(s) present, only that sulfur exists in the material. This is shown below in Figure 2.

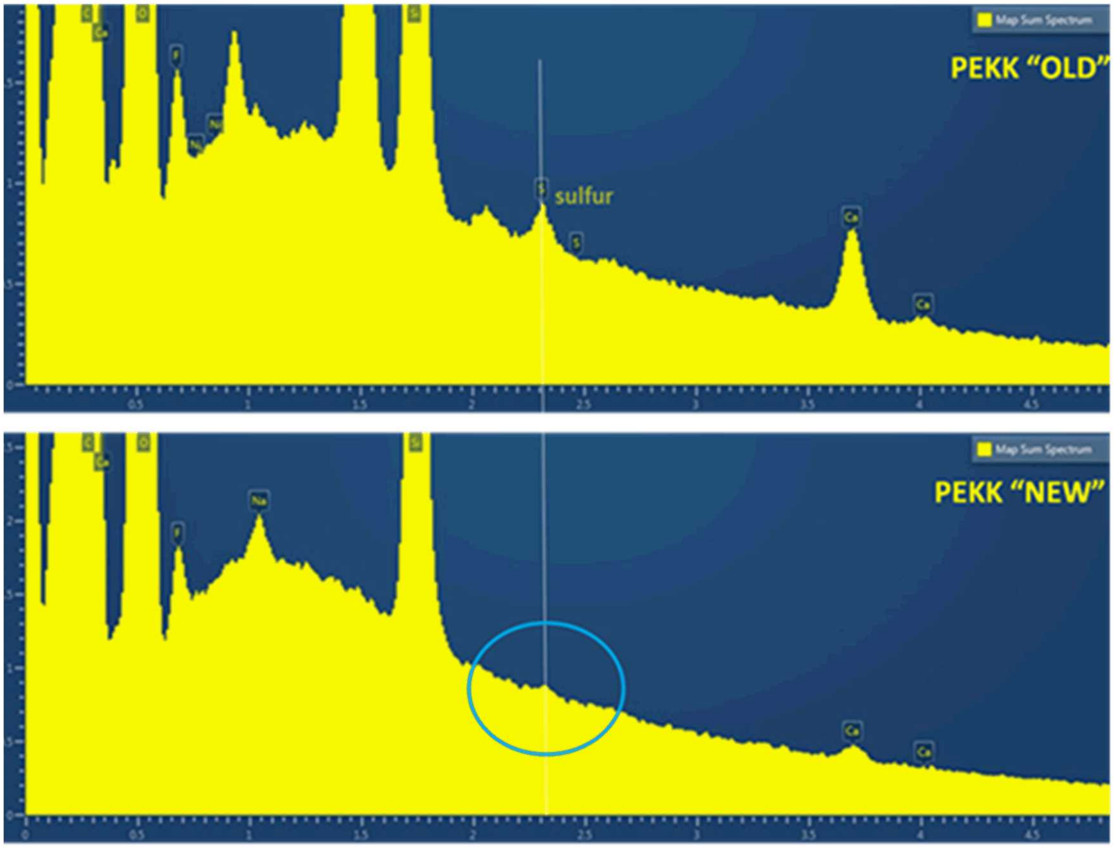

Figure 2. EDS spectrum of PEKK “Old” and “New” sample material. Sulfur was detected in both samples, though the chemical identity of the sulfur-containing compounds is not elucidated by this analysis.

In an effort to probe the specific identity of the sulfur-containing compound(s) in the PEKK “Old” and “New” materials, a direct solvent extraction was performed on remaining sample. A sample of 0.15 grams of PEKK “Old” and 0.46 grams of PEKK “New” were prepared and underwent extraction in DCM (Dichloromethane). (Note: The tool used to cut the sample was first cleaned, solvent-rinsed, and confirmed to be free of contamination.) Using GC-TOF/MS, the compounds extracted from the PEKK samples were identified, one of the most predominant which is Diphenyl sulfone, an organosulfur compound identified via library match with high confidence. This compound was identified in both the PEKK Old and New samples and was the only sulfur-containing compound identified. Other compounds identified in the extraction were 1,1,2,2-tetrachloroethane and 3-Fluorobenzoic acid, 2,2,3,3,4,4,4-heptafluorobutyl ester (both samples), and MIBK (Methyl isobutyl ketone) and Octadecanoic acid in the PEKK “New” sample. This can be seen below in Figure 3.

It should be noted that the goal of this analysis was simply to extract and identify any sulfur-containing species present in the PEKK samples, not to gauge absolute or relative concentrations. The solvent extraction was not performed according to a specific protocol (i.e., sample amount, immersion times, solvent evaporation ratios, etc. were not standardized), so estimations into the concentrations of compounds extracted from the sample can therefore not be made from the results of this analysis.

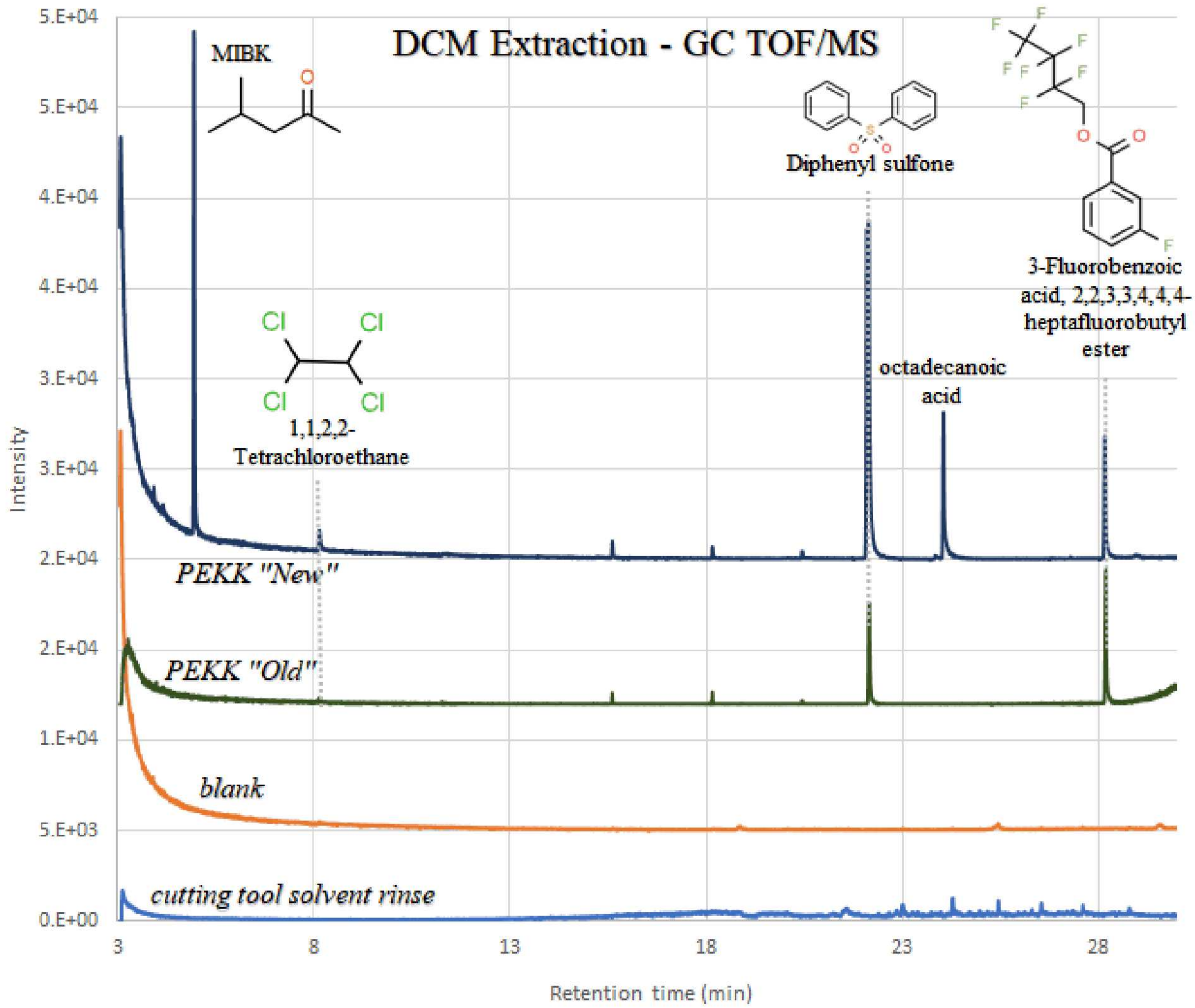

Figure 3. Total Ion Chromatograms for DCM extraction / GC-TOF/MS analysis of PEKK "Old" and "New" samples. Note: chromatograms are displayed on the same intensity scale but grouped and offset for clarity. Note: Peak intensities represented above are not necessarily representative of the sulfur concentrations in the original sample material; a relative comparison between PEKK "Old" and "New" TICs may therefore not be valid.

Follow-on Studies: 2 Additional PEKK Material Sample Sets

These results prompted further investigation into the presence of sulfur compounds in a range of other PEKK materials. Two additional sample sets of PEKK materials underwent outgassing analysis: the first set consisted of a range of PEKK powder materials (5 powders, 2 duplicates each) -the raw feedstock used in PEKK additive manufacturing processes. The second sample set consisted of 4 additively manufactured PEKK solids samples (2 duplicates each). Both material sample sets were provided by KCNSC or Solvay directly, and they are to be consulted for exact details of the sources/rationales of the samples. Each of the samples in the PEKK powder sample set underwent outgassing screening via cryo-GC/MS headspace analysis after aging each sample at 138 ºC for ~ 1 week, followed by DCM extraction / GC-TOC/MS. The PEKK "solids" samples underwent outgassing analysis but a DCM extraction was not performed. (The test matrix is summarized in Table I).

Cryo-GC/MS Headspace Analysis: Outgassing Screening

Both the PEKK powders (5 total, 2 duplicates each) and AM solids (4 materials, 2 duplicates each) underwent an outgassing screening using the same preparation and technique as used in the PEKK "Old" and "New" samples. Each sample was sealed under lab air in an all-metal ampoule (previously verified clean using cryo-GC/MS) and heated at 138 ºC for ~1 week. Prior to introducing the sample headspace into the instrument, a blank run was performed to verify the cleanliness of the sample port on each of the sample runs. A 1 ppm Carbonyl sulfide standard, prepared under the same conditions as the sample (~30 cc, 630 Torr) was used to verify identification of the COS peak in the samples and to generate a first-order approximation of absolute concentrations of that compound in the sample headspaces. Extracted Ion Chromatograms (m/z = 60, the COS parent ion) for the PEKK powders and AM solids sample sets are presented below in Figures 4 and 5, respectively.

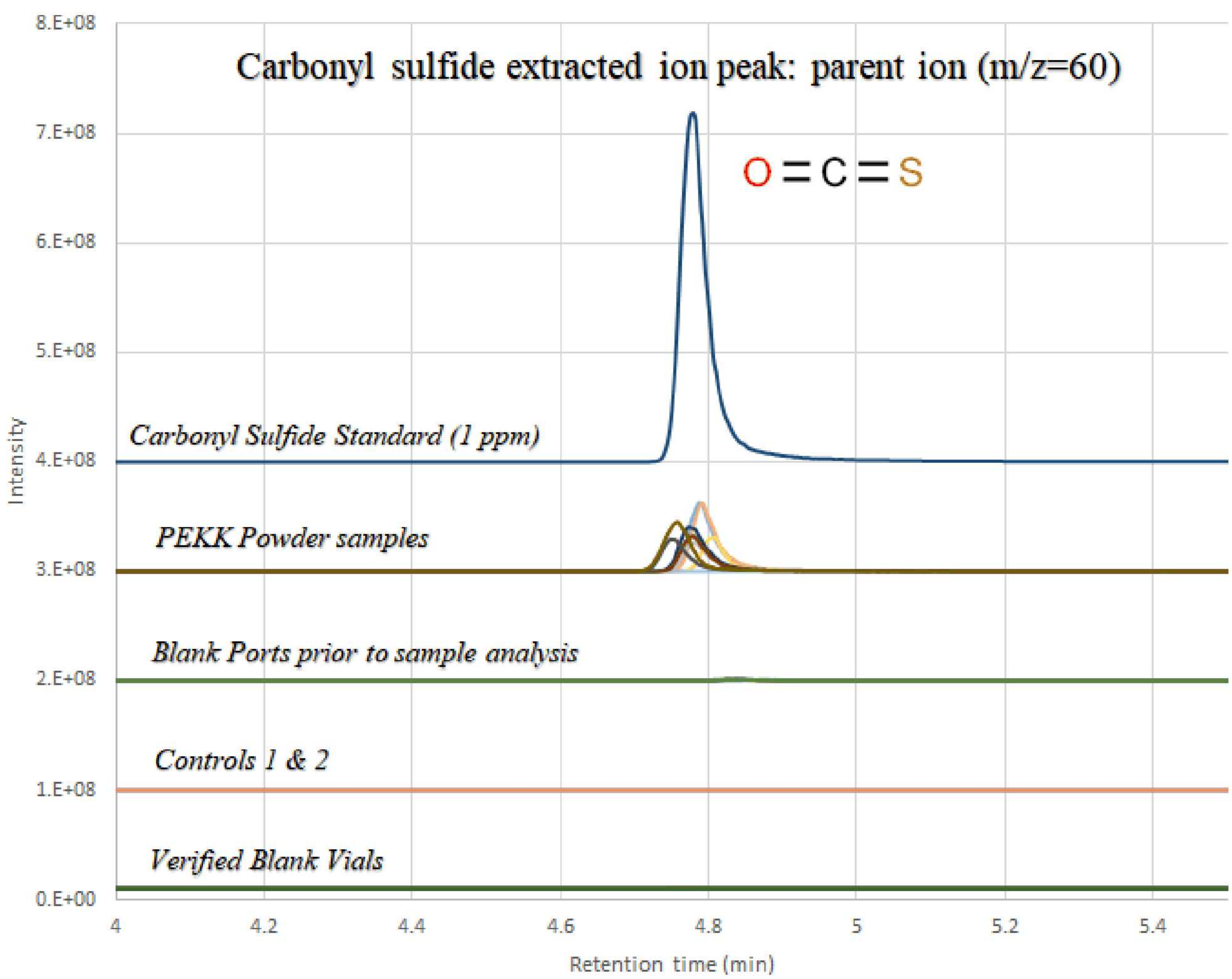

Figure 4. Extracted Ion Chromatograms for m/z=60 (parent ion of Carbonyl sulfide) in PEKK Powders study. Note: chromatograms are displayed on the same intensity scale but grouped and offset for clarity.

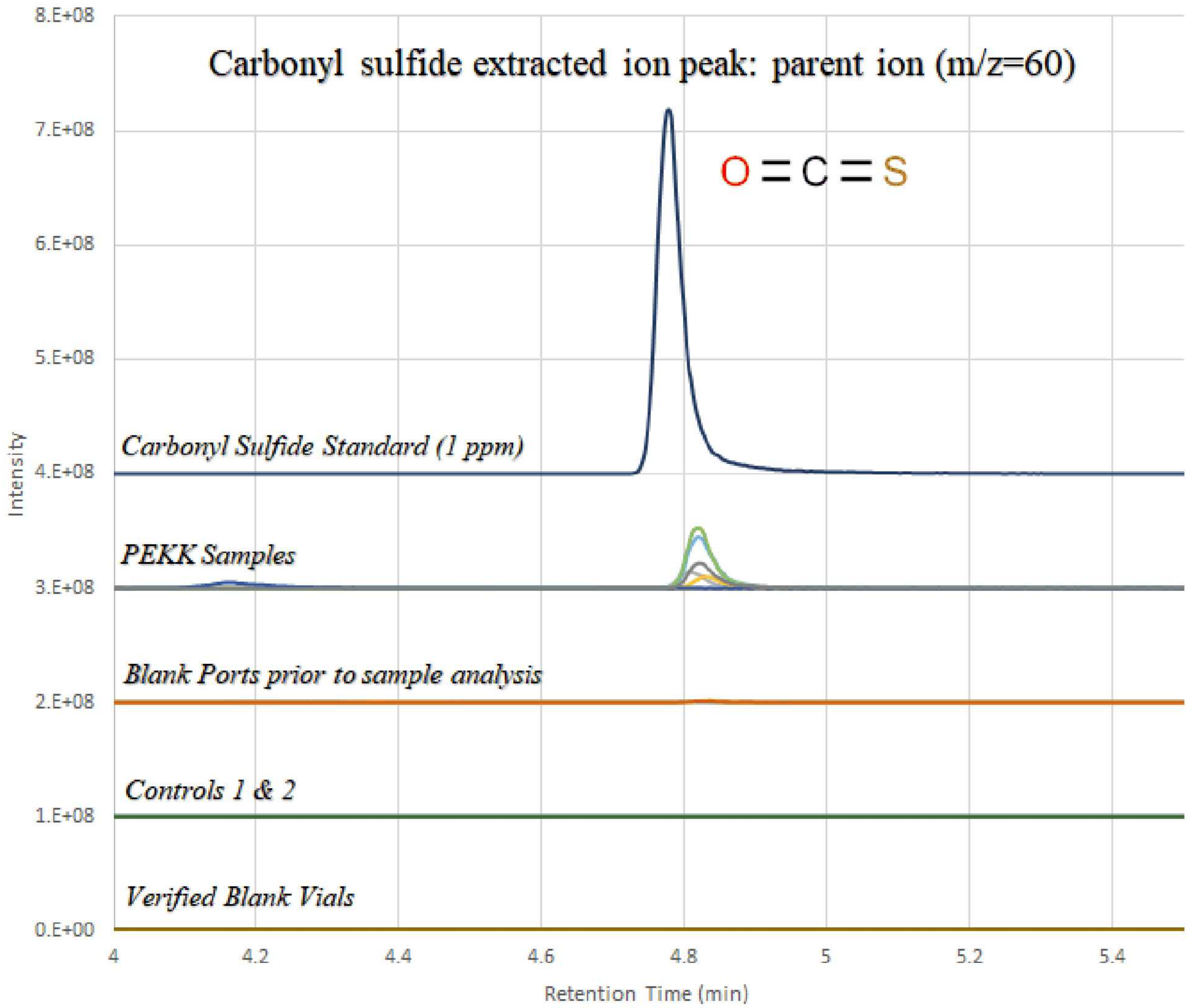

Figure 5. Extracted Ion Chromatograms for m/z=60 (parent ion of Carbonyl sulfide) in PEKK AM solids study. Note: Chromatograms are displayed on the same intensity scale but grouped and offset for clarity.

Extraction of PEKK material in DCM / GC-TOF/MS Analysis

The solvent extraction method performed on the PEKK "Old" and "New" samples was applied to the powders in Sample Set 2. The leftover powders from the headspace study underwent extraction in DCM and GC-TOC/MS analysis. As in the PEKK Old and New samples, three of the five powder types were shown to contain Diphenyl sulfone. Curiously, three of the powder materials did not exhibit any residual Diphenyl sulfone (or other sulfur-containing compounds), a result which was confirmed when the extraction was repeated on the as-received (unaged) materials. The results of the DCM extraction of the powders is shown below in Figure 6.

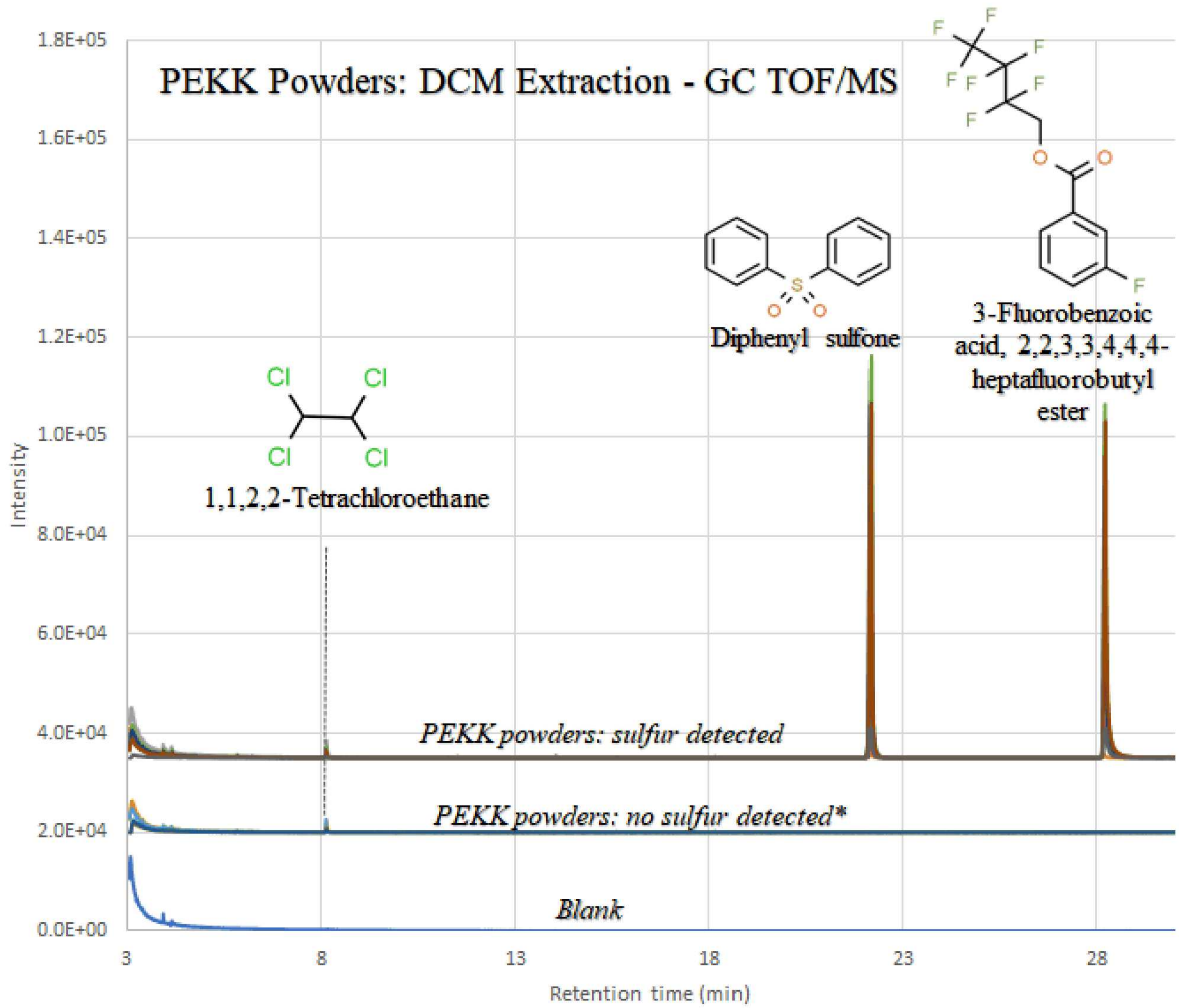

*Figure 6. Total Ion Chromatograms for DCM extraction / GC-TOF/MS analysis of PEKK Powders. Note: chromatograms are displayed on the same intensity scale but grouped and offset for clarity. *Powders with no sulfur detected underwent duplicate analysis with unaged sample material. Note: Peak intensities represented above are not necessarily representative of the sulfur concentrations in the original sample material; a relative comparison between PEKK "Old" and "New" TICs may therefore not be valid.*

Diphenyl Sulfone In PEKK

The observation of sulfur-containing outgassing compounds, and subsequently the detection of Diphenyl sulfone as an extractant directly from the PEKK materials in this study, was a highly unexpected result given that the chemical structure of the polymer does not itself contain sulfur. This led to speculation over the possible source of the observed sulfur compounds and a cursory investigation into the common synthesis techniques used to produce PEKK and related materials. As it turns out, a variety of sulfur-containing compounds, but in particular Diphenyl sulfone, appear frequently in the literature describing approaches to the synthesis of polymers in the family of materials to which PEKK belongs.

PEKK is an example of a class of high-performance semi-crystalline thermoplastics called poly(aryl ether ketones), or PAEKs, which display a range of desirable properties (thermal stability, good mechanical properties over a wide temperature range, good electrical performance, etc.).[6,7] Synthesis of PAEK polymers is generally accomplished through either a nucleophilic or electrophilic (Friedel-Crafts) polymerization process, each of which have a range of variations described in the literature. In the nucleophilic polymerization approach to synthesizing PEAK materials, the reaction takes place in a high-temperature solvent, which is almost ubiquitously described as being Diphenyl sulfone.[6,7,8,9,10] However, literature on the synthesis of PEKK describes most commercial production of that material as taking place through electrophilic polymerization approaches, rather than the high-temperature nucleophilic routes commonly employed for other PAEK materials (like PEEK). Nonetheless, Diphenyl sulfone is not exclusive to use as a solvent in nucleophilic syntheses; it is also described in at least one electrophilic polymerization process of PEKK, where it is used as a Lewis base complexed with an excess of $AlCl_3$ in a reaction at or below room temperature to form higher molecular weight polymers than in other approaches.[11]

Interestingly, a recent patent application by Solvay Specialty Polymers USA, LLC. (March, 2020)[12] presents a synthesis method for PEKK with improved thermal stability using a nucleophilic polymerization approach, wherein it is specified that the preferable solvent to be used in the process is "…at least 99 wt. % diphenyl sulfone." High-purity Diphenyl sulfone seems to be of import in the process, as reference is made to another patent (also submitted by Solvay) which details a method for removing impurities from that compound in order to improve the products of PAEK syntheses.[13]

Conclusions

Given the prevalence of Diphenyl sulfone in the literature describing the various approaches for the production of PAEK materials, it seems reasonable to hypothesize that the source of sulfur compounds observed in the PEKK materials in this study stem from residual impurities originating from the synthesis rather than from contamination picked up through improper storage / handling or subsequent processing. The precise mechanism by which these residual sulfur-containing impurities react to form the gas-phase volatiles observed in the cryo-GC/MS analyses (Carbonyl sulfide, Carbon disulfide, etc.) is not presently understood but is being pursued as an area of future study.

The solvent extraction technique applied in this study appears to represent a potential means by which PEKK (and similar materials) might undergo a screening for the presence of sulfur-containing impurities. Ideally, a protocol could be developed that would facilitate a relative comparison of impurity concentration between different lots of materials. However, it should be pointed out that a solvent extraction alone may not be definitive as a screening for sulfur impurities; this is illustrated by the fact that the PEKK powders in this study that "Passed" solvent extraction (no Diphenyl sulfone or other sulfur-containing compounds observed) were still found to outgas sulfurous volatiles. This could be the result of higher molecular weight sulfur-containing substances that are not readily soluble in the solvent chosen in this study; this will be further investigated in future work.

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