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Preparation of MnO_2 coated fibers for gamma spectrometric measurements - A comparison of four practical approaches

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Abstract: The analysis of natural radium-in-water activity concentrations is for two reasons of general interest: (1) radium in natural waters may pose a problem with regard to radiation protection and (2) radium isotopes in natural waters can be used as environmental tracers in hydrological studies. A state-of-the-art method for radium extraction from (generally large) water sample volumes is radium adsorption onto MnO_2 coated acrylic fibers. In our study we comparatively evaluated four methodical approaches for post-extraction preparation of the fiber to allow gamma spectrometric measurements. The methods included (1) straightforward measurement of the loose fiber, (2) compressing the fiber after mixing it with an adhesive, (3) combustion of the fiber and embedding the ash in candlewax, and (4) leaching of the fiber and embedding the resulting precipitate in candlewax. The aim of the study was to compare the advantages and disadvantages of the four preparation approaches with respect to their individual practicability. Even though the methodical fiber preparation approaches have been suggested in the literature before (as cited in this paper), results of their direct practical comparison have not been presented yet. Our study revealed that balancing practical sample preparation effort against data reproducibility suggests a measurement of the compressed fiber applying an adhesive to be the preferable approach.

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1 Introduction

The omnipresence of radium in natural waters can be seen from two ambivalent perspectives. On the one hand, elevated radium concentrations in waters that are used for drinking or irrigation can pose a serious health risk. Related problems have e.g. been reported for fossil groundwater originating from deep sandstone aquifers on the Arabian Peninsula and in Northern Africa (Schubert et al., 2011; Vengosh et al., 2009). Furthermore, radium in "produced" waters (brines) of the oil and gas industry may be of related concern (e.g. Vengosh et al., 2017; Rowan et al., 2011). On the other hand, the presence of radium in natural waters can also be considered beneficial. In a number of studies it was demonstrated that the four naturally occurring radium isotopes (^{224}Ra ($t_{1/2}$ = 3.7 d; ^{223}Ra ($t_{1/2}$ =11.4 d); ^{228}Ra ($t_{1/2}$ = 5.7 y); ^{226}Ra ($t_{1/2}$ = 1600 y)) can be used as tracers or indicators in a wide range of hydrological applications such as water migration investigations or seawater/groundwater interaction studies (e.g. Moore and Sarmiento, 2008; Moore 2003). In both cases, i.e. radium as a potential threat and radium as an environmental tracer, straightforward and reliable analysis of radium in natural waters is of key interest.

The water volume that is required for sound radium analysis depends on the radium activity concentration of the water and on the applied detection technique. For instance, if ^{226}Ra is the isotope of interest, detection by means of ICP-MS requires even at low activity concentrations (as they are observed e.g. in seawater (^{226}Ra ~ 1.3 mBq/l)) only rather small water volumes of about 200 - 300ml (Bourquin et al., 2011; Varga, 2008). If, however, all four natural radium isotopes are to be detected by means of gamma spectrometry much larger water volumes are necessary, thus requiring a pre-concentration of radium prior to analysis.

Pre-concentration of radium by means of enforced evaporation is only feasible for water sample volumes of up to several tens of liters. Such rather small sample volumes can also be treated by radium extraction from the water applying special adsorbents such as specific resins (Maxwell, 2006), MnO_2-coated polyamide discs (Eikenberg et al., 2001) or 3M EMPORE™ Radium Rad disks (Joannon and Pin, 2001).

The most appropriate extraction method for much larger sample volumes (up to several hundred liters) is adsorption onto MnO_2 coated acrylic fiber (e.g. Moore and Reid, 1973; Moore and Arnold 1996; Bourquin et al., 2008). This extraction approach requires pumping of the water sample with a flow rate of about 1 l/min through ~20 g of MnO_2 coated fiber that is placed in a column. A suitable state-of-the-art column is readily designed for subsequent analysis of the short lived ^{223}Ra (half-life 11.4 days) and ^{224}Ra (half-life 3.7 days) by means of Radium Delayed Coincidence Counting ("RaDeCC"; Moore and Arnold, 1996). It is common practice that after the RaDeCC analysis the long lived ^{226}Ra (half-life 1600 years) and ^{228}Ra (half-life 5.75 years) are determined by means of gamma spectrometry. This requires the adaptation of the MnO_2 coated fibers to the specific geometry of the gamma detector used, i.e. further preparation of the fiber is necessary.

Conventional fiber preparation methods are (i) quantitative combustion of the fiber (Charette et al., 2001, 2007) or (ii) leaching of the fiber to extract the radium for subsequent recovery as $Ra/BaSO_4$ precipitate (e.g. Moore, 1987; Moore et al., 1985; Moore and Santschi, 1986). Although both approaches show good results they have the disadvantage of being rather time-consuming and laborious. Moreover, the GEOTRACES inter-comparison study for radium isotopes showed rather poor agreement of the participating laboratories in the ^{226}Ra determinations, which may be also due to problems of adequately calibrating and preparing fibers for gamma spectrometric measurements (Charette et al., 2012).

In our study we comparatively evaluated four methods to prepare MnO_2 coated acrylic fiber for ^{226}Ra and ^{228}Ra measurement by means of gamma spectrometry. The four methods include: (1) placing the loose fiber into a defined gamma detection geometry without any further processing, (2) molding of the fiber into a defined pellet applying an adhesive, (3) combustion of the fiber and embedding the ash in candlewax, and (4) leaching of the fiber and embedding the subsequently produced Ra/$BaSO_4$ precipitate in candlewax. Aim of the study was to compare the advantages and disadvantages of the four procedures based on practical considerations including (i) the extent of the required practical preparation efforts, (ii) the reproducibility of the gamma measurement results and (iii) the magnitude of self-absorption resulting from the sample matrix.

2 Material and methods

From a certified ^{226}Ra stock solution (provided by the national German metrology institute Physikalisch-Technische Bundesanstalt) with a concentration uncertainty of 1.4 % twelve 1 liter aqueous sub-solutions with defined radium concentrations were produced (*cf.* Tab. 1). Distilled H_2O was used for the preparation of the sub-solutions. The twelve sub-solutions (with a pH around 7) were each filled in a 1 liter Marinelli beaker equipped with an inlet and an outlet port. For the production of twelve defined fiber specimens each beaker was connected in a closed loop to a peristaltic water pump and a column that contained 15 g of MnO_2 coated acrylic fiber (dry weight). Each sub-solution was pumped through its individual closed-circuit system at a pump rate of 2 l/min and a temperature of 20°C. In order to allow complete adsorption of the dissolved radium onto the fibers, each sub-solution was circulated for one hour, i.e. each sub-solution was pumped 120 times through its fiber column. For verification of quantitative radium adsorption onto the fibers each of the twelve residual sub-solutions was subsequently analyzed for remaining traces of dissolved radium by means of gamma spectrometry. If remaining radium was detected the quantity was taken into account for definition of the nominal radium activity of the respective fiber specimen. We assume any adsorption of radium on tubings, pump and beaker to be negligible.

The procedure resulted in twelve fiber specimens with known, i.e. nominal ^{226}Ra activities. Four of the specimens contained a comparably low and eight of the specimens a comparably high activity (*cf.* Tab. 1). After drying the twelve fiber specimens at room temperature, they were grouped in four sets with three specimens each, two of relatively high activity and one of relatively low activity. The four sets of specimens were treated in abovementioned four different ways of sample preparation (see below for details).

Due to the four different physical characteristics of the specimens resulting from the four ways of fiber treatment a different magnitude of self-absorption was to be expected for each of the four sets, thus requiring individual gamma efficiency calibrations of the four different matrixes. To achieve this, the specimen with the highest nominal activity from each set was defined as “standard” for this particular set. The remaining two specimens were considered as “samples” of the set (Fig. 1, Tab. 1). Thereby it could be guaranteed that the samples and the standard were handled in the same geometric setup and have the same physical and chemical characteristics (e.g. density) and hence the same self-absorption. The activity concentrations of the two samples of each set were then determined by relating the detected gamma counts to the corresponding counts detected in the standard of the same set applying the rule of proportion.

3 Experimental

In order to produce the four sets of fiber specimens the fibers were taken from the individual columns, dried and prepared as given in detail below and schematically illustrated in Fig. 1. The preparation resulted in the four specimen types shown in Fig. 2.

For “set #1” the fiber was transferred into cylindrical radon tight HDPE capsules, 7 cm in diameter and 3.5 cm in height. The fiber was not treated in any way but just placed in the HDPE capsules so that after closing and sealing the lids tightly, the fiber filled the capsules homogeneously.

For “set #2” the fiber was compressed into pellets by means of a hydraulic press applying 125 kN of pressure. The mold of the press allowed the production of round and flat pellets with a diameter of 7 cm and a height of 1 cm, which fitted tightly into the cylindrical HDPE capsules also used for “set #1”. First tests, in which the pure fiber was compressed, revealed that the fiber pellets do not hold their defined shape after pressure release, which made it impossible to obtain a constant and defined detection geometry. For stabilization of the pellet shape the fiber was hence mixed with powder sugar as an adhesive. The sugar was previously analyzed for traces of radium using gamma spectrometry, but no radium activity was detected. Other potential adhesive materials, such as talcum, milk powder and chalk had also been tested; however, the powder sugar showed the most satisfying results regarding handling and stability of the fiber pellets.

For “set #3” the fiber was slowly and carefully combusted in an open ceramic bowl at about 1200°C using a Bunsen burner. The process took about 30 min per specimen. Subsequently, after cooling, the ash was homogeneously mixed with fine grained pure candlewax (Merck). A blank of the wax was analyzed for traces of radium using gamma spectrometry with negative results. The homogeneous wax/ash mixture was subsequently compressed by means of the hydraulic press described above thereby producing pellets of the same dimensions as “set #2” that were also placed in the abovementioned HDPE capsules.

For “set #4” the fiber was leached using 6 N HCl at a temperature close to the boiling point. After quantitative leaching the fiber had turned its color to plain white, indicating the complete release of MnO_2 and hence of the adsorbed radium. Next the dissolved radium was quantitatively precipitated from the acid solution as Ba/$RaSO_4$ (Moore et al., 1985). The precipitate was dried and homogeneously mixed with fine grained pure candlewax as used for "set #3". The mixture was compressed by means of the hydraulic press again producing pellets that fitted tightly in the HDPE capsules.

The twelve HDPE capsules (four different sets, each with one "standard" and two "samples", *cf*. Fig. 1) where finally sealed by attaching the lid onto the capsule using a flexible glue (Hylomar® M) and additionally flexible sticky tape (Cellpack Premio 233) in order to minimize radon escape. An equilibration time of four weeks was allowed for radioactive equilibrium between ^{226}Ra, its daughter ^{222}Rn and the short-lived radon progenies ^{214}Pb and ^{214}Bi.

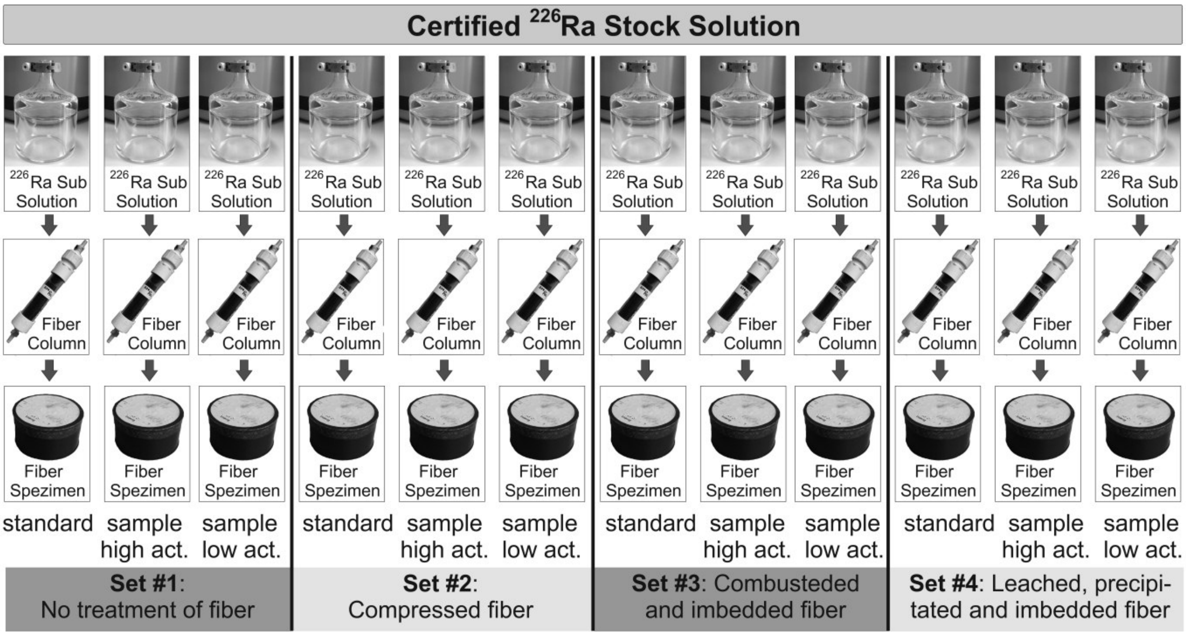


Fig.1: Fiber sample preparation scheme

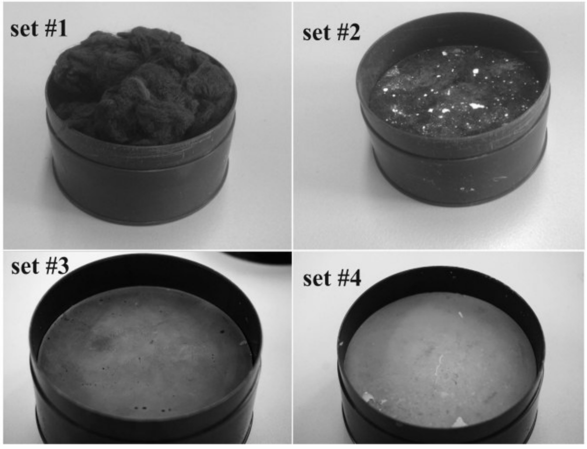


Fig. 2: Four different sample types: set #1 unprocessed fiber, set #2 compressed fiber, set #3 fiber combusted and mixed with candlewax, set #4 fiber leached and Ra/$BaSO_4$ precipitate mixed with candlewax (*cf.* Fig. 1)

Radium activity measurement of all four standards and eight samples was carried out by low-level gamma-spectrometry based on the distinct gamma emission energies of ^{226}Ra (186.1 keV) as well as of the short-lived radon progenies ^{214}Pb (295.2 keV, 351.9 keV) and ^{214}Bi (609.3 keV, 1120.3 keV, 1238.1 keV, 1764.5 keV, 2204.1 keV) using a coaxial Low-Energy HPGe detector, n-type (ORTEC), with an active volume of 39 cm^3 and a 0.5 mm Be window. Each measurement lasted for about 24 h. Spectra analysis was performed with the software GAMMAW® (Dr. Westmeier GmbH, Germany).

4 Results

Tab. 1 displays the detection results for the 4 x 2 samples. Given for each sample (i) its nominal ^{226}Ra activity (i.e. the target value), (ii) the activity that resulted from directly evaluating the 186 keV ^{226}Ra gamma line, (iii) the activity derived from the combined evaluation of the major ^{214}Pb and ^{214}Bi gamma lines, and (iv) the set specific cpm/Bq count rate at 186 keV as indicator for the individual intensity of self-absorption.

It has to be pointed out, that even though the two set #1 samples were filled homogeneously with fiber, no homogenous radium distribution could be taken for granted within the capsules. The reason for that is that, while pumping the sub-solutions through the fiber columns for radium extraction, radium that might have been preferentially extracted in the upstream part of the respective fiber column resulting in an unevenly distribution of radium in the fiber volume. Water flow along preferential pathways in the fiber may also have caused an inhomogeneous distribution of radium on the fiber. Hence the set #1 samples were measured twice, once upside-up and once upside-down. The specimen that was chosen as standard for set #1 showed identical results either way.

The activities displayed in Tab. 1 show that the measurements resulted in activities of the individual samples that match the corresponding nominal values within the counting uncertainties. The only exception is the set #1 sample with the lower activity. The concentrations derived from the ^{226}Ra gamma line differ significantly from the target value. As discussed above this disagreement can be explained with an inhomogeneous spatial distribution of radium within this particular capsule resulting in a larger (or if measured upside-down a smaller) distance between radiation source and detector giving rise to a lower (or if measured upside-down a higher) count rate.

Tab. 1: Nominal activities of the samples; Activity concentrations derived from the ^{226}Ra gamma line; Activity concentrations derived from the seven major gamma lines of the short lived ^{222}Rn progenies ^{214}Pb and ^{214}Bi; Set specific count rate [cpm/Bq] of the ^{226}Ra gamma line at 186 keV

	nominal activity [Bq]	^{226}Ra [Bq]	^{214}Pb & ^{214}Bi mean [Bq]	186 keV count rate [cpm/Bq]
Set #1: Unprocessed Fiber				
High (upside up)	310 ± 15.5	313 ± 16	325 ± 40	0.11
high (upside down)		315 ± 17	320 ± 33	
Low (upside up)	105 ± 5.3	94 ± 4	107 ± 14	
low (upside down)		115 ± 6	108 ± 25	
Set #2: Compressed Fiber				
High	325 ± 16.0	319 ± 16	337 ± 44	0.17
Low	155 ± 7.8	159 ± 7	153 ± 31	
Set #3: Combusted Fiber				
High	315 ± 15.8	315 ± 15	307 ± 30	0.12
Low	145 ± 7.2	148 ± 8	139 ± 18	
Set #4: Precipitated Ba/RaSO$_4$				
High	215 ± 10.8	212 ± 12	217 ± 24	0.06
Low	133 ± 7.0	138 ± 6	131 ± 20	

5 Discussion

The aim of the study was to evaluate the advantages and disadvantages of four different fiber preparation approaches for measuring radium adsorbed on MnO$_2$-fibers by means of gamma spectrometry. That evaluation of the four approaches was done by comparing (i) the amount of their individual practical preparation efforts, (ii) their individual reproducibilities of the nominal activities and (iii) the magnitude of self-absorption resulting from the sample matrix indicated by the individual count rate at 186 keV [cpm/Bq].

The measurement of samples without any fiber treatment (set #1) requires the least practical fiber preparation effort. The fiber was simply stuffed into the detection geometry (i.e. the HDPE capsules) and measured after decay equilibrium between radium and short-lived radon progenies had established. Still, as shown in Tab. 1 one of the two samples revealed a significant discrepancy between detected values and the nominal activity when the ^{226}Ra 186 keV line is evaluated (even though the mean value of two results agrees well with the nominal value within the uncertainties). This lower data reproducibility can be explained with the above mentioned poor degree of radium distribution homogeneity within the fiber.

A different picture emerges for set #1 when the ^{226}Ra activity of the samples is evaluated based on the short-lived radon progenies. Both values match the nominal value well. The explanation of this observation is that radon (as a gas) spreads homogeneously and independently of the radium distribution within the capsule, thus resulting in equal gamma activities of its short-lived progeny in spite of a potentially inhomogeneous radium distribution. Hence, the potential error that arises from a poor degree of radium distribution homogeneity within the fiber can be avoided by not relying on the ^{226}Ra line at 186 keV but by rather using the activities of the short-lived radon progenies. For reliable results sample capsules have to be sealed radon tight in order to exclude radon loss during the required 3 weeks equilibration time (Scholten et al. 2013). The low self-absorption due to the loose packing of set #1, on the one hand, and the rather large fiber volume of the samples that increases its effective distance to the detector thus decreasing the [cpm/Bq] count rate, on the other hand, keeps the count rate at 186 keV at a level comparable to that of set #3 (Tab. 1).

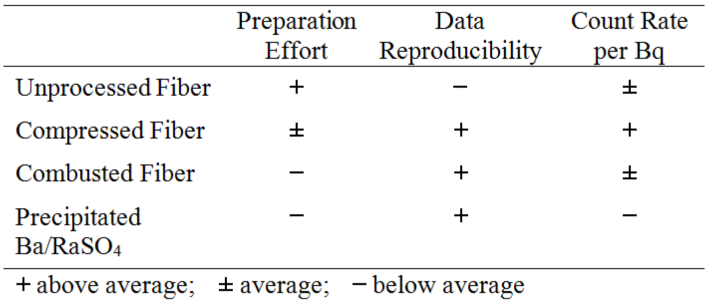
The fiber preparation applying a compaction of the fiber (set #2) is hardly more laborious than the measurement of the unprocessed fiber (set #1). Still, compared to set #1 the physical homogeneity of the set #2 samples is significantly increased due to the lower volume of the pellets, which is of general advantage for the data reproducibility. On top of that the relatively low self-absorption of the pellets and the short effective distance between detector and sample result in a higher [cpm/ Bq] count rate (Tab. 1). That makes this fiber preparation approach suitable for samples with low activity concentrations.

The two fiber preparation methods that involve combustion and leaching of the fibers (set #3 and set #4, respectively) are much more time consuming and laborious than the two methods applied for sets #1 and #2. On the other hand, a strong advantage is that the homogeneity of the sample sets #3 and #4 increases significantly due to the thorough mixing of either the ash or the precipitate with the candle wax. However, the addition of the candlewax increases the self-absorption of the samples, thus reducing the [cpm/Bq] count rate (Tab. 1). In the case of set #4 that effect is even more noticeable due to the strong self-absorption potential of the precipitated Ba/RaSO_4.

6 Conclusions

The described advantages and disadvantages of the four different sample preparation approaches are qualitatively summarized in Tab. 2. It can be stated that the approach, which is represented by set #2 (compressed fiber) turned out to be the preferable one. Requiring only a low sample preparation effort it leads to results that show a satisfying data reproducibility. The approach represented by set #1 (unprocessed fiber) shows comparable advantages if the radon progeny data is used to quantify radium activity concentrations.

Tab. 2: Advantages and disadvantages of the four different sample preparation approaches



	Preparation Effort	Data Reproducibility	Count Rate per Bq
Unprocessed Fiber	+	−	±
Compressed Fiber	±	+	+
Combusted Fiber	−	+	±
Precipitated Ba/$RaSO_4$	−	+	−

+ above average; ± average; − below average

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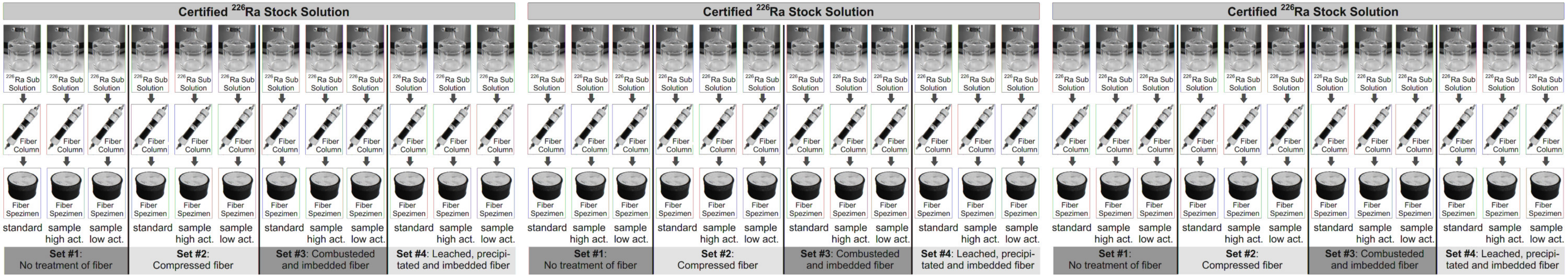
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Set #2: Compressed fiber
Set #3: Combusteded and imbedded fiber
Set #4: Leached, precipi-tated and imbedded fiber
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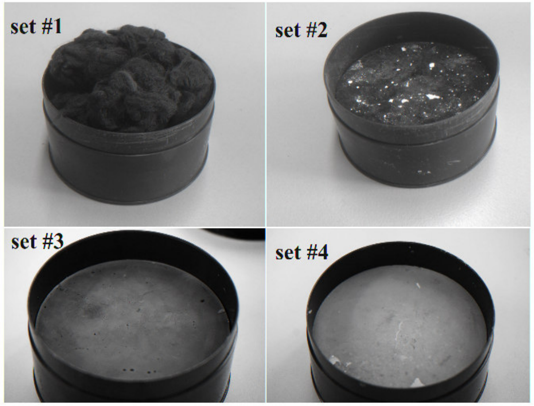
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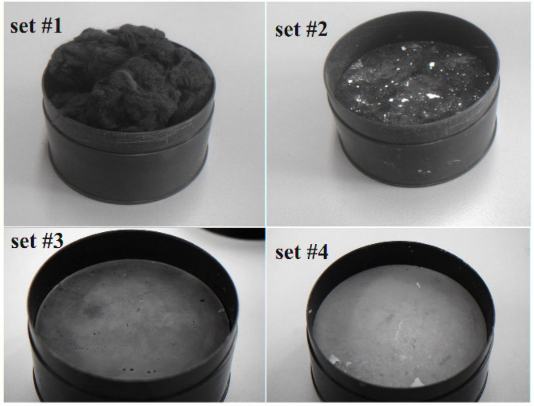
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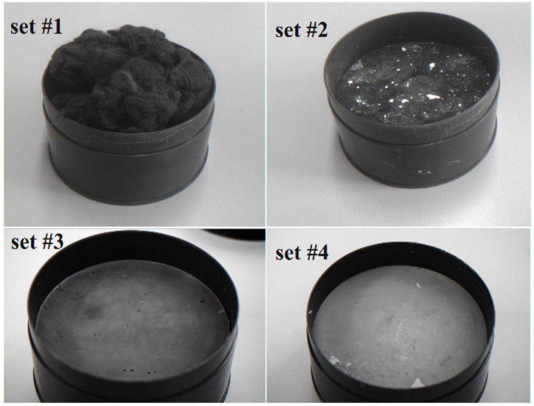
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