

# Establishment of both removal technique of PFOA as a by-product produced in a manufacturing low-molecular-weight PTFE powder and its extremely micro analysis method.

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## Abstract

We have manufactured various grades of poly-tetra-fluoro-ethylene (PTFE) powder by irradiation of high-energy beam followed by dry milling recent years. This powder production method produces small amounts of per-fluoro-octanoic acid (PFOA) in the PTFE fine grades with particle size of several micron meters. PFOA is a kind of environmental pollutant and harmful substance, so that this material should be removed away from the PTFE powder at least down to the REACH regulated value of EU (25ppb). We have attempted to establish the reliable removal technique of PFOA from PTFE powder and its microscopic analysis method. This paper introduces briefly our techniques and micro analysis method. The former technique is based on an extraction using organic solvent, and the latter method makes full use of a liquid chromatography/tandem mass spectrometry. In short, we succeed the removal of PFOA down to approximately 10 ppb, which is lower than the EU REACH regulated value (25ppb).

**Keywords:** PFOA (per-fluoro-octanoic acid) removal, recycle, extremely micro analysis method, PTFE (poly-tetra-fluoro-ethylene) powder

## 1. Introduction: Regulations for PFOA Concentration in Material

PFOA (per-fluoro-octanoic acid) is an organic fluorine compound that has been used as a fluororesin processing aid, fire extinguishing agent, water repellent, and paint. It is found that PFOA is hard to be decomposed and highly bio-accumulative, so there is a growing worldwide trend to regulate the concentration of PFOA and its salts in materials from the viewpoints of environmental pollution and health hazards. In response to this trend, European Union (EU) has added PFOA and its salt in the list of

restricted substances to the list of REACH regulation in 2020. The highest concentration of these compounds is less than 25 ppb. Accordingly, Japan has revised the regulation law (Act on the evaluation of chemical substances and regulation of their manufacture) in 22, Oct. 2021. By this the manufactured materials containing PFOA and their imported goods have subjected to regulation. However, this is not subject to regulation in case of a by-product, and as long as the concentration is controlled by the upper limit allowed by the three Ministries (Ministry of Health, Labor and Welfare, Ministry of Economy, Trade and Industry and

Table.1 Properties and applications of PTFE powder (TFW-P series)

|                                 | TFW-500                             | TFW-1000P                             | TFW-2000P               | TFW-3000P                         | TFW-3000FKP                     |
|---------------------------------|-------------------------------------|---------------------------------------|-------------------------|-----------------------------------|---------------------------------|
| Maximum particle size( $\mu$ m) | 100                                 | 30                                    | 20                      | 10                                | 10                              |
| Average particle size( $\mu$ m) | 25                                  | 10                                    | 6                       | 3                                 | 3                               |
| Bulk density(g/cc)              | 0.60                                | 0.58                                  | 0.62                    | 0.44                              | 0.44                            |
| Melting Point( $^{\circ}$ C)    | 320 <                               | Around 320                            | Around 320              | Around 320                        | Around 320                      |
| PFOA conc.(ppb)                 | PFOA free                           | <10 / <25                             | <10/ <25                | <10/ <25                          | <10/ <25                        |
| Application                     | resins, rubbers<br>flame retardants | resins, rubbers<br>paints, lubricants | paints, grease<br>films | inks, paints<br>lubricants, films | lubricants, insulation<br>films |

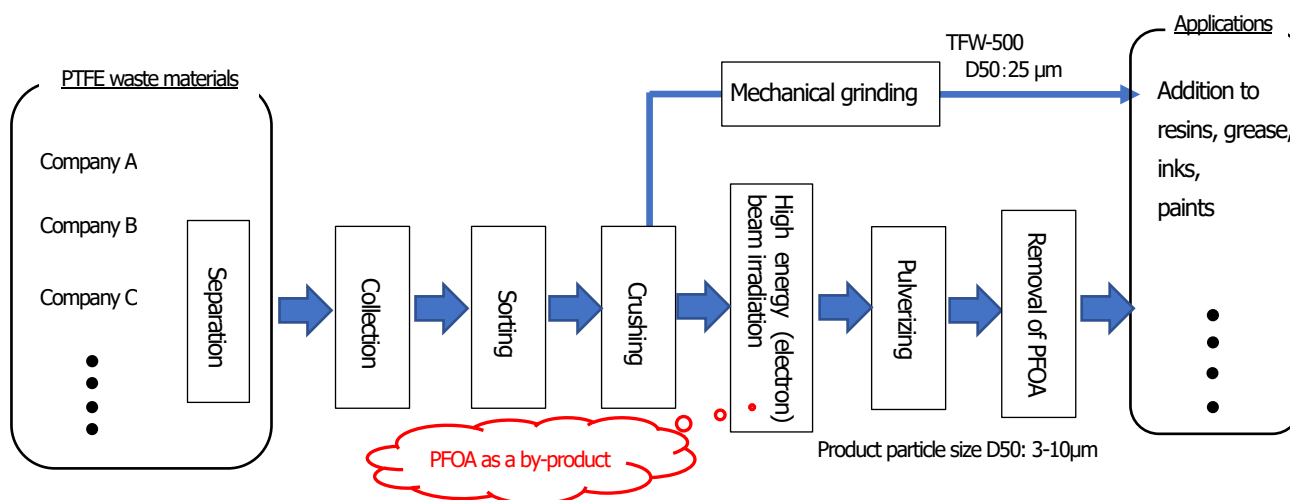


Fig.1 Manufacturing flow chart of TFW-P.

Ministry of the Environment), considering the idea of Best Available Technology /Techniques, so called “BAT”. Since our PTFE powders (TFW-1000P 2000P, 3000P and 3000FKP) have a low-molecular-weight due to irradiation of electromagnetic wave (electron beam), During the irradiation, very slightly amount of PFOA is reproduced so that we have reported the three Ministries. Even in the meantime, we have tried to improve the removal technique of this compound as well as its micro analysis method for years.

## 2. Manufacturing process of PTFE powder and PFOA reproduced during irradiation of electron beam into the raw PTFE material before grinding

### 2.1 Manufacturing process of PTFE powder

PTFE is an engineering plastic with excellent chemical resistance, electrical insulation, non-adhesiveness, low-friction and other applications such as plumbing tubes, lining materials, packings, wire coatings, heat exchangers.

Our company has sold five grades of PTFE powder with different particle sizes (Table 1). The raw materials are scraps and cutting waste emitted from molding manufacturers. They are roughly separated into relatively good-quality parts, and then higher quality material are done by sorting operation before grinding. The sorted material is then fed into the crushing and other operations.

The schematic manufacturing process for the PTFE powder is shown in Fig.1. In this process, the powder products of few tens of micron meters ( $\mu\text{m}$ ) in average size can be obtained by mechanical grinding using a certain type of mechanical grinding machine. As for the case of finer powder less than few micron meters in average size,

mechanical grinding alone cannot manage at all. However, our seniors found the fact that such finer powder can be obtained by the combination of the electron beam irradiation followed by pulverizing. So we have followed in their footsteps.

### 2.2 Production of PTFE fine powder of few micron meters and formation of PFOA as a by-product

As described earlier, the irradiation of electron beam into the raw PTFE material followed by pulverizing is very effective for manufacturing PTFE fine powder of few micron meters. The electron beam irradiation plays a big role to weaken the strength of PTFE as well as dissociate its molecule. Fig.2 shows the molecular weight of the PTFE powder as a function of the electron beam irradiation amount into the raw PTFE. As can be seen from the figure, the irradiation amount of 800 to 1000 kGy enables to reduce the molecular weight of PTFE of  $10^5$  to  $10^3$  levels. This is our own fine powder production technology enabling to obtain the PTFE fine powder of few micron meters. The only drawback is, as mentioned above, PFOA formation as a by-product at a very small amount in the PTFE powder. Based on our study so far, the concentration of PFOA is limited in the parts per million (ppm) level, which is pretty low but more than the EU as well as the Japanese regulated value. Therefore, our priority is the PFOA removal from the PTFE fine powder and the improvement of micro analysis method. To do that, it is important to understand the formation mechanism of PFOA in the PTFE powder when the electron beam is irradiated to the powder. This will be discussed in the later section. Now, we have set the PFOA removal process in the PTFE fine powder manufacturing process shown in Fig.1. To put it briefly, our PFOA concentration can be achieved

to the values at 25 ppb or less, and recent data have been maintained below 10 ppb level (refer to Table 1).

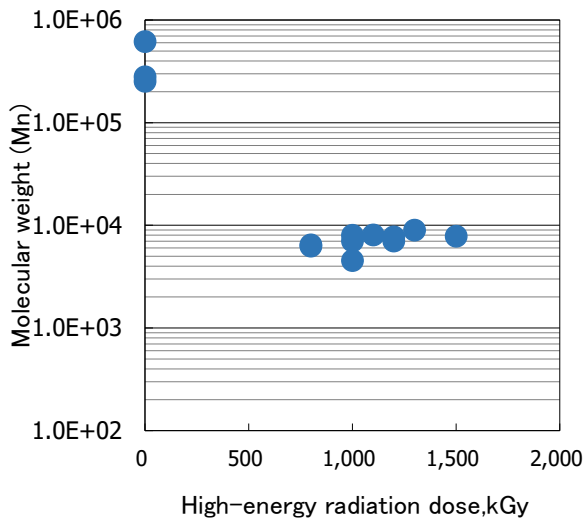
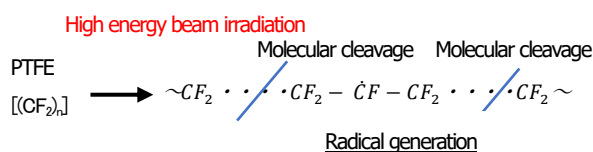


Fig.2 Relationship between the dose of high-energy radiation and the molecular weight of irradiated PTFE.

### 2.3 Formation mechanism of PFOA in the PTFE fine powder

As mentioned in the 2.2 section, the electron beam irradiation can reduce the strength of the raw PTFE material, so that the material is easy to pulverize into finer sizes by the operation. The size of the obtained PTFE powder is few micron meters. Contrary to this good point, the fine PTFE powder contains PFOA as a by-product. What we hear from the previous work done by others, this electron beam irradiation to PTFE may result in the formation of PFOA in it. Although the details of this formation mechanism are not fully confirmed yet, it might be recognized as follows<sup>1-2</sup>

First, when a PTFE sample is irradiated with the electron beam, the strength of the sample is weakened and cleaved it, and in the vicinity of the molecular cleavage area, activated points, i.e., radicals in the molecules are generated, reforming the following cleavage reaction.



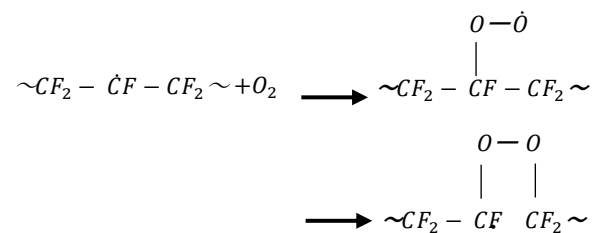
Here, n denotes the degree of polymerization of PTFE and  $\dot{\text{C}}$  denotes the carbon radicals.

When PTFE is irradiated with such electron beam under air

atmosphere, the molecules with radicals  $(-\text{CF}_2-\dot{\text{C}}\text{F}-\text{CF}_2-)_n$ , occur chain reactions with oxygen ( $\text{O}_2$ ) and water vapor ( $\text{H}_2\text{O}$ ), where n' is the polymerization degree of PTFE. The chain reactions can be classified by the following two kinds.

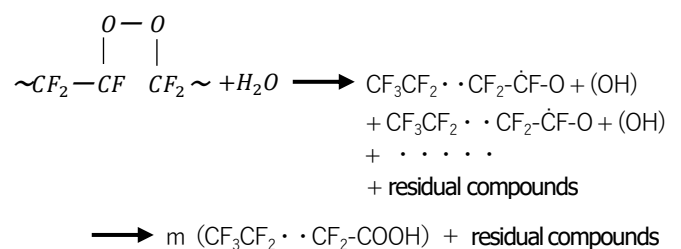
- 1) Reaction of radical molecule  $[(-\text{CF}_2-\dot{\text{C}}\text{F}-\text{CF}_2-)_n]$  with oxygen ( $\text{O}_2$ ) in the air:

An oxygen molecule ( $\text{O}_2$ ) is added to a radicalized carbon ( $\dot{\text{C}}$ ), then the both species act each other, resulting in the formation of the C-O compounds with radicals. At this time, the radicals ( $\cdot$ ) move on the unstable carbon sites (C). In this way, the reactions between C and O with radicals occur throughout the PTFE molecule.



- 2) Reaction of active molecule produced in the reaction mechanism in the section 1) with water vapor ( $\text{H}_2\text{O}$ ) in the air:

In the section 1), PTFE activated by the electron beam irradiation reacts with oxygen in the air, generating the radical molecules  $((-\text{CF}_2-\dot{\text{C}}\text{FO}-\text{OCF}_2-)_n)$ . Since these molecules retain the radicals, so that it can also react with water vapor ( $\text{H}_2\text{O}$ ) in the air. At this time, the (OH) group dissociated from the water molecule moves to the carbon radical sites ( $\dot{\text{C}}$ ), forming carboxyl group compounds ( $\text{CF}_3\text{CF}_2 \cdot \cdot \cdot \text{COOH}$ ). The PTFE main chain (C-chain) is cleaved in the random state, but this cleavage phenomena happens in the position at 8<sup>th</sup> carbon site from the end of PTFE molecule chain. The resultant compounds formed after this cleavage phenomena are  $\text{C}_7\text{F}_{15}\text{COOH}$ , that means PFOA. Thus, the reaction of the radical molecule  $(-\text{CF}_2-\dot{\text{C}}\text{FO}-\text{OCF}_2-)_n$  with water vapor, producing PFOA in the PTFE is schematically shown here.



### 3. PFOA removal technology

We have established the technology that can continuously separate and remove PFOA from the low-molecular-weight PTFE fine powder manufactured in our process. By introducing this technology into the PTFE fine pulverizing process, we can produce a large amount of high-grade PTFE fine powder (Fig.1) with low PFOA concentration less than 25 ppb. Furthermore, this PFOA concentration can be reduced less than 10 ppb by improving the technology in the even in 8 hours of continuous operation without any trouble, as shown in Fig.3. As can be seen from Fig.3, the PFOA concentration in the fine powder fluctuates slightly during the operation, but these average values are remained below 10 ppb.

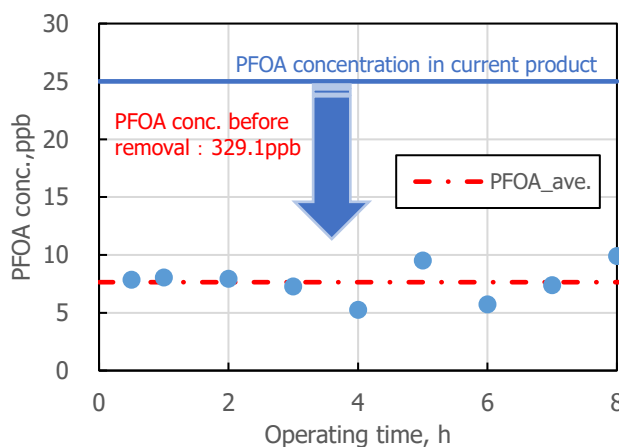


Fig. 3 Variation of PFOA concentration with the operating time in the continuous PTFE fine powder manufacturing process

### 4. Quantitative analysis method for extremely micro amount of PFOA in the PTFE powder

#### 4.1 PTFE sample preparation and liquid chromatography/tandem Mass Spectrometry (LC/MS/MS measurement)

As described in the first section, the PFOA concentration in PTFE powder is restricted below 25 ppb, which is the upper limit of the EU regulation, and it is desirable to keep it below that level. Our company have been struggling to develop an extremely micro analysis method focusing on a target of 10ppb as well as 25ppb. Our analytical procedure, shown in Fig.4 is consisted of pretreatment of the PTFE powder followed by the liquid chromatography/tandem mass spectrometry (LC/MS/MS). This is based on the techniques and conditions of CEN/TS 15968: 2010<sup>3</sup> in EU, saying “Determination of extractable perfluorooctane

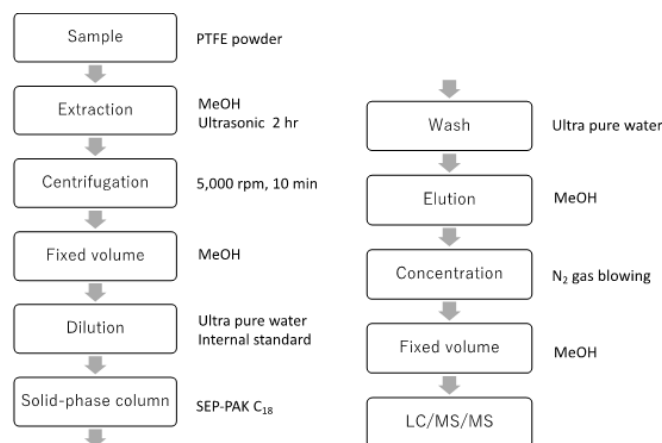


Fig. 4 PFOA analysis procedure

sulfonate (PFOS) in coated and impregnated solid articles, liquids and firefighting foams. Method for sampling, extraction and analysis by LC-qMS or LC/MS/MS”. In Fig.4, the PTFE powder (0.5 g) was suspended in methanol and sonicated at 60 °C for 2 hours to extract PFOA. PFOA can be more efficiently extracted by using methanol than ethanol. After that, the extract is separated from the solid powder by a centrifuge (5000rpm, 10min), the extract is diluted by ultra-pure water, followed by adding an internal standard (IS) solution (made by Cambridge Isotope Laboratories, Inc., USA). Then, the mixture is fed into a solid-phase column with SEP-PAK vac C18 cartridge (made by Waters Corporation, USA). The IS solution was added to correct for the loss of PFOA that occurs on solid-phase columns. The diluted extract flow into the solid-phase column could be done by a natural fall method, but we have done by a suction method using an aspirator. It is found that our method works quick and effectively and shows no trouble at all in the adsorption phenomenon of PFOA into the solid-phase column. After passing all into the solid-phase column, the column was washed with ultra-pure water, and the PFOA in it was eluted with methanol. The eluate was concentrated by heating with blowing nitrogen gas, and its volume was settled with methanol, then it was subjected to feed to the LC/MS/MS instrument.

In this analysis, extremely micro concentration of PFOA in PTFE can be quantified, but very close attention would be needed because contamination from ultra-pure water and other reagents is considered to affect greatly on the measured values as experimental error. Therefore, we have checked the both data between two samples with and without PFOA, using the extraction procedure shown in Fig.4.

The conditions for the Liquid Chromatography (LC) and the quadrupole mass analyzer; quadrupole mass spectrometer (MS/MS) are shown in Tables 2 and 3. A

calibration curve for  $^{13}\text{C}_8$ -PFOA as an internal standard solution was described by a ratio of PFOA peak area to  $^{13}\text{C}_8$ -PFOA peak area against a ratio of PFOA concentration to  $^{13}\text{C}_8$ -PFOA concentration obtained by adjusting the PFOA standard solution (0.25-15 ng / ml) diluted by methanol and measuring it with the LC/MS/MS instrument. Based on this calibration curve, the PFOA concentration of the actual treatment solution was given as a quantitative analysis value. **Fig.5** shows the calibration curve, which is judged to be highly reliable when the value of  $R^2 \geq 0.999$  is obtained, and this curve is used to determine the PFOA concentration of the PTFE sample.

Table 2 LC condition

|                  |                                                                |
|------------------|----------------------------------------------------------------|
| LC system        | UPLC                                                           |
| Column           | C <sub>18</sub> -ODS (1.7 μm x 50 mm)                          |
| Injection volume | 5 μl                                                           |
| Column Temp.     | 40 °C                                                          |
| Flow rate        | 0.2 ml/min                                                     |
| Mobile phase     | A: 0.5 mM CH <sub>3</sub> COONH <sub>3</sub> /0.1% Formic acid |
|                  | B: Acetonitrile                                                |
| Gradient         | B: 40% (0 min)→95% (13 min)→95% (18min)                        |

Table 3 MS/MS condition

|                                              |                                                         |
|----------------------------------------------|---------------------------------------------------------|
| MS/MS spectrometer                           | Xevo G2-S Q-TOF                                         |
| Ionization                                   | ESI-Negative                                            |
| Detection ion<br>(Precursor ion/Product ion) | PFOA 413.0/169.0<br>$^{13}\text{C}_8$ -PFOA 421.0/376.0 |
| Cone voltage                                 | 45 V                                                    |
| Collision energy                             | PFOA 20 eV, $^{13}\text{C}_8$ -PFOA 10 eV               |

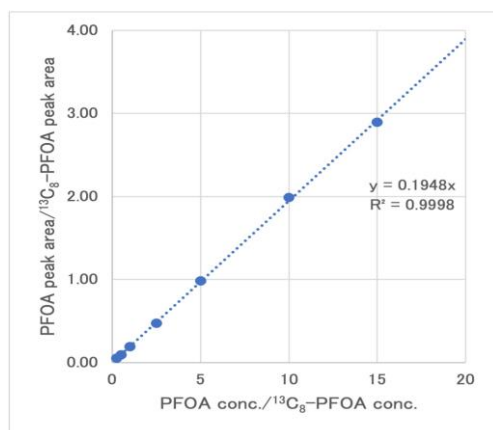


Fig. 5 Calibration curve of PFOA

## 4.2 Validation of PFOA analysis values

The validity of our PFOA analysis method in PTFE was checked by comparison of the data measured by us and an external analysis organization. To do so, we prepared the two samples in the same lot; the one was for us, and the other was for the external organization, which was Mie prefecture Environmental Conservation agency (MEC), Japan. Both measurements of PFOA concentration in the sample are shown in **Table 4**. Our measured values are slightly different from those done by the MEC agency, but the errors are quite small ranged from 10 to 12%. In addition to that, these errors are within the margin of few parts per billion (ppb) level. This means that our data are almost correct, then our analysis method is confirmed to be validity. In addition, it is necessary to check whether the measured PFOA concentration is dependent on the initial PFOA concentration, we have tried to measure the PFOA concentration in three different initial PFOA content samples, i.e.,  $1 \times 10^2$  ppb,  $1 \times 10^3$  ppb and  $1 \times 10^4$  ppb. As a result, the analysis values in PFOA concentration come close at any initial concentrations. Therefore, it is confirmed that our established PFOA analysis method is valid for determination of PFOA concentration in PTFE.

Table 4 Comparison of the concentrations (ppb) of PFOA

| Sample No. | Our measurement | MEC measurement |
|------------|-----------------|-----------------|
| 1          | 24.5            | 27              |
| 2          | 205             | 180             |
| 3          | 1240            | 1100            |

## 4.3 Confirmation of analysis accuracy

To confirm the analysis accuracy of the established analysis method, we performed repeated measurements for the three different PTFE samples with  $1 \times 10^2$  ppb,  $1 \times 10^3$  ppb and  $1 \times 10^4$  ppb in PFOA concentration. **Table 5** shows the mean values (ppb) and the standard deviation (SD: ppb) and the coefficient of variation (CV: %). The target value of CV was set below 20%, referring to the "Guidelines for Validity Assessment of Water Quality Testing Methods"<sup>4,5</sup> notified by the Ministry of Health, Labor and Welfare, Japan.

From Table 5, the CV values are close to the target one and all data are below 20%. This is due to look over change the amount of liquid used, increase in the repeated measuring number and other technological revision. As a whole, the average CV is 13.5% and the minimum one is 8.33%. Therefore, we have confirmed that our analysis method has an ability of highly accurate measurement for extremely micro amount of PFOA in PTFE powder.

Table 5 Accuracy (CV) of measurements of PFOA

| Sample No. | Mean of PFOA (ppb) | SD (ppb) | CV (%) |
|------------|--------------------|----------|--------|
| 1          | 5.7                | 1.00     | 17.5   |
| 2          | 6.0                | 0.50     | 8.33   |
| 3          | 24.1               | 4.50     | 18.7   |
| 4          | 35.2               | 3.10     | 8.81   |
| 5          | 628.6              | 94.5     | 15.0   |
| 6          | 961.0              | 119      | 12.4   |
| Av.        | -                  | -        | 13.5   |

## 5. Conclusion

Since there is a demand to further reduce the environmental regulation value of PFOA concentration in PTFE powder, it is our responsibility as a manufacturer to provide society with safe powder products that are below the regulatory value. Our company have manufactured the powder with below regulatory limits and sold it for years. Even during that period, we have attempted to develop a novel technique for reducing PFOA concentration in the PTFE powder as well as an analysis method for determining accurately low PFOA concentration below EU regulation value (25ppb). In this paper, we introduce the establishment of our technique to control PFOA concentrations in the powder, and an analysis method for determining accurately micro amount of PFOA concentrations. Of course, there is still room for improvement, we introduce here the present state reaching a certain level.

Our company specializes in powder characterization and analytical methods, demonstrated by, for example, particle size distribution, shape observation by microscope, bulk density, powder flowability. Moreover, as a powder manufacturer, we develop unique method for producing high quality and excellent grade powder materials for sale. In the activity period, we have attempted to develop the detection and removal methods of extremely small amounts of elements contained in powders, characterization of surface-active states, manufacture of powder products with more advanced characteristics and their new applications. The technology introduced here is a part of these efforts, and as a group of "professional powder engineers" manipulating freely powder design and structure, we intend to develop advanced technology to meet the many needs of our customers. We look forward to your continued patronage and encouragement.

## <Acknowledgment>

In the establishment of the analysis method and the actual work, we received a great deal of cooperation from the Food Development Laboratory of Tottori Prefectural Industrial Technology Center and the Scientific Analysis Department of Mie prefecture Environmental Conservation agency. Without their cooperations and supports, our effort would never have seen the light of day. We would like to express our deepest gratitude here.

**Please also refer to the following information regarding the TFW-P series.**

[TFW Series \(betterseishin.co.jp\)](http://betterseishin.co.jp)

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