

Chapter 2

Sampling, Handling, Treatment and Separation

Prior to analysis, the sample must be defined, described and subsequently extracted from the considered material, if necessary, and prepared for the analysis. A rigorous approach has to be followed before initiating any expensive analysis.

2.1 Sample Collection and Analysis Mode

In a first step, sample collection and analytical protocol need to be addressed.

2.1.1 Sample Selection and Collection

Prior to sample selection and data collection, a minimum of information is required on the sample to perform the sampling. Is the sample:

- Solid, liquid or gaseous?
- Heterogeneous or homogeneous?
- 1 m^3 , 1 mm^3 ... or 1 nm^3 in size?
- A sub-sample?
- A sample series in space and/or time?
- A major, a minor or a trace/radio-trace component in terms of its analyte?
- Analyzed for basic properties, e.g. mass, volume, pressure (total and partial), temperature, gradients and location (coordinates) fixed in the system?
- Representativeness defined?
- Homogeneous or with spatial variation?
- Size larger than the phase's size?

For practical and safety reasons it will be interesting to reduce sample size in order to reduce sample activity. For example, sampling will pass from 1 fuel element

(assembly) to 1 fuel rod, to 1 fuel pellet to 1 fuel fragment; the sample needs however to be representative, which requires careful sample selection, otherwise series of samples need to be selected.

In statistics, quality assurance and survey methodology, sampling is concerned with the selection of a sub-set of individual objects within a statistical set of samples to estimate characteristics of the material. Each observed properties (such as location, weight, color) are noted for independent or individual objects. In survey sampling, weights can be corrected to adjust the data for the sample design, particularly for stratified sampling. Probability and statistical theories are applied on the results to guide the analyst.

The sampling process comprises several stages:

- Defining a population of concern in the investigated material
- Specifying a set of samples possible to measure
- Specifying a sampling method for selecting samples from the material
- Determining the sample size
- Implementing a sampling plan
- Sampling and data collecting/recording
- Selecting data which can be handled.

In the most straightforward case, such as the acceptance of a batch of material from the production line, one could identify and measure every single specimen in the population and to include any one of them in the sample. However, this is generally not possible. The imprecise populations are not amenable to sampling in any of the ways below to which statistical theory could be applied.

Sampling method

Probability sampling is carried out when a sample from a population has a given probability of being selected from the set of samples, and when this probability can be accurately determined.

Non-probability sampling is any sampling method where some elements of the population have *no* chance of selection, or where the probability of selection cannot be accurately determined. Hence, because the selection of elements is non-random, non-probability sampling does not allow the estimation of sampling errors.

Advantages over other sampling methods:

- Focuses on important sub-populations and ignores irrelevant ones
- Allows use of different sampling techniques for different sub-populations
- Improves the accuracy/efficiency of estimation
- Permits greater balancing of statistical power of tests of differences between strata by sampling equal numbers from strata varying widely in size.

Disadvantages over other sampling methods:

- Requires selection of relevant stratification variables, which can be difficult
- Is not useful when there are no homogeneous sub-groups
- Can be expensive to implement.

Oversampling may be performed to minimize error. Choice-based sampling is one of the stratified sampling strategies. In choice-based sampling, the data are stratified on the target and a sample is taken from each stratum so that the rare target class will be more represented in the sample. The model is then built on this biased sample. The effects of the input variables on the target are often estimated with more precision with the choice-based sample even when a smaller overall sample size is taken compared to a random sample. The results usually must be adjusted to correct for the oversampling.

In imbalanced datasets, where the sampling ratio does not follow the population statistics, one can resample the dataset in a conservative manner called **minimax** sampling. Gaussian distribution may be selected to classify the worst case error over all the possible sample population.

Accidental sampling is a type of improbable sampling which involves the sample being drawn from a specific part of the population. The researcher using such a sample cannot scientifically make generalizations about the total population from this sample because it would not be representative enough but specific to a given area where sampling is carried out.

Finally, in a breakthrough or tailing, sampling may be performed on a logarithm scale frequency to reduce the population of samples.

2.1.2 Sampling from Analysis Mode

The material targeted for analysis may flow in a pipe or a channel. Several modes of analysis are possible to perform the assay on a fluid, i.e. gas, liquid, powder fluid bed (see Fig. 2.1), see Callis et al. (1987):

- Non-invasive
- In-line
- On-line
- At-line
- Off-line.

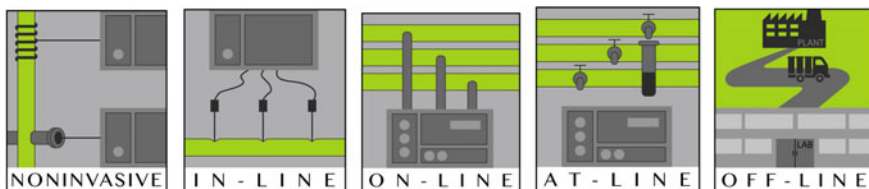


Fig. 2.1 Representation of five analysis modes based on sample location. Adapted from concept described in Callis et al. (1987), with permission © ACS

- The **non-invasive** analysis may be performed within a field through the pipe and be applied continuously or intermittently. Another possibility is to adapt a window and perform the investigation in transmission or in reflection. In both cases the information is provided without intrusion of a sensor in the pipe and without change in the thermodynamic conditions (P , T). The sample analyzed is defined by the beam, or the size of the sample passing in the field and back analyzed.
- The **in-line** analysis requires intrusion of a sensor, e.g. electrode or optrode in the pipe. There may be modification of the sampled material flow but no significant change in the thermodynamic conditions (P , T). The analysis may be performed in a continuous way; however, flow change may locally modify traces e.g. colloid's distributions, dissolved gases' fractions.
- The **on-line** analysis requires a deviation of the sample flux toward local analytical unit. Again, analysis may be performed in a continuous way; however, flow changes may locally occur, modifying the sample. The thermodynamic conditions (P , T) may consequently be slightly affected, potentially altering the sample.
- **At-line** analysis implies the sampling becomes intermittent with amount, mass (m) or a volume (V) of material collection. Here the thermodynamic conditions—including pressure and temperature of the sample—may significantly change, consequently affecting the sample.
- **Off-line** analysis also implies intermittent sampling, with potential significant change of thermodynamic conditions (V , P , T). Transport of fuel pins to hot laboratory with transfer in hot cell line is needed for non-destructive testing and sample preparation of irradiated fuel pins or irradiated structural materials. This would be the situation from one fuel rod in the reactor fuel pool (at-line) transferred to a hot cell of a hot laboratory to sample one fuel fragment from one fuel pellet from one fuel segment, from one fuel pin for example.

The concept of destructive versus non-destructive analysis may be introduced at this point, the latter allowing multiple analysis on the same sample.

2.2 Sub-sampling

The sampling and sample handling are performed taking into account (Salbu 2000):

- Representative samples and fractionation of samples
- Treatment in situ, at-site or shortly after sampling
- Dilution or pre-concentration and chemical yield control (efficiency of handling).

Sampling, pre-treatment, shipment to laboratory and analysis are areas where contaminations, losses or speciation changes can occur (Harvey et al. 1987). Corrections for these artifacts must be applied by use of isotopic tracers or specific handling conditions.

2.2.1 *Fluid Samples*

Samples of fluids may be gaseous and or liquids. Fluid samples may need physical or chemical treatments.

Gaseous samples are generally homogeneous, except in stratified large-volume samples with gases of high density differences. Some of them may include aerosols. They may be handled as delivered or after pretreatment for separation. Sampling is generally carried in loops (on-line) or in syringes (at-line). Gases are typically separated using chromatographic techniques. Analysis is then performed after separation if needed using analytical techniques described in Chap. 3.

In the cases of liquid samples, the sample may include gases, liquids and/or solids dissolved in the solvent. When gas, liquid and/or solid are dissolved forming a solution, segregation can occur falsifying the analysis of the solution (considered as a single phase). Re-homogenization is then mandatory prior to analysis. For apparent homogeneous fluid with dissolved species, such as reactor water, a separation technique such as ultra-filtration (colloids) or chromatography (ions) is needed prior to analysis of the separated species.

For heterogeneous fluid, such as suspension of organic phase in water (reprocessing), phase separation is also required prior to analysis in each single phase. Leached samples require full digestion (analytical leaching) using optimal leaching process as described in Sect. 2.2.2. In all cases an analytical sampling plan is required prior to determining the analyte properties.

- Treatments may be required at-site, shortly after sampling e.g. spiking acid for trace analysis (e.g. nitric acid prior to ICPMS analysis, see Sect. 3.2.18.4).
- Dilution of a suspension may be required prior analysis e.g. single particle analysis.
- Pre-concentration with chemical yield control (efficiency of handling) may be required prior to analysis, e.g. radiochemical analysis of a suspension.
- **Physical** separation may be performed:
 - field-free: by (ultra)-filtration, by gel-permeation or by volatilization, or
 - within a field: flow field fractionation, centrifugation, capillary or gel electrophoresis.
- **Chemical** separation: (co)-precipitation, ion exchange, extraction, electroplating, or chromatography; e.g. High Performance Liquid Chromatography (HPLC).
- Conductivity (Sect. 3.3) or spectrometer (Sect. 3.2) detectors are commonly used with ion chromatography.

2.2.2 *Solid Samples*

Sub-sampling can easily be performed at the macroscopic level on solid samples. The reduction of the sample size implies also the reduction of its activity, which is a

great advantage for its handling. The reduction in size may be performed by cutting, milling polishing collection of fragments (replicates), chemical etching, or physical milling by Focused Ion Beam (FIB). The produced macro- (for mechanical test), micro- (for spectroscopy test), nano- (for microscopy test) sub-sample can be prepared prior to its specific analysis.

Sub-sample preparations for transmission electron microscopy (TEM) analysis were recently reported and compared for nuclear materials by Aitkaliyeva et al. (2015). The preparation may include the following:

- Mechanical cutting and milling/polishing are physical subtractive processes. **Cutting** goes from crystal cleavage (using hard edge and a hammer shock) to cutting using a saw, e.g. a diamond powder coated disk or wire-saw. These two last techniques may require an inert cooling phase flow that reduces temperature excursion during cutting. The inert phase used for cooling must definitively be inert in a physical and chemical sense to avoid element dissolution or reactivity within the fluid flow. A further abrasive action including a polishing phase may be required prior to sample analysis. On the other side, **milling** may be used to produce powder that can be the sample to analyze. The milling material must be selected to avoid/reduce contamination of the powder.
- **Chemical milling** or **etching** is a subtractive reaction process. Using temperature-regulated baths allows chemical etching to remove material and to create an object with the desired shape. It is mostly used on metals, although other materials can also be treated. The process essentially involves bathing the cutting areas in a corrosive chemical known as an **etchant**, which reacts with the material in the area to be cut. Inert substances known as **maskants** are used to isolate the coated surface from the specific areas etched on the material.

For steels the etchant may be:

- Hydrochloric and nitric acids
- Ferric chloride for stainless steels
- Nital (a mixture of nitric acid and ethanol or methanol) for mild steels.

For ceramic the etchant may be:

- Hydrochloric and nitric acids
- Basic leaching with molten carbonate or hydroxide.

Protocol: the solid powder is treated by acid or basic contact. Temperature treatment by microwave (in situ) or heating (ex situ) affects the grain size distribution. Optimal size depends on type of analysis foreseen, e.g. macro- sub-sample for mechanical test, micro- sub-sample for spectroscopy test, nano- sub-sample for microscopy test.

Ion milling and etching

The use of **Focused Ion Beam (FIB)** is required for production of micron-sized samples with regular dimensions. Currently, this can be performed on low active

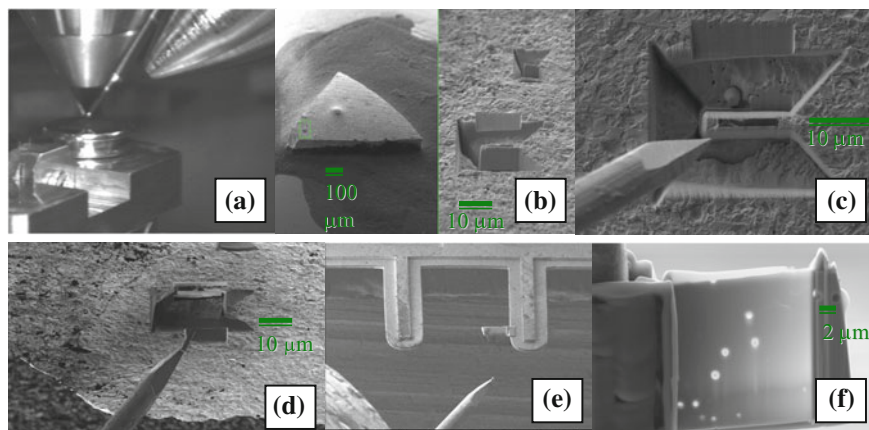


Fig. 2.2 FIBing a lamella sub-sample from a fuel “pie” piece. **a** set-up in the FIB unit, **b** fuel material excavation around the sub-sample, **c** approach of the pin for sub-sample transfer, **d** freed sub-sample and its transfer to sample carrier, **e** sub-sample fixed on sample carrier by carbon welding, **f** lamella obtained after fine abrasion. Details from Degueldre et al. (2013a), with permission © Elsevier

nuclear material (e.g. Degueldre et al. 2013a), or at very few other hot laboratories on irradiated fuel and active nuclear material samples, e.g. Teague and Gorman (2014). The sub-sample preparation is depicted through various production steps in Fig. 2.2. Such prepared samples can then be used for direct analysis in the FIB by scanning electron microscopy or synchrotron investigations (X-ray absorption or diffraction techniques), or for TEM, Degueldre et al. (2013b). A coating with thin film conductive material may be needed.

Other treatments

- Replicate sub-samples may be obtained by surface polishing, contact with adhesive tape and transfer of particles. To reach representativeness, several sub-samples from various places on the sample may be necessary. For example, the sampling requires cutting of the fuel rod, section handling and sub-sample preparation such as specimen cutting, cross-sectioning, possibly embedding in resin, and polishing with abrasive sand paper. Replicate (grain samples detach/attach) production may be performed using rotational grinding (detach) a fuel cross-section and transfer (attach) of fuel particles on adhesive tape pieces, e.g. Degueldre et al. (2011). The production steps are depicted in Fig. 2.3.
- Abrasion without field, may be upgraded by abrasion within a field, e.g. gravity (centrifugal), magnetic.

The size of the sample or sub-sample to analyze must be compared to the size of the spot analyzed.

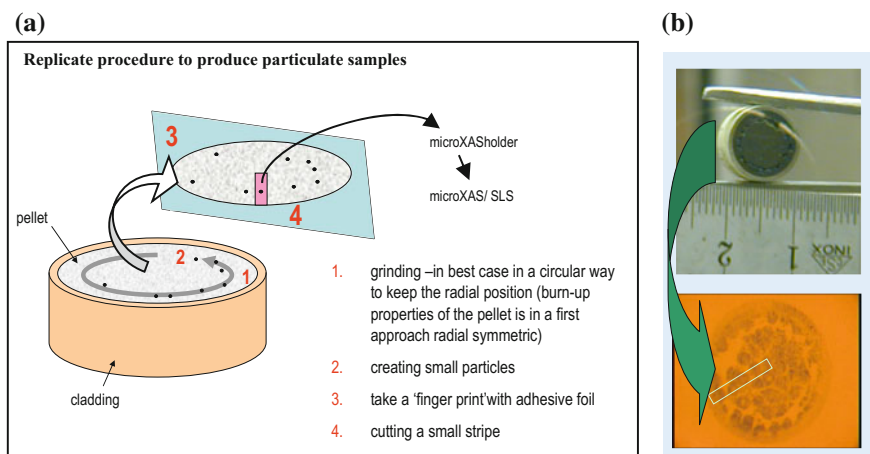


Fig. 2.3 Replicate procedure to produce particle samples on fuel cross-section. **a** Schematic procedure for sample preparation. **b.** Top fuel specimen prior to grinding, bottom: sub-sample obtained by contacting the adhesive Kapton foil on the grinded fuel section. A piece of sub-sample may be cut for activity reduction (below dose limit); Degueldre et al. (2016), with permission © Elsevier

2.3 Reference Materials and Calibration

2.3.1 Reference Materials

Certified Reference Materials are standards used to control the quality of the analysis, to validate analytical methods or for the calibration of instruments. Reference materials are important for analytical chemistry and nuclear material analysis. Since most analytical instrumentation is comparative, it requires a sample of known composition (stable, fixed fraction of components) for accurate calibration. These reference materials are produced under stringent preparation and manufacturing procedures. Certification and traceability of the data must be documented in detail. Quality management for laboratory accreditation requires metrological traceability and use reference materials for calibration (Calli 1979).

The certified reference material is “a material characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability”.

These reference materials may be:

- Pure substances; stoichiometric chemicals, characterized for major constituents.
- Chemical substances; characterized for major chemical and trace impurities.
- Standard solutions and gas mixtures, often prepared from pure substances.

- Matrix reference materials characterized for the composition of specified major, minor or trace chemical constituents. Such materials may be prepared from matrices containing the components of interest, or by preparing synthetic mixtures.
- Reference objects or artifacts, including microscopy specimens characterized for properties ranging from object type to sized specimens.

2.3.2 Calibration with Internal or External Standards

Internal standard methods are used to improve the precision and accuracy of results where volume errors are difficult to predict and control. A systematic approach has been used to compare internal and external standard methods in high-performance analytical techniques. The precision may be determined, with both analyte and internal standard combined. Precision using three methods of adding the internal standard to the analyte before final dilution may be examined. The internal standard method is used more frequently and more performing than the external standard methods in all instances.

A systematic approach was used to compare **Internal Standard (ISTD)** and **External Standard (ESTD)** methods used in high-performance analysis.

An internal standard in analytical chemistry is a chemical substance that is added in a constant amount to samples, the blank and calibration standards in a chemical analysis. This substance can be used for calibration by plotting the ratio of the analyte signal to the internal standard signal as a function of the analyte standard concentration. This is done to correct analyte losses during sample preparation. The internal standard is a compound that must show similar behavior to the analyte.

The external standard approach is similar but the assay on the standard is carried out independently, the analyte in one batch, the standard in a separate batch. This practice could however be slightly affected for its precision compared to the internal standard approach.

References

- Aitkaliyeva, A., Madden, J. W., Miller, B. D., Cole, J. I., & Gan, J. (2015). Comparison of preparation techniques for nuclear materials for transmission electron microscopy (TEM). *Journal Nuclear Materials*, 459, 241–246.
- Calli, J. P. (1979). The role of reference materials in the analytical laboratory. *Fresenius' Journal of Analytical Chemistry*, 297, 1–3.
- Callis, J. B., Illman, D. L., & Kowalski, B. R. (1987). Process analytical chemistry. *Analytical Chemistry*, 59, 624A–637A.
- Deguelldre, C., Martin, M., Kuri, G., Grolimund, D., & Borca, C. (2011). Plutonium—uranium mixed oxide characterization by coupling micro-X-ray diffraction and absorption investigations. *Journal of Nuclear Materials*, 416, 142–150.

- Degueldre, C., Borca, C., & Cozzo, C. (2013a). Curium analysis in plutonium uranium mixed oxide by x-ray fluorescence and absorption fine structure spectroscopy. *Talanta*, 115, 986–991.
- Degueldre, C., Schaeublin, R., Krbanjevic, J., & Minikus, E. (2013b). Electron energy loss spectroscopy investigation through a nano ablated uranium dioxide sample. *Talanta*, 106, 408–413.
- Degueldre, C., Bertsch, J., & Martin, M. (2016). Post irradiation examination of nuclear fuel: Toward a complete analysis. *Progress in Nuclear Energy*, 92, 242–253.
- Harvey, B. R., Lovett, M. B., & Boggis, S. J. (1987). Some experiences in controlling contamination of environmental materials during sampling and processing for low-level actinide analysis. *Journal of Radioanalytical and Nuclear Chemistry*, 115, 357–368.
- Salbu, B. (2000). Speciation of radionuclides in the environment. In R. A. Meyers (Ed.), *Encyclopedia of analytical chemistry* (Vol. 1, pp. 2993–3016). Chichester: John Wiley
- Teague, M., & Gorman, B. (2014). Utilization of dual-column focused ion beam and scanning electron microscope for three dimensional characterization of high burn-up mixed oxide fuel. *Progress in Nuclear Energy*, 72, 67–71.

<http://www.springer.com/978-3-319-58004-3>

The Analysis of Nuclear Materials and Their
Environments

Degueldre, C.A.

2017, XXIV, 288 p. 109 illus., 83 illus. in color.,
Hardcover

ISBN: 978-3-319-58004-3