10.3.4.9 Preparation of materials for analytical atomic spectrometry

The preparation of materials prior to spectrochemical analysis is one of the most important steps in the determination of elements, especially where these are at trace levels, and proposals are given below, for nomenclature on preparation of materials.

10.3.4.9.1 Sampling procedures and definitions

Sampling procedures not specifically related to spectrochemical procedures are dealt with in a report entitled "Nomenclature for Sampling in Analytical Chemistry" prepared by IUPAC Analytical Chemistry Division, Commission V-3 (See Note 1). The terminology adopted here is outlined schematically in Fig 10.14 and discussed below. The routes from "lot" to analysis in Fig. 10.14 are dependent on the *sampling plan* adopted. Referring therefore to Fig. 10.14 the nomenclature of the different sample types in the sampling hierarchy is outlined in the definitions below.

A *lot*: an identified quantity of material assumed to be uniform for the purposes of the investigation. It constitutes the total material to be sampled by using a particular sampling plan.

Sampling unit: the discrete identifiable portion suitable for taking as a sample or as a portion of a sample. These units may be different at different stages of sampling.

Bulk sample: the sample resulting from the planned aggregation or combination of sample units.

Laboratory sample: the sample supplied to the laboratory and often taken directly from a bulk sample; it may consist of sample units.

Composite sample: often prepared as a representative mixture of several different (usually bulk) samples, and from which the laboratory sample is taken.

Test sample: the sample taken or formed from the laboratory sample, by a process involving homogenization using physical or mechanical treatments such as grinding, drilling, milling or sieving. The test sample is then in a form suitable for *subsampling* for analytical purposes, for storing for future analysis or for use for test purposes other than analytical.

The *analytical sample*: the final product of sampling which serves for the determination of at least one *quality characteristic*. It is obtained by subsampling the test sample directly or by chemically or physically treating the test sample, or a subsample of it, to provide a form suitable for analysis. The analytical sample may be subdivided to enable,

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Note 1 *Pure & Appl. Chem.*, *62* 1193 (1990). See in Chapter 18.

for example, replicate measurements to be made. In some types of analysis only a part, unspecified in size, of the analytical sample is consumed in the analysis.

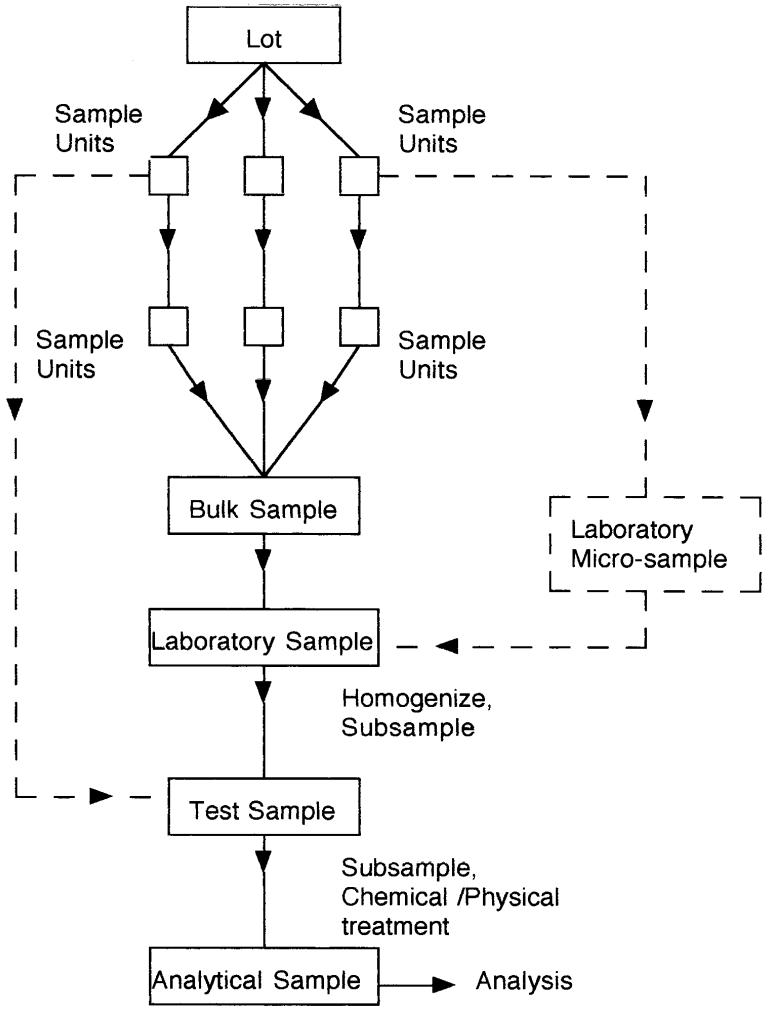

Fig.10.14 Schematic diagram of sampling stages and terminology

Where no homogenization or subdivision is necessary the laboratory sample, the test sample, and, if the latter requires no further chemical or physical treatment, the analytical sample are identical.

With some homogeneous materials such as waters or oils the laboratory sample may be taken directly from a sample unit and, if no further subdivision or homogenization is carried out, the laboratory sample is the test sample. Similarly, with *atmospheric particulates* collected on a filter, the sample unit is the laboratory sample and, if no further subdivision or homogenization is carried out, also the test sample.

In many spectrochemical techniques the physical and chemical form of the sample actually participating in the measurement, and contributing to the signal, may differ from that of the analytical sample. In these cases it may undergo several transformations from one state to another, for example, in flame atomic spectroscopy, into an aerosol and then a metal vapour or it may be converted into a gaseous hydride in the determination of hydride-forming elements. These forms might be considered 'instrumental samples' but since such transformations may not be fully under the control of the analyst they are excluded from consideration with respect to sample preparation.

The analytical sample should truly represent the laboratory sample, but this may not be the case in all respects in the case of partial digestion or because during its preparation, the material may have become oxidized or hydrated, dehydrated, carbonated etc. The preparation of such samples may require additional precautions, such as working under dry and/or inert gas atmospheric conditions.

With all methods of sampling and preparation the accidental introduction, i.e. contamination (see Note 2), or loss of one or more constituents can occur. This may be caused by the materials used in the preparation stages, the composition or physical properties of the containing vessels, the chemical used or the treatment employed. Therefore, all the preparation processes and the materials and chemicals employed must be chosen to minimise contamination with and losses of the analyte. Contamination can be avoided by the use of *dedicated laboratory-ware* for specific analyses. *Clean-room*, or *clean-glove-box* conditions and *laminar air-flow cabinets* may also be required for the reduction of *environmental contamination*.

Accurate sample *documentation* is essential not only for correct matching of samples and analytical results but, combined with documentation of *reagents* and consumable laboratory items such as filter papers and with regular measurement and recording of the *analytical blank*, also serves to identify (retrospectively) possible sources of contamination.

10.3.4.9.2 Metallic materials

Self-electrode samples are used for emission spectroscopic analysis and other techniques. The analysis of a metallic material is often carried out using the laboratory sample as the analytical sample. Laboratory samples which may be analysed directly, after a minimum of surface treatment, are *ingots*, *bar samples*, *forged samples*, *cast samples*, *cast-pin samples*, *chill-pin samples*, *splash samples*. Other types of sample in this category are *sheet samples*, *wire samples*, *rod samples* and *fabricated samples* (e.g. a machined component such as a gear-wheel). In some cases large components may be sampled or

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Note 2 *Pure Appl. Chem.*, **51**, 1201 (1979).

excited on site for direct analysis locally or remotely. Test samples from which the analytical sample may be taken directly include *drillings*, *sawings*, *chips*, *filings*, *millings*, *turnings* and *shavings*.

In order to obtain a uniform crystal structure, and overcome its previous metallurgical history, the analytical sample may be derived from the laboratory or test sample by some form of *heat treatment*, followed by *quenching*: a uniform crystal structure may also be achieved by *annealing* at a controlled temperature. The metallurgical history may also be overcome by subjecting the surface to an energetic electrical discharge and/or by *forging*, *hammering* and *rolling*. For some analytical purposes it may be desirable to melt or *vacuum-melt* the whole laboratory sample.

Prior to analysis, all or part of the surface can be *faced* mechanically to form a plane surface or machined to the required shape. Thereafter the metal surface may be prepared to various degrees of smoothness by using a *disc*- or *band-facer*, *belt-sander* or *linisher*. It may be mechanically polished and in some cases *spark erosion*, *sputtering*, *electrolytic etching*, or *chemical etching* may be used to clean the surface or to investigate surface characteristics. Many of these surface treatments are potential sources of contamination and suitable precautions should be taken.

For X-ray photo-electron spectroscopy (XPS) or electron beam excitation methods, use is sometime made of *vacuum-coating*, *vacuum-deposition*, *ion-implantation* or sputtering techniques to prepare or form the surface of the analytical sample and/or to prevent build-up of electrical charge during analysis.

A conductive sample prepared in one of the ways described above may be used as a self-electrode for analysis by optical emission spectroscopy using arc, spark or other methods of excitation (see Note 3). It may also be used for X-ray fluorescence analysis.

10.3.4.9.3 Non-metallic materials

Some types of laboratory sample of inorganic materials, including *cores*, *chips*, *pipe* or *spear samples* and *sievings*, may not be homogeneous and thus may require further treatment to produce a test sample of sufficiently small *particle size* to make representative sampling possible or to suit the method of analysis being employed. This can be achieved by *dry grinding* or *wet grinding* (i.e. grinding in a liquid which does not dissolve the sample) or shattering the material in a *mortar* (by hand or mechanically), *ball-mill*, *pulverizer*, *disc-mill*, *shatter-box mill* or *hammer-mill*. The materials from which such devices are manufactured must be carefully chosen to avoid contamination.

Note 3 Nomenclature, Symbols, Units and their Usage in Spectrochemical Analysis-V, Radiation Sources, *Pure Appl. Chem.*, **53**, 1913 (1981).

Subsampling of powdered materials may require the use of *rifflers*, *dividers* or the technique of *coning and quartering*.

Massive laboratory samples of organic material may be difficult to prepare in a form from which a representative test sample can be taken. A dry sample (such as plastic) may be prepared by *shredding* or a wet sample (such as sewage sludge) by homogenizing in a *blender* or *tissue-blender*. Alternatively, some organic materials may be made brittle by freezing in liquid nitrogen (but by no means in liquid air because of the explosion hazard), the *frozen material* thereafter being shattered into fragments from which the test sample is taken. Care should be taken to report results as being either on a *dry-matter* or *wet-matter* basis. In some cases the entire laboratory sample must be used as the test sample. Examples include tissue sections, skin and hair. Some biological materials are in liquid form (i.e. blood, urine, spinal fluid) from which the test sample can readily be taken. In other cases the laboratory sample must be treated to provide a homogeneous test sample. Depending on the elements being determined, the laboratory sample may be *oven-dried*, *vacuum-dried* or *freeze-dried*. The dried laboratory sample is then homogenized by one of the methods given above, to form the test sample from which the analytical sample is taken. For some purposes the freeze-dried laboratory sample, for example a freeze-dried tissue section, may be analyzed directly. For materials with a *complex composition*, i.e. consisting of non-homogeneous particles mixed at random or particles contained in a liquid, e.g. wear metals in oils, the test sample and the analytical sample must be taken by an appropriate method in which prescribed conditions are usually laid down (e.g. temperature, mixing procedure, etc.) to ensure obtaining representative test and analytical samples.

It may be useful to take a *laboratory micro-sample* (see Note 4) directly from the sample unit, e.g. blood from an animal. Such samples, however, may not be fully *representative samples*. A laboratory micro-sample in the form of an isolated piece of material or particle, obtained for example in forensic work, may be used directly for *micro-analysis*. A *selective micro-sample* results where a small portion has been separated from the lot or laboratory sample by selective means such as *magnetic-*, *density-*, or *manual separation*, or by *micro-drilling*, or by *centrifugation*, e.g. the separation of magnetic minerals from a geological material, or the separation of metal particles from a lubricating oil. If individual particles are analysed the term *individual particle analysis* is applied. The analysis of specific *micro-areas* or *micro-volumes* of a larger sample, e.g. the analysis of an inclusion in a metal, is also classified as micro-analysis (See Note 5). In these cases, the test or analytical sample is prepared from the laboratory sample in such a way that a small portion of its surface can be analysed without removal from the surrounding bulk. This enables an *in situ micro-analysis* or a *surface analysis* to be carried out (See Note 6).

Note 4 One definition of a micro-sample is given in compendium of Analytical Nomenclature, H.M.N.H. Irving, H. Freiser and T.S. West, Pergamon (1978) 130, as a sample of weight between 1 and 10 mg.

Note 5 *Pure Appl. Chem*. *57* 1453 (1985)

This may be *non-destructive*, i.e. does not change the physical or chemical nature of the sample, or may require *micro-surface removal* of the surface area of interest. These techniques can give *depth profiles* of element distribution.

The preparation of a sample for analysis will depend on whether the final determination is to be carried out in solution or on a solid. In the terms given below, there is some overlap. For example, a *fused sample* may be analysed directly as a liquid melt or the cooled solid or it may be treated further to provide a solution. Alternatively the fused sample may be ground and *pelleted*.

10.3.4.9.4 Materials analysed in solid form

A metallic test sample in the form of drillings, sawings, or chips etc. may be analysed directly or it may be formed into a *pressed-disc*, or *pellet* by means of a *pelleting press*. *Metallic glasses* may be recrystallized by heating to aid in dissolution.

A non-conducting inorganic test sample may be mixed with an *additive*. An inorganic powder can be mixed, prior to pelleting, with a *binder* which may be an electrical conductor. For X-ray fluorescence analysis, a *low* or *high absorber* is sometimes employed. For some purposes, for example when only a small amount of material is available, the pellet may be *faced* by the pure binder or other metal, one face only of the pellet being composed of the sample/binder mixture.

Some organic materials can be analysed without pretreatment. More usually, however, the material is ashed or mineralised. The ash, or mineralised residue (with or without additives) may be used for direct analysis, or alternatively, a solution of the sample may be prepared from it. (See below). The material may be *dry-ashed* in a *muffle furnace* at a controlled temperature. Alternatively it may be mineralised by *low temperature ashing*, in, for example, an atmosphere of oxygen or fluorine which has been excited by a radio-frequency discharge. In order to determine elements which are easily volatilized, or are present as volatile species, organic material may be ashed in oxygen in a *closed oxygen combustion system*. One such method is *oxygen-flask combustion* by which the test sample is burned in a closed flask containing oxygen and an absorbing solution in which the analytes are subsequently determined. Other closed oxygen-based combustion systems such as pressure bombs can also be used. (See below). For some biological fluids a *deproteination* or *haemolysis* stage may be required in the preparation of the analytical sample.

In order to achieve homogeneity or to destroy the crystalline structure of, for example, a non-metallic sample, it may be heated with a *fusion reagent* or *fusion mixture* to form a *fused sample* (the use of the term flux is discouraged). The molten, fused sample may be poured on to a cold, flat surface to produce a glass which can be analysed directly, e.g. by

X-ray fluorescence spectroscopy, or it may be cooled, ground and thereafter analysed. To facilitate grinding the hot brittle solid can be *shattered* by dropping it into cold water, or some other liquid which does not dissolve the glass.

Solid materials in powder form can be prepared for analysis as a *slurry* of the powder in an aqueous or liquid medium. These may be stabilized by using a sufficiently fine powder or by means of *emulsifiers* or *thixotropic agents*. For materials of complex composition, prescribed conditions for representative sampling may be necessary.

10.3.4.9.5 Dissolution of materials

For some methods of analysis it may be required that the analytical sample be in a liquid form - the *sample solution*. The material may be brought into solution by *acid-digestion* in an open vessel at atmospheric pressure. Acid-digestion with a suitable acid, or a combination of acids, may be used not only to dissolve the material but also to remove a matrix constituent by *selective volatilization*, e.g. silicon by the use of hydrofluoric acid. Organic materials may be decomposed by the use of oxidants such as nitric, sulfuric or perchloric acids. The term *oxidative acid-digestion*, rather than the term wet-ashing, should be used. *Acid vapour-phase attack* may be used to dissolve material in one vessel by the attack of the vapour from an acid in another vessel. The system may be either open to the atmosphere or enclosed. Some materials may not be fully dissolved by acid-digestion at atmospheric pressure. A more vigorous treatment involves *bomb-digestion* in pressure vessels lined with polytetrafluoroethylene (PTFE), glass, silica or vitreous (glassy) carbon or in sealed silica tubes. The test sample and acids are heated in such a closed vessel, so that the digestion is carried out at higher pressure and temperature. The test sample may also be transformed into an acid-soluble form by *sintering* it with a suitable reagent.

In *partial digestion* and/or *selective digestion* procedures only part or some of the analytes present are brought into solution. This may be preferred to *total decomposition* if relative concentrations of the analyte in the test samples provide sufficient information (e.g. materials for geochemical exploration). According to the reagents used and treatment applied (e.g. agitation and heating etc.) the extracted portion may correspond to the analyte present or bound in a particular form. *Chemical leaching* may thus provide a means of analyte *speciation* or *phase analysis*.

Some materials, either inorganic or organic, may be dissolved by digestion with bases. For organic materials in particular *solubilization* with bases is often efficient.

Decomposition of organic materials (e.g. starch, sugars, proteins etc.) can be achieved by *enzymic decomposition*, in which the enzyme converts a high-molecular-mass compound into lower-molecular-mass species. The process can be regarded as an example of *enzymic degradation*.

Aqueous materials, such a natural waters, may contain organically-bound elements. These can be converted into inorganic form by *photochemical effects* (*radiolysis*). The efficiency of the process may be increased by the use of an additive and/or accelerated by the addition of an oxidant.

Pyrolytic techniques are used for the high-temperature *thermal decomposition* of a test sample or for its conversion from one chemical form to another. Although not primarily intended as a method of preconcentration, pyrolytic techniques can be used to separate the analyte or analytes from the matrix of the test sample. In a technique called *furnace-pyrolysis*, a flowing stream of gas (hydrogen, oxygen, nitrogen, chlorine, etc.) required to produce volatile species of the elements being determined, is passed over the test sample in a heated furnace. The analytes leave the furnace in the gas stream, or are entrained by a carrier gas. The analytes in the gas stream may be collected in an absorbing solution, on a carbon or other filter or by condensation on a cool surface. In the case of mercury this can also be done by *amalgamation* with a noble metal. The analytes may then be swept and released from the trap, by heating, into a sampling source for analysis. The test sample may also be mixed with a reagent to produce a volatile compound which is volatilized by heating and separated by *distillation*. Metallic samples can be dissolved by *anodic oxidation*. This technique may also be used to oxidize and dissolve inclusions or base metal phases from metals and alloys.

10.3.4.9.6 Preconcentration and separation

In order to improve the limit of detection and the reliability for the determination of some analytes it may be desirable to employ some form of *preconcentration* and *separation* to increase the analyte to matrix ratio or to reduce interference effects. The terms for collection and concentration methods have been summarized in earlier IUPAC documents (see Notes 24,25). Methods not covered by these reports are (1) concentration by *fire-assay*, involving heating of the test sample of an ore with a special fusion reagent, and finally removal of base metal by the oxidative process of *cupellation*, (2) *cementation* of elements in solution on to a metal cementant by spontaneous electrochemical displacement and (3) preconcentration on *activated carbon*.

Separation of the analyte from the matrix can also be achieved by transforming it into volatile species using chemical reactions at approximately room temperature. The volatile analyte thus separated may be passed either to a *collecting device* such as a *cold finger* or *cold trap*, condensed on a cold electrode, or supplied directly to the sampling source (see Note 7). Wide use is made of chemical vapour generation of volatile species such as metal hydrides, halides, chelates and oxides for separation or preconcentration of the analyte (see 10.3.4.6.).

Note 7 *Pure Appl. Chem.*, *51*, 1201 (1979)

10.3.4.9.7 Speciation of elements

The term *speciation* is applied to the identification of the particular combinational form or oxidation state (e.g. molybdenum as molybdate, mercury as methylmercury etc.), in which an element exists in a material and to the determination of the element in that form.