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SAMPLE DIGESTION FOR THE DETERMINATION OF ELEMENTAL TRACES IN MATRICES OF ENVIRONMENTAL CONCERN

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INTRODUCTION

Many methods for the determinations of elements require that all element containing species are converted in one single form which is uniform and well defined; i.e. that all forms of binding present in a particular sample are converted into one or more simplified stages (e.g. ionic). Methods requiring sample treatment are, amongst others, atomic absorption or emission spectrometry and voltammetry; in some cases (e.g. in XRFA) a complete digestion of the sample to avoid matrix interferences is not required; here dilution of the sample or digest, or a comparison of the results with those of a certified reference material (with approximately the same matrix composition) is often sufficient. The various applicable techniques of element determination do not all require the same degree of sample matrix break-down, e.g. voltammetry is more prone to errors caused by (complexing) organic matrix fragments, than flame atomic absorption spectrometry. Atom spectrometric techniques (AAS, ICP) can be used for solutions which are not completely converted into simple products (i.e. H_2O, CO_2 and ions), because at the higher temperatures of the measurement, possible complexes dissociate. Voltammetric techniques on the other hand, require that the ions to be determined are free and not bound to other ions or fragments of an organic matrix. Certain biotic matrices are sufficiently digested with nitric acid in a bomb, if atom spectrometric techniques are to be used; whereas for voltammetry a further digestion with perchloric acid is necessary.

The choice of a digestion technique should take into account the particular requirements of the end determination. For some cases (e.g. XRFA), a complete digestion of the sample is not required. Especially in various control determinations, an incomplete digestion which consumes less time and labor, is often acceptable for a special well-described purpose. Typical examples of accepted but incomplete digestions from various fields are the determination of the Kjeldahl nitrogen content (food analysis), the determination of the aqua regia soluble metal contents (agriculture, soils and sludges, ground water pollution estimates) etc...

However, when one wants to know the total contents, one has to apply a digestion technique which, in combination with the chosen end determination, allows a determination of the total content. Such a total digestion should be applied wherever the establishment of an element balance is needed, where element pathways through various eco-compartments have to be found in order to construct environmental or biological models, where "worst-case" strategies are necessary because the fate or the species of an element are as yet unknown (e.g. total Hg vs methyl-Hg). Needless to say such a total digestion and determination is always more cumbersome than the determination of a methodologically defined parameter. Unfortunately, there is no digestion technique able to cope with widely differing matrices which is as well suited for a large number of determinations per day. For every case a selection of a possible optimal digestion technique has to be made taking into account factors such as: method of end determination, kind of matrix, element concentrations, possible interferences, losses or contaminations, practicality in the laboratory and safety hazards.

Usually, one arrives at a suitable digestion procedure for a particular laboratory applicable to one or a few similar matrix types. This report is not intended to point to the best technique if any, but to discuss the factors considered when dealing with the necessity for a sample digestion prior to the end determination. Extensive surveys of possible techniques have been given for specialized fields as well as more general surveys by e.g. Tschöpel (50), Bock (51), etc. It would be beyond the scope of this report to deal with the matter again in such a detailed way. Some general remarks can be made, however, and a general survey can be presented.

In trace analysis problems, the demands, risks or errors increase strongly with decreasing content; characterisitics for the µg/g range do not necessarily hold at the 100 ng/g range or lower. Before applying a method of digestion, careful checks on accuracy and completeness of of digestions (e.g. with certified reference materials or radiochemistry) are necessary. With decreasing contents, the errors due to both contamination and losses increase. The lower the content to be determined, the more one should consider the following remarks.

Besides the content of contaminants or interferences in the digestion reagent, the amount of the reagent is important. An active and efficient less pure reagent may be preferred over a rather inactive, but extremely pure one, if a smaller amount is sufficient. Preferably, acids which can easily be purified such as $HClO_4$, $HClO_3$, HCl, HF, HNO_3, and to a lesser extent H_2SO_4, are frequently and successfully applied. However, these reagents should be of a high purity in extreme trace analysis. In most cases sub-boiling point distillation is necessary, as well as storage and use under clean-room conditions.

Every digestion takes place in a suitable vessel. In trace analysis, not only is the shape and size of the vessel important but the wall material must be chosen to avoid (cross) contamination as well as losses by adsorption. If the wall surface is large compared to the content of the vessel, adsorption losses easily occur. These losses in turn may cause contamination of the next sample (memory effects). A material such as PTFE, although seemingly perfectly stable and inert, may gradually increase its surface area (cracks) after use Glass and especially quartz-glass have more favourable properties but they cannot be used if a silica containing matrix (e.g. soils, rocks, sediments, some plants, coal, etc.) is to be completely digested using of hydrofluoric acid. Glassy carbon if sufficiently resistant against the reagents used, is often a good alternative.

A good way to reduce the amount of required reagent is by operating under pressure in closed vessels at higher temperature to increase the oxidation potential and thus the reactivity. The smaller amount of reagent and the closed system decrease the risk of contamination by reagents and by laboratory air. Therefore, pressurized digestions are often recommended (e.g. by IUPAC V2). The demands made on the inertness of the vessel walls are, however, considerably higher. At high temperatures (200 °C) PTFE cannot be used many times. Moreover trace elements are easily leached from glass by digestion acids and should not be considered for high temperature pressure digestions of materials with low contents. Quartz-glass is a suitable material but in case of silica-containing matrices, a separate attack with e.g. hydrofluoric acid in a PTFE vessel at lower temperatures is necessary. This, of course, requires a transfer step from a quartz-glass to a PTFE vessel, increasing the risk of losses or contamination. If possible the whole digestion should be carried out in one closed system, without transport of material. If this is not possible, the transport should be undertaken in a closed system, (e.g. hydride formation, sorption on a carrier such as an immobilized reagent, ion exchanger or the like) or under clean-room or clean-bench conditions. The avoidance of contamination must involve a careful cleaning of all surfaces contacting the sample or digest. Including polishing to reduce the surface area if necessary. Elaborate procedures have been developed out using in the final stage, cleaning reagents of highest purity (e.g. sub-boiling point distilled HNO_3 applied for a prolonged period).

Losses may occur not only by adsorption but also by volatilization, which occurs especially in open vessels (e.g. dry ashing, fusion). If, in the course of a destruction at the applied temperature a volatile compound can be formed, volatilization must be considered. Sometimes a carefully selected temperature programme can, depending on the matrix, avoid a measurable volatilization. It is highly recommended to apply proper ashing acids (e.g. mixture of Mg-oxide and nitrate or nitric acid) in dry ashing procedures. Possible volatile compounds formed in a closed vessel digestion can be attacked by the digestion reagent. The design of the closed vessel should allow such attack. This is easily achieved in a high temperature, high pressure closed bomb digestion. One may conclude that a digestion with a pure gas or with a minute amount of acid of highest purity under high pressure at high temperature in a closed vessel, should be regarded as most effective for trace analysis.

In the following a brief summary of the various possibilities will be presented. Techniques which use the addition of spike (e.g. isotope dilution mass spectrometry) require a vigourous attack of the whole matrix to make sure that the endogeneous element is present in the same form as the spiked element.

Table 1 summarizes some methods and the matrices for which they can be applied.
In Part 2 of this paper we shall deal with recent findings concerning the most common techniques and in Part 3 with two examples to illustrate the general statements made before.

1. NOTES TO SOME COMMON MINERALIZATION TECHNIQUES

In recent literature many surveys of techniques have been presented often accompanied by critical remarks with reference to factors such as difficulties, labour intensity, cost and reagent quality (1-5). Presently the techniques most commonly in use are: UV-irradiation and oxidation with dissolved oxygen, wet digestion, (dry) combustion and fusion. Some notes will be made in the following with regard to their use.

A. Oxidation using UV-light

Oxidations under the influence of UV-light and possibly with the acid of an oxidizing agent (e.g. hydrogen peroxide or peroxodisulphate) are mainly used for aqueous solutions (6). Dissolved organic molecules and complexes of the analyte metals are broken down to yield free metal ions. The technique is applicable for sea-water (7-9), waste water (10), fresh water (11) and wine (12). Equipment is commercially available and further improvements and developments are still being made (13). Stinger et al. (10) compared UV-irradiation (4h) with an acid digestion (hydrogen peroxide/sulphuric acid) for the determination of As in waste water. Both methods gave comparable results. The method does not oxidize all organic components possibly present in water; chlorinated phenols, nitrophenols, hexachlorobenzene and similar compounds are only partly oxidised (14).

TABLE 1

Kind of digestion	Method	Reagents	Application
Fusion	acid/alkaline	persulphate/NaOH	inorganic
	oxid./reducing	Na_2CO_3, $NaNO_3$	inorg./organ.
	Freiberg	Na_2CO_3 + S	inorg.
Wet	open vessel		
	acid	HCl (HF)	inorg.
	oxidizing	e.g. $HNO_3/KMnO_4$/(HF)	inorg./organ.
		$HClO_4$	organ.
		Catal. oxid.	
		H_2O_2 (Fe (II) as a catalyst)	
	UV-oxid.	S_2O_7; H_2O_2	waters
	closed system; static	bomb digestion with e.g. HCl, HNO_3, $HClO_4$	inorg. + organ.
	closed system; dynamic	HNO_3-reflux *	inorg. + organ.
Combustion	open vesel	dry ashing with air	organ.
	closed system; static	oxygen flask	organ.
	closed system;	Wickbold, Trace-O-Mat R	organ.
Pyrolysis		organ.	
Halogenization			Br_2, Cl_2 inorg.
Reduction		H_2 or C	inorg. + organ.
Electrolysis		solns./inorg.	
Enzymatic		urease	urea fertilizer
Hydrolysis		Tetra-alkylammonium hydroxide	organ.

* closed through a liquid slot.

B. Acid digestion

Acid digestions are commonly used for nearly every type of matrix. For more rapid treatments or lower element concentrations a pressurized digestion (closed system) is the choice. For siliceous matrices, treatment with hydrofluoric acid in PTFE-lined vessels (HF) at or after the digestion is necessary. Pressurized digestion systems also allow the addition of HF together with the other (oxidizing) acids. The advantages and disadvantages of pressurized digestions were dealt within a previous report of the IUPAC Commission V2 (micro and trace analysis) written by Jackwerth and Gomiscek (15). Bajo et al. (1) present a survey of several acid digestion techniques.

Knapp (16) treated sources of systematic errors in digestion and gave the following possibilities to reduce the risk of errors:

1. the amounts of reagents should be as small as possible (contamination);
2. the ratio mass: surface should be as large as possible;
3. the vessel material should be inert and pure;
4. the whole system should have the possibility of sealing and keep ambient air out.

This leads to the recommendation to use pressurized digestion to avoid losses and contamination. The high pressure digestions accordingly developed have gained wide

acceptance especially for matrices with trace levels below 500 ng/g. The vessel walls should preferably be made of quartz. Other authors recommend glassy carbon (17) or PTFE. A major drawback of a PTFE vessel is that after some period of use it shows minute cracks into which a part of the digest diffuses, thus causing losses and memory effects. Temperatures above about 200 °C are not recommended as the material becomes soft. As discussed above, digestion time, temperature and choice of reagents depend strongly on the type of matrix and the chosen method of final determination. Different authors come to different conclusions because they have studied different matrices. Not all biotic, organic or mixed matrices (soils) are equally difficult to digest. When following the recommendations laid down in the literature the user should be aware and develop optimal conditions for the type of sample. Certified reference materials could be of great help (18).

Recent literature has presented some interesting experiences which can act as guidelines. For food materials a pressurized digestion with nitric acid can be sufficient; with 300 mg sample size and digestion at 150 °C (19). Stoeppler et al. (20) investigated the digestion of an organic matrix with nitric acid in more detail. They measured the pressure changes during the digestion and studied the influence of the type of matrix, the temperature programme and the amount of acid. They found that the digestion never oxidized all organic fragments completely. This could pose difficulties in voltammetry. This is confirmed by Adeloju et al. (21) who determined Se in biotic materials. Digestion with HNO_3 yielded poor results when using cathodic stripping voltammetry; a mixture of nitric and sulphuric acid gave better results, but even here the matrix influence was considerable as the voltammettric peak shifted from one sample to another.

Chloric and perchloric acids may cause severe explosions if used with large amounts of oxidisable matter. It is recommended to use these acids to complete the digestion, adding them in a later stage of the digestion (to a transparent digest). Perchloric acid is often required if voltammetry is applied. A safe and efficient technique consists of the evaporation of the digest to dryness followed by a treatment with $HClO_4$ till fuming (or even evaporation of the added acid). Addition of the strong oxidant chloric acid ($HClO_3$) to the nitric acid increases the power of oxidation: no losses of As, Cd, Hg or I could be observed when digesting 70-400 mg of an organic sample at 130 °C for 70-90 min (22). Stable matrices such as graphite, charcoal or some environmental were successfully attacked after addition of perchloric acid, sulphuric acid or sodium dichromate to the nitric acid (23).

May et al. (24) digested up to 4 g of dry material with a nitric-perchloric acid mixture in a 250 ml quartz vial placed in a heating block with a temperature of 200 °C. Typical digestion times were: tissues and plants: 1.5 hours, fats: 3 hours, and sludges: 8 hours. The blanks were of the order of magnitude of ng/g. The mixture did not fully dissolve the metals, possibly bound to silica. To obtain the total content of some metals treatment with HF was necessary (25, 26).

Open vessels often lead to losses due to volatilization. Kaiser et al. (27) studied losses of mercury (using spikes of labelled Hg) in digestions with chloric/nitric acid mixtures at heating block temperatures of up to 200 °C. They observed losses unless special long-neck Kjeldahl-type flasks were used. Conditions of temperature and time were critical. Fats caused difficulties and had to be removed prior to digestion. Blanks were high in open systems.

The addition of spikes may demonstrate the power of a digestion technique. The added spike should preferably be an organic stable compound when analyzing an organic matrix (28). Where possible, administration of labelled compounds to living organisms helps to verify post mortal digestion of their tissues. Koops (29) applied subcutaneous injections of labelled iodine to cows and checked the recovery in their milk. Yang et al. (30) fed rats with labelled Zn and checked the Zn-recovery from their livers. These authors digested with a mixture of nitric/sulphuric acids in an open system until white fumes appeared; afterwards 14% of the Zn was still bound to organic compounds.

The elements I, Hg and Se are easily volatilized during digestion, so in principle open systems should be avoided. Se often volatilizes when charring with concentrated sulphuric acid (e.g. 31). If the oxidation potential is kept at a very high value (i.e. sufficient to oxidise all I to iodate or further) during the whole of the digestion period, volatilization losses do not appear. Haas and Krivan found, using radiotracers that no losses of Hg occurred in an open wet digestion with aqua regia provided that, hydrogen peroxide was added continuously during the whole digestion period (32). Perchloric acid can also maintain the oxidation potential sufficiently high to avoid losses of Se (34). Schlieckmann et al. (33) used chloric acid in combination with HF and HNO_3 in the digestion of dust samples at temperatures of 80 °C, 130 °C, and 150 °C. The chloric acid caused losses of Cr (as chromyl chloride) at higher temperatures.

A relatively new technique using microwave energy in closed PTFE-vessels at elevated temperature and pressure is able to achieve very rapid decomposition. The microwave energy is directly absorbed by the acid and some types of samples. Moreover closed polymer vessels are transparent to microwave energy. Kingston and Jassie (49) demonstrated the

decomposition of biological or botanical samples with nitric acid in 10 minutes with temperatures of 185 °C attained within 3 min. A method of calibration and prediction of time to temperature or the required amount of power to produce a certain temperature allows modeling of temperature decomposition using closed microwave systems. The rate of decomposition and retention of volatile trace elements is an advantage of this closed system acid decomposition system.

C. Combustion

A frequently used method for biotic and organic materials, coal and food is dry ashing, where the matrix is oxidized with ambient air at 450-600 °C. The method is not labour intensive and many samples can be handled simultaneously. In the case of siliceous materials the residual ash is treated with HF. Contamination, e.g. by atmospheric dusts, is a severe risk, therefore, the method cannot be recommended for low trace contents. Volatilization may introduce other sources of error (35). In an experiment with dry ashing of oils several elements were partially lost (36) but additives (e.g. Mg-nitrate/nitric acid) in combination with programmed heating sometimes helps to overcome the problem (34, 35). Combustion of organic matrices in oxygen in a closed system is a good technique, because as pointed out previously, gases can be purified relatively easily. Oxygen bombs can handle large amounts (e.g. 20 g) of sample (37, 38).

An elegant combustion system is the so-called Trace-O- Mat R (e.g. Table 1) which enables not only combustion in a closed system but also further treatment (39-40). Experience has been gained on a variety of matrices and elements. Even rocks and soils often release their volatile trace metals at the high temperature of combustion (addition of cellulose). The volatile elements are condensed on a cold finger (liquid nitrogen) in the system. Later they can be dissolved by refluxing with e.g. nitric acid. Elements which have been successfully determined are: Cr, Cu, Fe, Mn, Zn, Cd, Pb, Hg, As, and Se.

Low temperature ashing (LTA) is a technique in which the samples are oxidized in a stream of activated oxygen at temperatures up to 120 °C. Little attention is required once the sample is placed in the device; the blanks are low, there are no hazards (aggressive liquids, explosions), a reaction between container and sample does not occur and the rate of the reaction can be monitored (e.g. N-emission line at 675 nm). Volatilization is not a significant problem except when fluorides can be formed (B, Si, Ti, U, W). The technique is expensive, few samples can be ashed at a time, the ashing requires hours and the samples must be dry (27).

Fluorine seems to catalyse LTA-combustion processes. The reaction rates are increased by PTFE which has advantages over CF_4 (41). Quartz containers and equipment should not be used in combination with fluorine additions. In 1962, Gleit and Holland (42) obtained oxidation rates of about 1 g/h using a 300 W oscillator at 13.56 MHz and temperatures below 100 °C (42). In a recent study (30), it was shown that using an 80 W source for 3 hours 47 % of Zn in rats' livers was still bound to an organic ligand. This suggests that LTA can hardly be combined with voltammetry. A recent paper describes the use of a 27.12 MHz source (16).

D. Fusion

Fusion (especially alkaline fusion) is a powerful technique especially both for organic matrices and those with a high silica and alumina content (e.g. rock, dust, slags, ashes) having relatively high trace element contents (43). Since solid and aggressive fusion reagents are difficult to purify, fusion cannot be recommended as a technique for ultra trace analyses. A second disadvantage is that the method is carried out in contact with ambient air. Risks of volatilization are large; e.g. chlorides have to be removed prior to the fusion step to avoid losses of, say, Cr as CrO_2Cl_2 or As as $AsCl_3$. As a result of the high salt content following the treatment, some spectrometric techniques such as flame atomic absorption spectrometry may present difficulties. A combination of a lithium tetraborate melt by electrothermal atomic absorption spectrometry has given good results for fly ash, sediment and dust (44). For difficult matrices such as aluminosilicate ashes formed at a temperature of 600-800 °C, alkaline oxidative fusion (preceded by a sulphuric acid treatment) was shown to be the only alternative for a prolonged (8 days) acid (HF, $HClO_4$, HNO_3) digestion at 180 °C (45).

2. EXAMPLES

Many of the above suggestions are based on the authors' experience. For every new case for the laboratory, the efficiency of the digestion procedure has to be tested, verified and if necessary a modified or new procedure has to be applied. Recent examples with experienced laboratories will be summarised below. Two cases will be considered: (1) the digestion of a very resistant material with relatively high contents (an incinerator ash with a considerable amount of aluminosilicates) and (2) a low-fat total organic matrix with low contents (skim milk powder).

A. Incinerator ash

The contents of "trace" elements in such a matrix are high (e.g. Cd 470 mg/kg, Hg 31 mg/kg, Se 4 mg/kg, Cr 260 mg/kg, Ag 3 mg/kg, Br 300 mg/kg (46). Since most elements are present at levels above 50 mg/kg, the risk of contamination by solid reagents is low. However, inter-element interferences may be anticipated as well as difficulties in the digestion.

Preliminary x-ray and electron microprobe investigations have indicated that a large number of particles have an aluminosilicate matrix. This class of compounds does not dissolve easily in hydrofluoric acid. It was necessary to apply a pressurised digestion with oxidising acids and HF for about 100 h to completely dissolve the matrix to obtain a 100% recovery. Fusion methods can therefore be applied provided that losses do not occur. This is not easily achieved because of the high contents of halides (volatilisation of chlorides or bromides). Thus, prior to a fusion attack the material should be treated with a reagent such as fuming sulphuric acid to remove most of the halides and thus obtain correct values for elements such as As, Tl, Ni. A standard attack fully suitable for a coal (fly) ash would have given poor results for this type of ash.

B. Milk powder

Unlike (fly) ash the matrix of a milk powder is easily digested; the difficulties here lie in the very low contents present in the material (e.g. Cd 3 ng/g, Hg 1 ng/g, Cu 0.5 µg/g, Fe 2 µg/g and Pb 0.1 µg/g) (47).

Although neutron activation analysis should not suffer from contamination, one laboratory had to perform their weighing prior to irradiation with a balance placed in a clean room. Even the short time necessary for the weighing (e.g. 1 min) was sufficient to cause a considerable mercury contamination. This confirms similar observations (48).Dry ashing is not recommended for matrices with such low contents of trace elements of concern (0.5 - 1000 ng/g). The risk of losses and contamination is considerable. Programmed dry ashing done in a very clean oven and with clean air is possible only if carried out by experienced workers. The best digestion should take place in a closed system (e.g. pressurised acid digestion or a Trace-O-Mat R system) in which high purity reagents (sub- boiling point distilled acids, oxygen gas) can be used. Digestion in open systems e.g. Kjeldahl-type flasks gives unacceptable results.

3. QUALITY CONTROL

Experience has shown the paramount importance of verification of digestion efficiencies by using reference materials with matrices with a similar or identical composition. As many biotic materials, soils, sludges etc. vary widely in trace element and matrix composition this testing should involve as many materials as possible. The difficulties of digestion posed by the analysis of these matrices may be even greater than the ones encountered in daily practice.

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