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General Aspects of Trace Analytical Methods — VI

ACID PRESSURE DECOMPOSITION IN TRACE ELEMENT ANALYSIS

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ACID PRESSURE DECOMPOSITION IN TRACE ELEMENT ANALYSIS

Wet decomposition procedures within sealed systems (pressure decomposition) provide efficient methods for sample dissolution in trace element analysis. Vessels produced from high-purity materials (PTFE, glassy carbon), contained by compact pressure casings (stainless steel, aluminium alloys) are used in this technique. At temperatures of about 170°C the reaction capacity of acids and oxidizing decomposition agents increases so that inorganic and organic samples of a most widely differing composition are dissolved in a relatively short time.

In this report, an attempt is made to compile the specific advantages of, and the problems posed by, pressure decomposition procedures such as increased reactivity, faster reaction, decrease in blank values, avoidance of trace element losses, easy control of precision and calibration, completeness of sample decomposition, possible formation of explosive products etc.. At the same time, the properties of materials used for vessels and casings and the critical constructional features and their effect on operational efficiency and working safety regarding vessel, casing and heating system are discussed.

1. INTRODUCTION

The most common analytical techniques applied nowadays in trace element analysis of organic materials and minerals possessing complex matrices are spektroscopic and electrochemical methods of determination that normally begin with the dissolution of the substances to be analysed. Therefore, biological samples, as well as rocks, ores, slags, glass etc., are rarely analysed for trace elements without having received chemical pre-treatment, during the course of which solid matter is brought into solution by decomposing and destroying the sample matrix. A decomposition process also has other advantages, such as the removal of inhomogeneities, elimination of analytical interference by matrix compounds, and improvement in the calibration process. Sample decomposition increases the accuracy and precision of the analysis of numerous substances. The preconcentration of trace elements which may result from the destruction of organic matrices, also leads to an improvement in detectability. A comprehensive list of literature and working specifications are to be found in some monographs (refs. 1 - 3).

Particularly in the field of trace analysis, decomposition processes should be controlled to prevent falsification of analytical results due to sample contamination through air and chemical pollution in laboratories, through dirty equipment and through losses caused by volatilization, adsorption etc. (refs. 4 - 7). Systematic errors of this kind increase as the concentration of the element to be determined in the sample decreases. It is therefore essential to avoid such sources of errors not only by controlling the individual analytical steps after sample preparation, but also during sampling and sample storage (ref. 8).

During the last few years, the method of 'wet' sample preparation within closed containers has become widely applied. A predecessor of this technique was that published by Carius as early as 1860 (ref. 9), when he described the oxidation of a weighed quantity of sample with concentrated nitric acid within a sealed strongwalled glass vial. The vial is heated within a strong steel tube for several hours at 250 - 300°C. After cooling, the top of the vial is broken off. A partial or complete loss of volatile compounds during the release of excess pressure cannot be avoided. This rather painstaking and dangerous mode of operation was replaced by the utilization of dismountable tube furnaces made of stainless steel lined with platinum or other noble metals in order to minimize corrosion (ref. 10). Such furnaces are often used in the analysis of silicates.

Since 1955 numerous modified pressure systems have been described involving, as an inner chamber, a vessel made of polytetrafluoroethylene (PTFE) (refs. 10 - 19). The pressure increase during decomposition caused by vapours and reactant gases is contained by encasing the vessel in a strong metal housing, which is readily disassembled. Constructions, in which several individual vessels are combined to give one larger compact unit, are especially suited to serial analysis (refs. 20 - 22). Although the internal pressure is often an unwanted product of the decomposition process, the method is described as 'pressure decomposition'. Many publications describe wet decomposition procedures for samples of widely differing composition, making use of dissolving and oxidizing acids within closed systems.

Some authors recommend the use of sealed vessels of synthetic materials without any protective metal encasement for the wet decomposition of silicates (ref. 23), steel (ref. 24), food (ref. 25) etc., if temperatures below 100°C are sufficient for the reaction. Several such vessels may be heated simultaneously within one pressure heater (ref. 26). However, there should be a warning about the use of unprotected synthetic vessels, because of the possibility that spontaneous occurrence of high temperatures may soften the vessel walls and the highly acidic contents may spurt out under pressure (ref. 27).

For reasons of operating safety and case of handling, the samples of organic substances used in this method should not generally exceed 100 - 300 mg. Very few decomposition devices, including those operating with oxygen as oxidizing agent, are expressly designed for samples of more than 10 g; the cost of construction of appropriate equipment for large samples is accordingly high (refs. 28, 29).

In this report, an attempt is made to compile the specific advantages of, and problems posed by pressure decomposition procedures in which acids and other substances are used as decomposition agents. At the same time, critical constructional features and their effect on operational efficiency and working safety are discussed, albeit without specific reference to commercially available equipment.

2. PRESSURE DECOMPOSITION PROCEDURES AND THEIR ADVANTAGES

The wide application of pressure decomposition procedures in trace element analysis is based on a series of advantages which this method possesses over wet sample preparation in open vessels.

2.1 INCREASED REACTIVITY - FASTER REACTION

As a rule, the energy and rate of reaction with decomposition agents increase in proportion to the reaction temperature. This is related to the increase in oxidization potential and the formation of intermediate reactive products such as free radicals which facilitate the chemical attack on the compounds to be decomposed. Thus, numerous substances which fail to react with concentrated nitric acid can be decomposed without difficulty by utilizing a closed reaction vessel, at temperatures above the normal boiling point. The same applies to the reaction of hydrofluoric acid with silicates. The number of decomposable materials is therefore considerably increased, and the time required is usually considerably less than that in decomposition methods utilizing unsealed vessels.

2.2 DECREASE IN BLANK VALUES

The high temperatures required for the decomposition of stable materials can be achieved in flames, plasmas or molten-salt reactors under normal or reduced pressure. For the decomposition of organic substances there is a whole range of highly efficient combustion procedures available (refs. 1, 3, 6). Fusion decomposition procedures are far less favoured in trace element analysis, as many salts are highly contaminated compared with their respective acids and as they can only be purified with difficulty. Blank value problems are enhanced, because the quantity of decomposition agent which has to be used, exceeds often many times the weight of the test material. Samples are generally not capable of ultra-trace analysis after decomposition by fusion has been carried out.

On the other hand, the acids used in pressure decomposition are commercially available at a much higher level of purity, and are easily purified further by isothermal destillation (refs. 4. 7, 20). In comparison to decomposition methods utilizing unsealed vessels, the quantity of acid required for pressure decomposition methods is considerably reduced which further decreases the blank values. Finally, the sealed vessel system eliminates contamination, otherwise unavoidable, from pollutants of laboratory air. Thus, by carefully controlling all sources of contamination, any contribution to blank values occurring during the course of the decomposition process may be reduced to such an extent that analysis of substances difficult to decompose can be made even in the $ng \cdot g^{-1}$ range.

2.3 AVOIDANCE OF TRACE ELEMENT LOSSES

Particular problems in all decomposition procedures are the volatility of trace elements or their compounds and trace element losses due to sorption processes at vessel walls. By completely enclosing the sample and decomposition agent, the escape of volatile species before the analytical determination can be avoided. This is especially true for a series of biologically essential or toxic trace elements such as As, Be, Cd, Cr, Hg, Pb and Se in routinely analysed environmental materials. A number of other elements may also be changed into volatile compounds at the onset of the decomposition process, especially those in organic substances, at which stage complete or partial losses occur from unsealed vessels.

Trace losses by adsorption at or occlusion into the surface of a decomposition vessel are not entirely avoidable by the choice of a vessel of suitable material, but investigations carried out with the aid of radio-tracers show that such losses are generally negligible (refs. 18, 21). A dissolved sample can be pured from a PTFE vessel which is wetted only slightly by the acid, leaving almost no residual analyte. Any amount that does remain may be rinsed out with a few drops of wash liquid. Thus, the volume of the resulting trace concentrate remains small.

2.4 EASE OF CONTROL OF PRECISION AND CALIBRATION

It is essential in the application of any decomposition method that experimental proof is obtained that the trace elements to be determined completely reach the sample concentrate. Therefore, the recoveries of known quantities of trace elements added to the sample as aliquots of a dilute solution or as radio-tracers, prior to commencing the decomposition process, must be investigated. Often, no consideration is given to the possibility that elements bound in the sample do not react in the same manner under decomposition conditions as added trace compounds. For this reason, in experiments made in unsealed vessels, no reliable statement can be made as to the recovery of all components of the sample. Decomposition processes in sealed vessels, however, are far less problematic, because it may be expected that added trace elements and their compounds and those of the sample, will undergo fast chemical reactions, thus changing them to identical compounds, such as salts of the decomposition acid.

Analogous problems occur if a trace element content is to be established with the aid of a standard addition method. Here too, systematic errors can only be excluded, if it has been ascertained that sample and additive are present as identical compounds, i. e. in identical chemical and physical states. For samples of unknown composition, this is best achieved by application of a solution or decomposition process making use of a sealed vessel.

3. PROBLEMS ARISING WITH THE APPLICATION OF PRESSURE DECOMPOSITION

Despite the undeniable advantages which pressure decomposition methods offer, there are some problems arising from material properties and construction details of pressure vessels and casings some of which are connected with the decomposition actions occurring in such vessels. The most serious difficulties encountered are discussed below. Figure 1 depicts a simplified sketch of a typical pressure system which is commercially available in numerous variations.

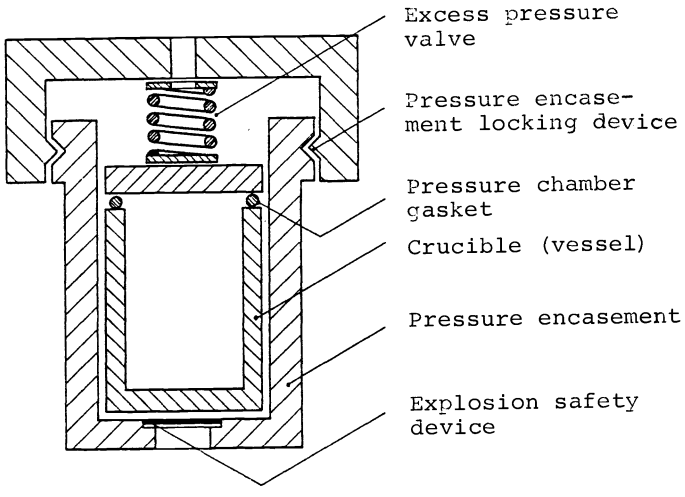

Fig. 1 Simplified illustration of a pressure decomposition vessel

3.1 POLYTETRAFLUOROETHYLENE (PTFE) AS VESSEL MATERIAL

The most commonly used material from which vessels for pressure systems are made is PTFE produced by catalytic polymerization of tetrafluoroethylene (commercially known as Algoflon, Fluon, Halon, Hostaflon, Polyflon, Soreflon, Teflon). Other materials have been proposed only in isolated instances (section 3.5). Because of its very stable C-F bonding, PTFE is extraordinarily resistent to chemicals and is of high thermostability. Owing to this resistence, but also because of its low content of trace metals when compared with other synthetic materials, PTFE is one of the materials preferred for the manufacture of apparatus used in trace element analysis (ref. 4).

PTFE is only seriously attacked by molten alkali metals or their solutes in liquid ammonia and by elemental fluorine, chlorine trifluoride and other fluorine compounds which are extremely reactive. However, under the conditions of a pressure decomposition process, there is also minor attack on PTFE from the most important acids used for oxidation such as nitric, perchloric or sulphuric acid (ref. 30). PTFE is practically completely resistent to hydrofluoric acid (ref. 4). Because in the polymerization process 'metalfree' peroxide catalysts are employed, the main impurities encountered which give rise to blank values, particularly when first using a new pressure decomposition vessel, probably originate from the machining process. These mostly adhering impurities can be removed to a great extent by heating for some time or by 'steaming' out with acid (ref. 7), but best of all, by simulating decomposition conditions. For ultra trace contents, however, this can only be stated with reservation, as was shown for mercury by Kaiser et al. (ref. 31).

It has only been occasionally observed that from cleaned, repeatedly used vessels, dependent on the manufacturer and material, irreproducible amounts of certain elements have found access to the sample concentrate, even when the work was done in high-purity locations. These are presumably 'conglomerations' copolymerized into the PTFE which are set free during surface attack by the decomposition acid (ref. 4). In order to keep these blank values low, vessels of the smallest suitable capacity, and with the smallest possible inner surface area should be used.

As has been established by tests carried out with radio-tracers, losses of trace elements caused by adsorption to the PTFE are in general (at least in the $\mu g/g^{-1}$ and in the sub-$\mu g/g^{-1}$ ranges) negligible (refs. 18, 20). In respect of the pg/g^{-1} range, no detailed systematic investigations have been carried out. Of some significance is the slight gas permeability of PTFE due to which noticeable amounts of nitrogen oxides, water or acids (ref. 4) and also traces of iodine and mercury (refs. 18, 31) may be occluded by the vessel walls, so that loss of trace elements and also memory effects may result.

Some properties of the PTFE are of significance with regard to the shaping and sealing of the vessel (refs. 32, 33). These are thermal expansion and flow behaviour under pressure. The thermal stability is of secondary interest in this connection: it is only above 400°C that PTFE begins to decompose. The thermal expansion depends, among other factors, on the high degree of crystallization of PTFE. Between 18 and 25°C and at 327°C, the crystallites possess transition points which can cause a change in volume of several percent. Between room temperature and 370 - 380°C, at which PTFE granulates sinter (in the absence of pressure) a reversible increase in volume of about 28 % occurs. So, it is advisable to use a highly pre-compressed material of low specific thermal expansion as a material for decomposition vessels. Under pressure application, PTFE tends to flow at a temperature far below sinter temperature. Because of this, the working temperature quoted for pressure decomposition procedures should generally be limited to < 200°C, although the maximal temperature for several pressure systems including PTFE vessels now commercially available, is given as 285°C.

The appreciable thermal expansion of PTFE and its tendency to flow under pressure must be taken into consideration when calculating the dimensions of the vessel and its pressure casing, as well as in respect of the shape of the pressure gasket. A space left between the vessel and the inner base of the metal casing should be large enough to permit expansion of the vessel at temperatures below those which cause considerable increase in inner pressure. It is only in this way that deformation causing possible damage to the gasket can be avoided, permitting the vessel to be removed from the metal casing without problems at the end of the decomposition procedure. In the construction of some of the commercially available pressure systems, this has not been given sufficient consideration and the danger exists that the vessel lid, although equipped with a pressure spring, may be trapped by the inner wall of the metal casing when the vessel regains its original shape on cooling. In such an event, vapours and reactant gases escape causing losses of trace elements and corrosion of the inner wall of the metal casing.

Attention must also be given to ensure that longitudinal expansion of the vessel does not strain to such degree, the spiral or laminated spring positioned at the excess pressure valve, so as to cause the safety device to malfunction. This can also happen, if the PTFE is deformed causing blocking at the lateral openings of the valve in the pressure casing.

A special problem is posed by the shape of the vessel and lid with regard to the tightness of the gasket. Thus, the thermal expansion and flow behaviour of the PTFE must be considered carefully to avoid trace element losses and to ensure proper functioning over a long period of time. Most commercial systems are equipped, in numerous variations, with a conical gasket or an O-ring seal affixed within a groove of the vessel or the lid. While an O-ring is easily changed when defective or deformed, a defective conical gasket generally leads to the loss of the vessel and/or the lid.

Finally, the upper edge of the vessel should be shaped in such a way that it will not come into contact with the metal of the pressure casing. Otherwise, contamination by elements of this metal cannot be avoided when the vessel is opened and while pouring out the sample solution.

3.2 SAFETY DEVICES

Each wet decomposition procedure in a sealed vessel is inavoidably connected with an increase in pressure caused by the vapour pressure of the acid and water at the decomposition temperatures and also by the pressure of the reactant gases and the air contained in the vessel. Depending on the weight of the sample, the temperature and the reactions involved, this pressure may reach values of > 50 bar (ref. 34). There are decomposition systems which permit the measurement of pressure during the reaction.

Figure 2 shows the pressure increase in a sealed vessel system from 100 to 200°C during wet decomposition of an organic substance.

The curve is the result of a model calculation based on the following values and simplifications: the vessel volume is assumed to be 30 cm^3 containing 1.5 g of 100 % nitric acid, the sample is a water-containing organic compound comprising 100 mg of carbon. During decomposition, the sample is completely converted to carbon dioxide and water, the nitric acid to nitrogen monoxide and water. A simplification is the assumption that nitrogen monoxide and

carbon dioxide behave like ideal gases and that, apart from the enclosed air, a total of 3 ml water is included in the calculation. Another simplification, for ease of calculation, is the assumption that at 100°C, decomposition is already complete.

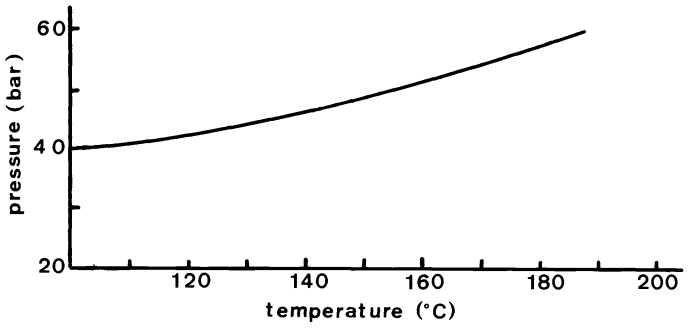

Fig. 2 Pressure estimate under decomposition conditions

The pressure behaviour during the decomposition of real sample materials therefore, may be different in detail: in the pressure temperature measurements, Stoeppler et al. (ref. 34) observed the formation of sharp pressure peaks during the heating phase. They showed that experiments of this kind may be very helpful in estabilishing suitable conditions for a harmless decomposition of organic samples.

In order to keep the decomposition vessel gas-tight at such high pressures, the vessel lid is pressed onto the gasket by means of a pre-tensioned spring. In an efficiently functioning valve, the spring constant determines the maximum pressure which can be tolerated. The escape of vapours and gases is only possible, when the spring, compressed by pre-tension und by the thermal expansion of the vessel material, can still be more compressed to facilitate the lifting of the lid. The excess pressure escapes via openings within the metal pressure casing and the valve closes again. As mentioned in section 3.1, attention should be paid during the construction of the apparatus to ensure that the valve openings do not become blocked by parts of the vessel deformed by pressure and high temperature; also, the valve exits should be angled to prevent acid spurting out, in a high-pressure stream.

Some commercially available pressure decomposition systems are produced without any such safety valves. A pressure spring often serves exclusively as a means of sealing the vessel. Pressure release in the case of a vigorous reaction can occur only by destruction of the vessel or of an explosion safety membrance usually positioned underneath the pressure casing (Fig. 1). As it often proves difficult, especially during testing, to employ optimal ratios of sample to decomposition agents, unexpectedly high pressure may build up and must be discharged. Also, when accidental excessive heating of the apparatus occurs, the pressure increase can reach a dangerous level. To avoid such dangers, the pressure decomposition apparatus must either be equipped with an efficiently functioning safety valve or it must be of such firm construction that a pressure discharge involving irreversible damage to parts of the apparatus is ruled out.

A particular danger may arise, if compounds react with oxidizing or nitrating agents resulting in the formation of highly explosive products. For example, by the addition of concentrated nitric acid to fat-containing samples, to oils, cellulose etc., nitro compounds may be formed which may detonate under certain conditions (refs. 34 - 36). Similar effects may be encountered as a result of reactions with perchloric acid used as a component of the decomposition agent, when added to organic samples (ref. 30). The pressure wave caused by a detonation is often so fast that a spring valve cannot open in time to release the high pressure. Complete destruction of the apparatus can therefore only be avoided, if the metal casing is equipped with a suitable rapid pressure-release membrane which, since it is the weakest part in the system, would burst and release the excessive pressure. In such an event, parts of the decomposition apparatus and heating system, as well as the vessel contents are projectiled by a powerful force. Thus, entrance by unauthorized personnel to the special room in which pressure decomposition work must be performed, should be strictly prohibited (ref. 22).

Results of tests made on one of the commercial systems regarding the stability of the vessel and its casing have been published (ref. 37). By exploding different amounts of lead azide or tetranitropenta erythritol ('nitropenta') within the decomposition vessel, it was established that the metal pressure casing remained intact, even after detonation of 300 mg of lead azide and 750 mg of 'nitropenta'; however, the PTFE vessel was destroyed in the process. With 300 mg of lead azide and 450 mg of 'nitropenta', the PTFE vessel remained intact. It was concluded that for this apparatus, any materials of a possible explosive nature should not be subjected to decomposition procedures, except in weights between 100 and 300 mg.

The optimal volume of the vessel is related to the weight of sample subjected to the decomposition procedure. As mentioned before, with an increasing inner surface area of the vessel, problems of contamination and adsorption also increase, so the chosen vessel volume should not exceed 10 to 20 times the volume of the decomposition mixture. Vessels containing volumes of between 5 and 250 cm^3 are commercially available. In some models, the pressure casing is capable of holding vessels of different capacities, as required.

Although in most operating instructions, attention is drawn to dangers arising from adding excessive weights of certain samples, the temptation for inexperienced analysts to work with greater than admissible amounts, in order to obtain a higher response signal, in spite of the warning, should not be underestimated.

3.3 PRESSURE CASING

The material and shape of the pressure casing have considerable bearing on sample contamination as well as on the handling of the decomposition system. In the majority of commercial pressure systems, casings made of stainless steel or of an aluminium alloy are used. If corrosion occurs, allowances must be made for high blank values, especially in respect of Fe, Cr, Ni, Mo and V or of Al and the respective alloying elements.

By designing a suitable shape for the PTFE vessel and pressure casing, contamination dangers may be diminished. Corrosion of the pressure casing may further be diminished by gold plating, or lining of the inner walls with PTFE or other thermostable synthetic material. Corrosion products forming on pressure casings made from stainless steel can be removed with concentrated phosphoric acid (ref. 30).

The ease of handling of the pressure decompositon apparatus may be hampered by difficulties encountered when opening the pressure casing and removing the vessel. Some of the systems with a large diameter screw thread tend to jam under pressure; the threaded parts of the casing can thus be separated only with difficulty, necessitating the employment of massive auxiliary tools. This problem is worsened by corrosion of the threads. Less problematic to open are pressure systems with a bayonet locking device; here, a clamp screw pressing onto a spring provides the force required to keep the pressure vessel closed, while any force caused by pressure originating during the heating process is contained by the bayonet lock.

3.4 HEATING SYSTEM

For heating pressure decomposition vessels, various types of devices can be recommended: dry chambers, heating baths, heatable magnetic stirrers or heating blocks equipped with temperature regulators. The final temperature in each instance is kept constant via contact thermometers or temperature sensors. From a point of view of working safety, a metallic heating block serving as an additional casing for the pressure vessel is to be preferred. After termination of the decomposition procedure, the pressure system may be cooled by air circulation or in a doublewalled heating block by the circulation of water until room temperature is reached.

3.5 COMPLETENESS OF SAMPLE DECOMPOSITION

In order to determine trace elements in the residue of a pressure decomposed sample without interference, some methods with a high power of detection require the complete absence of organic decomposition products. This is particularly the case for all polarographic and voltammetric determinations in which such undefined artefacts cause 'ghost signals' and/or irreproducible responses for the metals to be determined as consequence of the inhibition of their electrode processes (refs., 30, 38 - 40). Interferences caused by

incomplete decomposed organic residues also occur in atomic spectroscopic methods, if these substances change, for instance, the volatility of trace elements within the spectrochemical emission source. Furnace methods of atomic absorption spectrometry are especially prone to such effects. Problems caused by residues of organic matrices are often observed in the trace analysis of fats, proteins and heterocyclic compounds which present difficulties in decomposition.

According to investigations carried out by Kotz et al. (ref. 30), at 170°C, the maximum temperature said to be permissible for PTFE vessels, the oxidation potential of nitric acid is insufficient to completely decompose all organic substances, even if the reaction time is extended to 10 h. Stoeppler et al. (ref. 34) have shown by gas-chromatographic analysis of the reaction products and by calculating of the resulting carbon balance, that in no case complete destruction of different organic materials was found. They observed a decreasing tendency of decomposition with increasing protein content of materials, and also samples with considerable amounts of fat were only partially decomposed. In any case, artefact interferences are only safely removed when perchloric or sulphuric acid is added at the termination of the decomposition procedure and the sample residue is evaporated. With this additional procedure, however, the risk of contamination grows.

Decomposition temperatures of up to 220°C are allowed if PTFE is replaced as vessel material by glassy carbon and merely the gasket is made of PTFE (ref. 30). For a number of otherwise problematic organic materials, this temperature increase proves sufficient for complete mineralization. Glassy carbon possesses, apart from high thermal resistence and the required resistance to nitric acid and hydrofluoric acids, several further advantageous properties: it is impervious to gases and vapours, and it has little tendency to adsorb traces. The high purity of this material makes it suitable even for analysis at extremely low concentration ranges. Because of their smooth and high-density surfaces, vessels made of this material can easily be cleaned (ref. 30).

4. SELECTION OF DECOMPOSITION CONDITIONS

As has been discussed earlier, optimal conditions for pressure decomposition (sample weight, nature and volume of decomposition reagents, reaction temperature and reaction time) depend on the sample and on the decomposition system available. The sensitivity of the subsequent trace determination procedure as well as its susceptibility to interference caused by undecomposed matrix residues must also be taken into account. This means that, as a rule, decomposition conditions must first be established by initial tests which are specifically suitable for each individual analytical problem. Data contained in tables included in publications can merely be considered as approximate.

4.1 INORGANIC SAMPLES

Many inorganic substances may be pressure-decomposed without problem by hydrochloric and/or nitric acid. Silicate minerals or glasses are decomposed mostly by 40 % hydrofluoric acid to which, as required, other acids such as H_3PO_4, $HClO_4$, H_2SO_4, HNO_3, HCl und HBr may be added (ref. 17). As it is very unlikely that an explosive decomposition will occur during the procedure with ordinary inorganic substances, samples weighing 1 g and more may be decomposed. The decomposition reagent added should be 5 to 10 times greater in quantity than the sample. The decomposition times (110 - 170°C) in general are 0.5 - 2 h. The particle size of the pulverized sample is of great importance in respect of the reaction rate: by stirring the reaction mixture, the decomposition procedure may be sped up considerably. In order to avoid precipitation of poorly soluble metal fluorides and to convert samples of different composition to a similar state, it is possible to add, after termination of the sample decomposition, a quantity of saturated solution of boric acid, which reacts with the excess fluoride to form tetrafluoroborate (refs. 16, 41). Working instructions for decomposition of minerals have been published: quartz (refs. 30, 42), silicon-containing materials (refs. 11, 17, 41, 43 - 47), bauxite (ref. 48), iron ore and slags (ref. 49), ferro-silicon (ref. 50), sulphide ores (ref. 51).

4.2 ORGANIC SAMPLES

The majority of organic samples including those of biological origin, can be decomposed by concentrated nitric acid at 170°C so effectively that determ-

ination of trace elements is possible if an analytical procedure (such as flame atomic absorption spectrometry) is used which generally is insensitive to minute residues of undecomposed organic material. For the decomposition of samples limited to 100 - 300 mg, for safety reasons, 0.1 to 1 ml of 65 % or higher concentrated nitric acid is sufficient in most cases. At 160 to 170°C, decomposition times of 05. to 3.5 h are generally required. Mixtures of nitric acid and other acids (such as H_2F_2, $HClO_4$, H_2SO_4, $HCl/HClO_4$) have also been proposed for decomposing organic matrices. When using such mixtures, however, it is imperative to consider the danger of the formation of explosive nitrated compounds, which is much more likely than when using nitric acid alone (refs. 35, 36). In the event of interference due to undecomposed matrix during subsequent determination steps, an additional oxidization procedure will be necessary (see section 3.5) or else an alternative decomposition procedure will have to be chosen. Working instructions concerning the decomposition of organic samples, particularly biological substances, are available (refs. 18, 22, 30, 34, 42, 52 - 61).

5. PRESSURE DECOMPOSITION IN COMBINED PROCEDURES

In order to limit as far as possible the number of contamination sources and possible losses of trace elements, it is advisable to give preference to analytical procedures requiring a minimum of working steps and operating vessels. Especially for analysis involving very low concentration ranges, attempts should be made to combine the individual analytical steps in such manner that they can take place in one and the same vessel.

According to proposals made by Tölg (ref. 42), the vessel utilized in a pressure decomposition system is also suitable for direct use as a reaction vessel in subsequent separation steps. For example, the excess acid may be evaporated and the remaining trace elements extracted within the decomposition vessel by addition of a suitable organic solvent. For the phase separation within the vessel, some auxiliary instruments are available. Finally, trace element determinations can also be carried out by electrochemical procedures without changing the vessel.

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