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Characterization of waste - Digestion of waste samples using alkali-fusion techniques

Aufschluss von Abfallproben mittels Alkalifusion

Caractérisation des déchets - Digestion d'échantillons de déchets par mise en solution par fusion alcaline

Ta slovenski standard je istoveten z: CEN/TR 15018:2005

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Characterization of waste - Digestion of waste samples using alkali-fusion techniques

Caractérisation des déchets - Digetsion d'échnatillon de déchets par Mise en solution par fusion alcaline - Guide de bonnes pratiques pour la mise en solution par fusion - Les différentes méthodes et protocoles existants

Aufschluss von Abfallproben mittels Alkalifusion

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Foreword

This Technical Report (CEN/TR 15018:2005) has been prepared by Technical Committee CEN/TC 292 “Characterization of waste”, the secretariat of which is held by NEN.

This Technical Report is the translation of the French guideline BP X 30-428 "Digestion by fusion – Good practice guide for digestion by fusion: the different existing methods and protocols" and adoption as a CEN/TR. It gives information about the digestion of the waste samples using alkali-fusion techniques.

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Introduction

EU regulations (e.g. hazardous waste, waste incineration, European waste catalogue) ask in many cases for the total content of certain elements. In the European landfill directive, knowledge of total composition is given as an example of waste property-based criteria and is part of the basic characterization of waste.

In these special cases the total content of certain elements has to be determined. The standard based on acid digestion of waste samples (EN 13656) is in almost all cases applicable. However for some elements or waste composed of very refractory matrix (e.g. silicates, carbides, oxides), or when some residue is left after acid digestion, alkali-fusion may be used to bring the waste sample completely into solution.

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1 Scope

This Technical Report describes digestion methods for the determination of element contents of waste samples by using different alkali-fusion techniques.

2 General information

2.1 Digestion of samples

The determination of the elemental chemical composition of waste material includes a pretreatment of the sample comprising several stages:

- sampling for analysis (drying, crushing, homogenisation, sample reduction);
- digestion.

This last stage of digestion is essential because it allows to obtain a homogenous medium compatible with current analytical methods (atomic absorption spectrometry AAS, inductively coupled plasma and atomic emission spectrometry ICP/AES, inductively coupled plasma mass spectrometry ICP/MS, molecular absorption spectrometry MAS, X-ray fluorescencespectometry XRF).

The diversity of the materials is such that this stage remains very complex and can give rise to major errors due mainly to:

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- contamination of the sample by digestion reagents;
- incomplete digestion;
- loss of elements by adsorption onto the mineralization residue, onto the filter, or onto the walls of the mineralization reaction vessel;
- loss of elements by volatilisation (over and above those connected with drying and crushing);
- loss by reprecipitation in the form of hardly soluble salts.

Digestion is generally conducted in two stages. The attack, which consists in destroying the sample's organic matter and in dissolving the mineral residue by possibly modifying the specification by a very aggressive medium, followed by a dilution of the residue by a liquid allowing to obtain a homogeneous solution compatible with the subsequently implemented analytical techniques. Specific methods have been developed for volatile elements.

While numerous digestion methods exist, none is universal. The choice depends, on the one hand, on the nature of the sample (matrix type) and, on the other hand, on the sought after element(s) or on the targeted objective : determination of the total content or search for exogenous contaminants. Digestion can be performed by a wet (acid attack) or dry (fusion, calcination, combustion) technique.

The purpose of this code of good practices is to inventory those fusion methods which allow the mineralisation and digestion of waste for which acid attacks do not give satisfactory results.

2.2 Digestion by fusion

Fusion is often employed for the digestion of mineral materials (silicates, alumino-silicates, ...) and more particularly of certain refractory oxides (zircon, chromite, ...), but it is unsuitable for the digestion of volatile elements.

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Digestion by fusion requires the use of a specific flux which determines the nature of the reaction involved:

- acid-alkaline reaction:
  - alkaline fusion (carbonates, borates, hydroxides);
  - acid fusion (disulphates and pyrosulphates, fluorides, boron oxides);
- redox reaction:
  - oxidizing fusion (alkaline fluxes + oxidants, peroxides);
  - reducing fusion (alkaline fluxes + reducing agents, sulphides).

Fusion is conducted in platinum, porcelain, silver, nickel, iron, vitreous carbon, zirconium, graphite or terracotta crucibles. The choice of the crucible depends on the nature of the substance to be decomposed and on the type of flux.

Heating can take place in muffle ovens, induction ovens, tunnel ovens, over flames (Mecker burner) or more recently in microwave ovens. The time and temperature vary depending on the sample, crucible and flux being used.

The dilution of the fusion product is generally carried out in water or acidified water (water acidified with hydrochloric or nitric acid up to 5 % ml/l) which is heated in order to solubilise the solid formed at time of fusion.

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3 Fluxes

Several types of salts or other chemicals are proposed for the fusion of rock samples: alkaline borates, sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), sodium peroxide (Na_2O_2), equivalent potassium compounds, potassium pyrosulphate (mixture of $K_2S_2O_7$ and $KHSO_4$), alkaline fluorides (e.g. : KHF_2). These fluxes have specific applications.

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In general, the efficiency of a flux for attacking silicate rocks increases from $Na_2CO_3 < NaOH < Na_2O_2$. Table 1 gives a non exhaustive list of the fluxes together with their melting point and the generally used crucibles.

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Table 1 — Fluxes used for the fusion of silicate rocks

Salt		Melting point (°C)	Fusion crucible
Lithium metaborate	$LiBO_2$	845	Pt + 5 % Au or graphite
Lithium tetraborate	$Li_2B_4O_7$	930	
Sodium carbonate	Na_2CO_3	851	Pt or Ni
Potassium carbonate	K_2CO_3	891	
Sodium hydroxide	NaOH	318, 314[a]	Zr (or Au, Ni, Ag)
Potassium hydroxide	KOH	360	
Sodium tetraborate (borax)	$Na_2B_4O_7$	741	
Sodium peroxide	Na_2O_2	480 d, 675 [a]	Zr
Potassium superoxide	KO_2	380	
Potassium fluoride	KF	846, 856 [a]	
Potassium hydrogen fluoride	KHF_2	225 d, 239 [a]	
Potassium pyrosulphate	$K_2S_2O_7$	300, 414 [a]	
Sodium pyrosulphate	$Na_2S_2O_7$	401 [a]	
Lithium carbonate	$LiCO_3$	720 [a]	
Cesium carbonate	$CsCO_3$	610 [a]	
Sodium Potassium carbonate	$NaKCO_3$	500 [a]	
Ammonium hydrogen sulphate	NH_4HSO_4	147 [a]	
Sodium hydrogen sulphate	$NaHSO_4$	185 [a]	
Potassium hydrogen sulphate	$KHSO_4$	214 [a]	
Ammonium hydrogen fluoride	NH_4HF_2	125 [a]	
Sodium nitrate	$NaNO_3$	306 [a]	
Potassium nitrate	KNO_3	339 [a]	

[a] d : decomposes.

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3.1 Alkaline fluxes

3.1.1 Carbonates

Fusion using sodium carbonate is the most generally employed method of attack for the digestion of silicates (rocks and glasses). One can use either sodium carbonate which melts at 850 °C, or a mixture of potassium carbonate and sodium carbonate in equal parts, an eutectic mixture which melts at 700 °C. Sodium and potassium carbonate ($NaKCO_3$) has a melting point of 500 °C.

Potassium carbonate is rarely used alone. Mixed with sodium carbonate, it is used for analysing silicates because the fusion temperature is lower than that of the sodium carbonate alone. This mixture can therefore be used for the determination of volatile elements such as chlorine, fluorine.

Sometimes a little nitrate is added in order to stimulate the oxidation of chromium for example.

Fusions using carbonates generally take place in platinum crucibles at 900 °C. These fusions shall be performed preferably in an inert atmosphere in order to limit the formation of soluble sodium platinate.

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Conversely, when the sample under analysis contains iron, the fusion shall be conducted maintaining an oxidising atmosphere inside the crucible in order to prevent the reduction of the iron and the attack of the platinum crucible.

During fusion using carbonates, Hg and Tl volatilise completely, As and Se partially.

After attack, the majority of the anions are dissolved in the water; metals which do not produce any anions remain in the state of oxides, but these oxides are generally able to be attacked by acids. Fe (III), Ti (IV), Zr (IV), Be (II), rare earths remain insoluble in the water in the state of oxides. Al (III), V (V), P (V) are dissolved in the state of anions, as well as chromium in the state CrO_4^{2-} after oxidation by the air during fusion. U divides into parts; likewise for Zn which is in the state of $ZnO_2^{\ 2-}$ and of $ZnCO_3$. Mn^{2+} changes partially to the state of MnO_4^{2-}; post-dilution boiling or the addition of a drop of alcohol produces MnO_2 which precipitates.

In presence of SiO_2 and Al_2O_3, sodium silicoaluminates form that are hardly soluble and very difficult to filter when diluted by the water. Where anion separation is not required, it is preferable to directly dilute the attack product by an acid, and to insolubilise the silicium oxide [3] and [8].

Procedure : 0,8 g to 1 g of finely crushed1) sample is mixed in a platinum crucible with 4 g to 5 g of the equal parts mixture of anhydrous sodium and potassium carbonates. First of all heat gently for 5 min, then to fusion for 30 min. When there is no longer formation of CO_2 bubbles, heat as high as possible during 10 min. Allow to cool, solidifying the content in a film on the walls of crucible. Fill up to a third with water; heat gently. Remove the solid. If unable to do so, place the crucible in a beaker in presence of water. Heat up until disintegration [3].

Fusion with sodium carbonate mixed with SiO_2 has been used for the determination of the fluorine and chlorine present in geological materials [10]. Fusion takes place in a platinum crucible at 900 °C for 30 min.

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It shall also be noted that alkaline carbonates can be used mixed with:

- a compound of boron for the analysis of highly refractory products (natural oxides or calcined aluminium or silicium, corundums, zircons, cassiterites, chromites, ...);
- a MgO or ZnO oxide in order to increase the fusion temperature (use of a porcelain crucible);
- sulphur for the analysis of tin oxide and materials forming soluble sulphurs compounds in an alkaline medium;
- an oxidant (alkaline peroxide or nitrate) for the determination of the chromium and sulphur in silicates and chromites containing lead;
- ammonium chloride.

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3.1.2 Molten borates

Lithium metaborate and tetraborate

These are widely used fluxes. Metaborate is more alkaline than tetraborate. It is used for dissolving acid materials: silicate materials, siliceous sands, acid oxides [13]. Lithium metaborate is used preferably in view of analyses by AAS or ICP after dilution.

Tetraborate, more acidic, is used for the attack of alkaline materials such as alkaline oxides, highly aluminic materials, alumino-silicates, bauxites.[13].

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1) Gradings not exceeding 200 µm - 300 µm are recommended.

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The metaborate/tetraborate mixture in a 4/1 ratio constitutes a practically universal flux. The eutectic point of this mixture is one of the lowest; it is efficient in 95 % of cases, just as much for the fusion of siliceous rocks as for aluminic rocks or siliceous limestones, hence its superiority compared with meta- or tetraborates alone. Furthermore, the rapidity of the dissolution of the bead of this flux mixture in 3 % or 4 % nitric acid is in the region of 10 min to 15 min versus 40 min to 60 min for meta- and tetraborates alone [2]. The combined attack is therefore recommended for the majority of silicates, except for extra-aluminic materials which must be attacked by tetraborate and extra-siliceous materials by lithium metaborate.

Procedure: These fusions using alkaline borates are conducted most often in vitrified graphite crucibles, placed in graphite jackets fitted with lids, if the operation is carried out in muffle ovens in an uncontrolled atmosphere. Fusion lasts 15 min to 30 min and the temperature borders on 900 °C – 1 000 °C. But the use of induction ovens in presence of an inert gas (Ar or N_2) allows to reduce the fusion time by 3 min to 4 min, at a temperature of 1100 °C, and to extend the lifetime of the crucibles 40 to 50 fold.

At lower temperatures, the obtained attack bead is often too viscous, the silicium oxide can be incompletely attacked and the dissolutions, even by 4 % nitric acid, can exceed 60 min.

The attack is generally performed on test portions of 0,1 g to 0,2 g2) with a flux/sample ratio between 8 and 1 depending on the refractory properties and the granularity of the products under attack [2].

Crucibles made of platinum iridium (5 %), gold or gold-platinum-rhodium (GPR) alloy are also used at 1 000 °C during 15 min in a muffle oven. Boron nitride crucibles are to be used in order to prevent contamination by traces of silicates.

Lithium metaborate alone

A 5 to 1 flux/sample ratio can be applied to the majority of the samples [1]. It can be lowered to 3 where it is wished to minimise the influence of the matrix at time of analysis. The purity of reasonably priced lithium metaborate and the low interferences generated by this reagent make it the best flux able to be used in ICP-MS [1]. Fusion takes place from 900 °C to 1 050 °C in Pt-Au or graphite crucibles in a muffle oven and the fusion product is recovered in nitric acid.

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It has been demonstrated by Totland et al. [20] that fusion using lithium metaborate allowed a better solubilisation of the elements Si, Cr, Hf and Zr, and of the elements of rare earths than acid mineralisation in an open vessel.

Procedure: For rock and soil samples2), it is possible to use lithium metaborate alone in a graphite crucible. The obtained bead is solubilised by shaking in a hydrochloric medium [8]. The major sample-solution dilution (factor 10 000) reduces the field of application to the principal elements: Al, Si, Fe, Ca, Mg, Na, and K [9]. Fusion is conducted preferably in platinum crucibles; those made of graphite have a shorter lifetime. The sample is mixed with excess lithium metaborate and fusion is performed from 900 °C to 1 050 °C during 15 min to 30 min in a muffle oven [7]. Certain authors limit the fusion temperature to 900 °C in order to prevent the low loss of alkaline compounds by volatilisation [7].

Borax ($Na_2B_4O_7$, 10 H_2O)

This flux has been much used. Its fusion point is 878 °C. It shall firstly be dehydrated. It allows to solubilise certain natural oxides which are not easily attackable by other processes, e.g. ZrO_2, calcined Al_2O_3, corundum.

Procedure: Place 0,3 g of powder2) together with 4 g of anhydrous borax in a platinum crucible. Melt and heat around 1000 °C – 1200 °C until it becomes transparent (30 min to 1 h). Dilute with 2 Mol/l hydrochloric acid (150 ml) in a water bath.

For highly aluminic products: two parts of anhydrous borax and 10 parts of anhydrous sodium carbonate are heated until a clear liquid is obtained. The sample is added to this liquid. Fusion is performed as previously [3].

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2) Gradings not exceeding 200 µm - 300 µm are recommended.