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

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British Standards

National foreword

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English Version

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

This Technical Report was approved by CEN on 6 December 2004. It has been drawn up by the Technical Committee CEN/TC 292.

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Contents

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.

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.

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:

- 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.

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.

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.

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.

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.

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.

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 crushed[1)] 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.

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.

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.

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.

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.

3.1.3 Hydroxides

Sodium hydroxide allows the disintegration of a large number of silicates (kaolins, clays, feldspars) and easily fusible products (glass), of certain oxides (TiO_2, SnO_2), phosphates (monazite) or sulphates and of various ores (Cr, Sn, Zn, Zr). Sodium hydroxide melts at 318 °C.

Caustic potash, of which the fusion point is at 360 °C, has a more vigorous action than sodium hydroxide and allows to solubilise chromites. On the other hand, its salts are less soluble which leads to a longer washing of the precipitates and to a possible occlusion of these salts.

Fusion using hydroxides is performed in silver, iron, nickel or zirconium crucibles.

This mode of attack is far more vigorous than with carbonates and allows fusion at lower temperatures. During the course of attacks by hydroxides, Sn, V, W, Mo, As, Sb, P, S, B and halogens produce sodium and potassium salts which are water soluble in an alkaline medium, whereas Fe, Ti, Zr, Co remain insoluble in the form of hydroxides or carbonates.

Procedure: Melt 10 times to 20 times the mass of the sample to be attacked3) of sodium hydroxide in pellet form. Heat gently in order to expel the water. Allow to cool. Introduce the sample in powder form. Heat to fusion with a low flame. 400 °C – 450 °C shall not be exceeded. Under these conditions, the nickel crucible is not attacked. Leave 10 min to 15 min.

For silicates, a flux/sample ratio of 10 to 12/1 is used.

For the analysis of soils and rocks by atomic absorption, silver crucibles are used.

Procedure: Weigh in a 30 ml to 40 ml silver crucible 100 mg of crushed3) and dried rock. Add 1,5 g of sodium hydroxide. Place on an electric hot plate for 15 min. Next progressively heat the crucible over a gas burner, shaking during 1 min. Cool and place the crucible in a 250 ml beaker containing 100 ml of distilled water and 20 ml of 2,5 N sulphuric acid. Heat the beaker until the residue has completely dissolved. Discard the crucible.

NOTE The method is used for the solubilisation of rocks, soils and sediments. The high quantities of iron (10 – 20) % are sometimes difficult to solubilise. The solution lends itself to the determination of silicium and aluminium; calcium and magnesium can be determined if their content is higher than 0,1 %. Nickel crucibles are sometimes used: the attack is more delicate and difficult to control [8].

3.2 Acid fluxes

3.2.1 Pyrosulphates

Fusions by pyrosulphates of alkaline metals or NH_4HSO_4 are very vigorous and are used for certain alkaline refractories (chromium-magnesium oxide), complex alloys, Fe_2O_3, TiO_2, Nb_2O_5, aluminium oxide, a large number of ores (Al, Sb, Cu, Cr, Co, Fe, Mn, Ni, Ta...), steels, phosphates and slags. These fusions are used whenever alkaline borate fluxes are inefficient. In all cases, the silicium oxide remains insoluble. The operation can be performed in platinum or quartz crucibles. After attack, one dilutes by diluted sulphuric acid.

$K_2S_2O_7$ has a melting point of 415 °C and $Na_2S_2O_7$ of 400 °C. The pyrosulphate behaves like a mixture of neutral sulphate and of SO_3 : SO_3 combines with the oxides to give SO_4^{2-}.

Sulphate-based reagents are unfavourable for certain elements such as lead, barium and calcium on account of the poor solubility of their sulphates.

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

Procedure : 0,5 g of powder[4] is attacked by 5 g to 7 g of pyrosulphate. Heat for 20 min to 30 min, just to melting with a low flame, avoiding the loss of SO3. Next bring the crucible up to 600 °C – 700 °C and heat until the liquid is limpid (e.g. 1h). Cool down. Place in a beaker containing 250 ml to 750 ml of water and 25 ml of concentrated sulphuric acid. Heat and filter the silicium oxide. Wash.

Platinum crucibles undergo very slight attack by the disulphate and the traces of Pt which are dissolved can present difficulties for certain determinations. Consequently, operations will be performed in quartz crucibles [3].

3.2.2 Alkaline fluorides (KF, KHF_2, NH_4F)

The use of alkaline fluorides allows the disintegration of the resistant silicates and of Be, Nb, Ta, and Zr oxides. These fluxes allow to have a higher digestion temperature than with HF. The KHF_2 melting point is 240 °C, 857 °C for KF. NH_4F looses NH_3 at 145 °C to produce NH_4HF_2 which melts at 124,6 °C. These are low temperature fluxes.

Operations are generally performed in platinum crucibles [3].

3.2.3 Boron oxide and others

Sands, aluminium silicates, tourmaline, corundum, enamels are attacked by boron oxide B_2O_3 which melts at 580 °C. Difficulties are encountered for silicates having a high magnesium and calcium content and for chromium ores which are not attacked [13].

3.2.4 Lithium tetraborate

(see subclause 3.1.2).

3.2.5 Other boron fluxes

A boric acid-potassium carbonate mixture has been used as a flux. This fusion shall be followed by an acid dissolution and a separation of the cations on a resin ion exchanger. The cations are then eluted with hydrochloric acid. On the eluate, it is possible to determine the major elements (Fe, Al, Ca, Mg, Na, K) and the trace elements (Rb, Ba, Sr, Cu, Cr, V, Ni, Co...) insofar as their concentration is sufficient, namely approximately 50 mg/kg in the sample. It is possible to determine the silicium in the initial effluent solution. This method offers the advantage of separating the silicium oxide more rapidly than with the traditional methods [9].

3.3 Oxidising fluxes

3.3.1 Sodium peroxide

In many cases, the attack by sodium peroxide is more efficient than fusions with other fluxes. This attack is suitable for a large number of Sb, As, Cr, Mo, Ni, V, U, Sn ores, for certain chromium alloys and steels and for chromium oxide or refractory oxide-based products (ZrO_2, Al_2O_3). Its oxidising action is used as a last resort when the other fluxes have failed. By bringing up to a red heat, Na_2O_2 decomposes, giving off oxygen. Its action is identical to that of sodium hydroxide, but here all the elements are at their upper oxidation stable state.

Operations are performed in a nickel, iron or zirconium crucible. These crucibles are attacked as from 600 °C to 700 °C. One operates just to melting at 500 °C. The disadvantage of peroxide fusions resides in the production of a violent reaction (also in presence of organic compounds) which results in the destruction of the bottom of vitreous carbon, iron or nickel crucibles. In presence of Na_2CO_3 or of magnesium oxide-based calcareous or refractory ores, the reaction is much less violent.

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

Procedure: Add to 1 g of powdered material[5] 10 g of sodium peroxide. Heat gently to melting and leave 15 min to 20 min. Cool and dilute with water. Boil during 15 min in order to destroy the excess sodium peroxide and the hydrogen peroxide which has formed. Highly reducing compounds are oxidised and cause an explosion [3].

Sometimes sodium peroxide is used mixed with sodium hydroxide. This allows the determination of the rare earth elements. These two fluxes attack platinum; one therefore uses gold, silver, nickel or zirconium crucibles which are subject to less attack. However, traces of the crucible constituent material are found in the analysed solutions. The commonly used sample/flux ratio is 1/4 and the fusion is performed at around 800 °C for 15 min to 30 min [7].

3.3.2 Nitrates

Where it is wished to avoid the use of sodium peroxide and where the product is not too refractory, a mixture of caustic alkali with an alkaline nitrate, which is the oxidising agent, can be used. The chromites can thus be attacked. The attack of the crucibles is consequently less significant than in the case of sodium peroxide.

3.4 Reducing fluxes (alkaline fluxes + reducing agents, sulphides)

- Melted sulphur and sodium carbonate.

This method of attack is suitable in the case where one of the major constituents produces a soluble sulphide in an alkaline medium (complex sulphides). Example: attack of SnO_2 (cassiterite) [3].

3.5 Digestion by sintering

Certain fluxes (sodium peroxide, carbonate, metallic oxides) can be used by sintering (reaction between solid phases). For this, either the fixed temperature is slightly lower than the melting temperature but sufficient for the solids to react, or it is higher but with a quantity of flux insufficient for completely dissolving the sample, but sufficient for disintegrating it, making it soluble in an acid medium.

This method of attack is interesting because:

- it allows to have a smaller flux/sample ratio;
- as the temperature is generally fixed lower than the melting temperature, the crucibles are subject to less attack.

The success of sintering with Na_2O_2 depends on the granulometry, on the flux/sample ratio, on the temperature, on the time and on the resistance of the materials to be attacked. These factors shall be carefully determined for each material.

Procedure: The attack takes place in a zirconium crucible in a tunnel oven at 450 °C and the sintering product is dissolved by a 10 % solution of HCl. 34 major and trace elements are determined simultaneously.

4 The crucibles

4.1 Platinum

Platinum is used in fusions with alkaline carbonates, alkaline pyrosulphates, fluorides, borates and silicates. Platinum is excluded in a large number of cases. It is attacked by the following substances [6]:

- chlorine and all substances which give off chlorine;
- nitrates (where they are used as fluxes, they shall be mixed with excess sodium carbonate);

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[5] Gradings not exceeding 200 µm - 300 µm are recommended.

- alkaline oxides, hydroxides, peroxides;
- cyanides, sulphides, arsenides and phosphorides;
- in presence of charcoal: acting as a reducing agent, sulphates, arsenates and phosphates can transform into sulphides, arsenides and phosphorides;
- free metals (Pb, Ag, Bi, Zn, Sb, Sn, ...);
- sulphur, charcoal, silicium oxide (silicium combines with the platinum and makes it fragile);
- do not use a reduction flame.

Platinum can be used in the case of refractory oxides together with sodium peroxide provided that the temperature does not exceed 500 °C [4].

NOTE Platinum interferes when analysing chromium by ICP-AES.

4.2 Silver

Silver is used for sodium hydroxide or potassium carbonate (potash) fusions. As silver does not withstand high temperatures (it melts at 960 °C), it must not be heated above red heat. Since nickel is less fusible, nickel crucibles covered inside with a layer of silver have been used [6].

4.3 Nickel

It has the same applications as silver, but offers the advantage of withstanding higher temperatures (it melts at 1 455 °C) and of being cheaper [6].

4.4 Vitreous carbon

Vitreous carbon crucibles are used in replacement of platinum ones. They are slightly cheaper, but present the disadvantages of sometimes retaining a part of the fusion product and have a short lifetime (5 fusions to 6 fusions per crucible). The fusion of samples rich in free metals (e.g. Cu, Pb) is performed in carbon crucibles [1].

4.5 Iron

Iron oxidises easily. It can only be used for reducing fusions [5]. It has restricted applications, but can be interesting for determining lead in a lead glance (galena). Iron therefore serves as a reducing agent and desulphurising agent (formation of FeS) [6].

4.6 Porcelain

Porcelain crucibles are used in the majority of cases where platinum cannot be used. They are well suited for the heating of sulphides, phosphates, for the reduction of oxides by C or H [5]. Porcelain crucibles are attacked by alkaline bases, alkaline earths, metallic oxides and by the mixture sodium carbonate + potassium carbonate, as well as by potassium hydrogen difluoride [6].

5 Protocols currently used within industry

5.1 Analysis of 16 metallic elements in crushing residues [11]

5.1.1 Principle

Fusion with lithium metaborate in an oven at 1 100 °C during 1 h in a platinum or vitreous carbon crucible.

The fusion product is diluted with diluted hydrochloric acid.

Analysis by ICP-AES or by flame atomic absorption spectrometry (FAAS) or graphite furnace atomic absorption spectrometry (GFAAS).

5.1.2 Field of application

This method is applied to automobile crushing residues and for the following elements and concentration ranges (limit values):

Al	1 mg/kg to 7 %	**Zn**	1 mg/kg to 7 %	**Sb**	17 mg/kg to 0,33 %
Ca	1 mg/kg to 17 %	**Cd**	2 mg/kg to 0,33 %	**Ti**	3 mg/kg to 0,67 %
Cu	1 mg/kg to 10 %	**Co**	4 mg/kg to 0,33 %	**Sn**	13 mg/kg to 6 %
Fe	2 mg/kg to 33 %	**Cr**	2 mg/kg to 0,67 %	**V**	20 mg/kg to 0,33 %
Mg	1 mg/kg to 7 %	**Mn**	1 mg/kg to 0,33 %		
Pb	1 mg/kg to 7 %	**Ni**	8 mg/kg to 0,67 %		

This method does not apply to volatile compounds.

5.1.3 Operating protocol

Calibration range

The calibration range for major elements differs from that for minor elements. The analysis of the major elements is carried out using a calibration range containing Al, Ca, Cu, Fe, Mg, Pb and Zn to which is added 5 ml of fusion salt in order to place oneself in the same conditions as the samples.

The analysis of the minor elements is carried out using a calibration range containing Sb, Cd, Cr, Co, Sn, Mn, Ni, Ti, and V to which is added the quantity of copper and iron found at the time of analysis of the major elements. This allows to have a calibration range which is more representative of the matrix of the samples when determining the minor elements.

Preparation of samples

So that the test portion of 1 g is the most representative possible of the sample, it is necessary to crush the latter to a granulometry below 1 mm and to homogenise after crushing.

After crushing, the sample is dried in the oven at 105 °C during at least 3 h.

Fusion

Weigh exactly approximately 1 g of dried sample directly in the platinum or vitreous carbon crucible and 10 g of lithium metaborate and 0,1 g of lithium iodide. Mix.

Initiate the fusion with a Mecker burner, then place the crucible in an oven at 1 100 °C for 1 h in order to obtain as clear as possible a fusion bead.

Remove the crucible from the oven.

Heat the fusion bead and a little more the edge of the crucible with the Mecker burner in order to recover a bead which will be poured into a beaker containing 20 ml of water and 10 ml of hydrochloric acid, while undergoing magnetic stirring.

Having stopped the stirring, put the crucible in the beaker, add possibly a little water and place the beaker on the sand bath at 150 °C.

When the crystals have detached themselves from the crucible, withdraw it after having rinsed it with deionised water.

Filter the solution through a white strip filter and recover in a 500 ml volumetric flask.

Analysis by plasma emission spectrometry.

The major elements (Al, Ca, Cu, Fe, Mg, Pb, Zn) are determined after an appropriate dilution of the solution obtained after fusion. The minor elements (Sb, Cd, Cr, Co, Sn, Mn, V, Ti, Ni) are determined directly in these solutions, if permitted by the total concentration of dissolved matter.

5.2 Determination of Si, Al, Fe, Mn, Mg, Cr, Ti, and F in slags [12]

5.2.1 Principle

Fusion of the test portion with lithium tetraborate in a vitreous carbon crucible in an oven at 1 200 °C during 20 min.

Digestion of the (fusion) bead by diluted hydrochloric acid.

5.2.2 Field of application

The contents in the slags under study are:

SiO_2	9 % to 66 %
Al_2O_3	1 % to 42 %
FeO	0,15 % to 35 %
CaO	0,5 % to 35 %
MgO	0,8 % to 20 %
MnO	0,15 % to 22 %
Cr_2O_3	0,1 % to 5 %
TiO_2	0,08 % to 4 %

These fields can be extended as a function of the demand, at least as far as the upper limits are concerned and provided that one disposes of calibration solutions covering the anticipated contents and by diluting if need be.

5.2.3 Operating protocol

Calibration range

Prepare several standard solutions each containing a mixture of the elements Si, Al, Fe, Ca, Mg, Mn, Cr, Ti at diverse concentrations and 10 g/l of lithium tetraborate and 80 ml/l of hydrochloric acid.

Fusion

Dry the finely crushed[6] sample at 100 °C during 2 h and leave it to cool down in a desiccator.

Weigh (200 ± 0,1) mg of sample and place it in a vitreous carbon crucible.

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[6] Gradings not exceeding 200 µm - 300 µm are recommended.

Weigh (2,5 ± 0,000 1) g of lithium tetraborate. Around 2 g are mixed with the sample, the remainder of the flux being deposited over the mixture.

The vitreous carbon crucible is deposited in a nickel crucible and the entire assembly is placed in a muffle oven brought up to 1 200 °C, during 20 min.

On removal from the oven, dilute the fusion product by a circular movement of the outer crucible, and leave to cool down.

The vitreous carbon crucible is placed in a PTFE beaker and stirred with a magnetic rod in 20 ml of hydrochloric acid and 150 ml of cold water for 1 h.

When the fusion product is totally dissolved, the solution is decanted into a 250 ml volumetric flask and the volume is adjusted with demineralised water.

Analysis by plasma emission spectrometry

5 ml of calibration solution and 5 ml of solution obtained by redissolution of the fusion product are mixed in 50 ml volumetric flasks containing 2 ml of hydrochloric acid. The volumes are adjusted with water.

The measurements are conducted in "ratio" mode taking lithium as an internal standard.

Remark

Too high a presence of silicium in the solutions can lead to the hydrolysis of the Si, particularly in those solutions containing the most silicium, and to the precipitation of the silicium oxide. It can be necessary to perform a separate calibration range for silicium.

5.3 Fusion with carbonate or borate mixture [15]

5.3.1 Principle

Fusion of the sample with a sodium carbonate / potassium carbonate mixture (ratio 40 % / 60 %), or fusion with a lithium metaborate / lithium tetraborate mixture (ratio 20 % / 80 %).

5.3.2 Field of application

Analysis in wastes, sludges, sewage waters.

5.3.3 Operating protocol

Na_2CO_3 / K_2CO_3

The sample/flux mass ratio is fixed at 1/10. 200 mg of sample are placed in a platinum crucible. This crucible is placed in a cold oven. The temperature is programmed in order to rise up to 1 000 °C in order to eliminate the organic matter present in the sample. When the oven reaches 900 °C, the crucible is removed and the ashes are intimately mixed with 0,8 g of sodium carbonate and 1,2 g of potassium carbonate. The complete mixture is then brought up to 1 000 °C during 1 h.

After cooling down, the content of the crucible is recovered with 10 ml of 50 % hydrochloric acid. The redissolution is carried out within 15 min to 30 min. It is sometimes necessary to heat the solution in order to complete the redissolution.

If the redissolution is not complete, the residue is filtered then rinsed; the rinsing waters are added to the sample. The liquid fraction is then made up to 100 ml in order to obtain an analysable solution.

The use of hydrochloric acid and of sodium and potassium ions leads to matrix effects and certain interferences when conducting the analysis by atomic absorption or emission.

Lithium metaborate / lithium tetraborate.

The attack mixture is composed of 0,4 g of lithium metaborate and of 1,6 g of lithium tetraborate. The fusion temperature is 1 100 °C during 1 h. The dilution of the (fusion) bead is conducted by a 4 % nitric acid solution.

5.4 Fusion with lithium borate [14]

5.4.1 Principle

Fusion with a lithium metaborate / lithium tetraborate mixture.

5.4.2 Field of application

Mineral waste (incineration ash of waste, sediment, MSWI bottom ash).

5.4.3 Operating protocol

The lithium metaborate / lithium tetraborate ratio is equal to 4/1. The crucible is in platinum. 1 g of sample mixed with 3 g of flux is brought up to 1 100 °C during 1 h. The dilution is carried out in 500 ml of 5 % V/V nitric acid.

5.5 Standards (non exhaustive list)

5.5.1 EN 955-2, Chemical analysis of refractory products — Part 2: Products containing silicium oxide and/or alumina (wet method) (July 1995).

Flux: equimolar mixture of sodium and potassium carbonates.

Crucible: platinum.

Mixture: 3 g of flux and 0,4 g of boric acid together with 1 g of crushed sample.

Heating: 10 min on a gas burner, then during 10 min at 1 200 °C in a muffle oven.

Dilution: 10 ml of water and 15 ml of hydrochloric acid and 1 ml of diluted sulphuric acid.

5.5.2 NF B 49-421, Refractory products: Analysis of alumina, silicium oxide, silicium carbide, metallic carbon and silicium-based refractories (November 1990).

For the determination of silicium carbide: after sulpho-hydrofluoric attack, an oxidising fusion is performed on the residue and the silicium carbide is determined by gravimetry of the silicium oxide.

Flux: sodium peroxide + sodium carbonate.

Crucible: vitreous carbon.

Mixture: 500 mg of sample with 6 g of sodium peroxide and 2 g of sodium carbonate.

Heating: 750 °C during 30 min. Complicated sequence.

Dilution: 150 ml of hot water, hydrochloric acid, perchloric acid.

5.5.3 FD A 10-010, Chemical analysis of ferro-alloys: Determination of phosphorous — Molecular absorption spectrometry (MAS) method (December 1986).

Oxidising fusion.

Flux: sodium peroxide.

Crucible: nickel.

Mixture: 500 mg of sample and 5 g of flux.

Flame heating: maintain fusion 5 min.

Dilution with water, final dilution 0,5 g/50 ml.

5.5.4 NF A 10-809, Chemical analysis of ferro-tungsten: gravimetric determination of tungsten (October 1984).

Flux: Potassium and sodium carbonate ($NaKCO_3$).

Crucible: Platinum.

Mixture: 1 g of sample and 5 g of flux.

Heating: over burner 30 min.

Dilution: 10 ml of water and sodium peroxide.

Filtration and re-fusion of the residue.

5.5.5 FD A 10-186, Chemical analysis of ferro-silicium — Determination of aluminium by atomic absorption spectrometry (AAS) (December 1977).

After dissolution of the sample with nitric, hydrofluoric and perchloric acids, separation and fusion of the residue.

Flux: Sodium carbonate and boric acid.

Crucible: Platinum.

Mixture: filtration residue + 1 g of sodium carbonate and 0,5 g of boric acid.

Heating:15 min at 1 000 °C.

Dilution: filtrate of the acid attack, final dilution: 1 g/100 ml.

5.5.6 FD A 10-101, Chemical analysis of ferrosilicium, ferromanganese-silicon and of ferrochromium silicon, Gravimetric determination of silicium (December 1976).

Transformation of the silicium oxide into silicate by oxidising fusion.

Flux: sodium peroxide (or mixture of sodium peroxide and sodium carbonate).

Crucible: Iron, vitreous carbon, nickel, zirconium.

Mixture: 500 mg of sample and 15 g of flux.

Heating: over flame, 5 min.

Dilution: water and hydrochloric acid.

5.6 Fluxes and their applications

Flux and their applications are illustrated in Table 2.

Table 2 — Fluxes and their applications

Fluxes		Applications	Disadvantages
Alkalines	Sodium or potassium carbonate	Determination of volatile elements (chlorine, fluorine).	Hg and Tl completely volatilise As and Se volatilise partially.
	carbonate (Na or K) mixed with	Analysis of highly refractory products (natural oxides or calcined aluminium or silicium, corundums, zircons, cassiterites, chromites...).	
	— a compound of boron		
	— an MgO or ZnO oxide	To increase the fusion temperature (use of a porcelain crucible).	
	— sulphur	For the analysis of the tin oxide and of the compounds forming soluble sulphides in an alkaline medium.	
	— an oxidising agent (alkaline peroxide or nitrate)	For determining the chromium and sulphur in silicates and chromites containing lead.	
	Boron salts		
	— metaborate (alkaline)	These are fluxes in very wide use. Metaborate is more alkaline than tetraborate. It is used for dissolving acid materials : silicated materials, siliceous sands, acid oxides.	
	— tetraborate (acid)	Alkaline oxides, highly aluminic materials, alumino-silicates, bauxites ...	
	— metaborate/tetraborate (ratio 4/1)	Efficient in 95 % of cases : siliceous, aluminic or siliceous limestone materials.	
	— borax	Hard-to-attack natural oxides, ZrO_2, calcined Al_2O_3, corundum, ...	
	Hydroxides	Used for the solubilisation of rocks, soils and sediments. They lend themselves to the determination of silicium and of aluminium ; calcium and magnesium can be determined if they are over 0,1 %.	Fe, Ti, Zr, Co remain insoluble in the form of hydroxides or carbonates. High quantities of iron (10-20 %) are sometimes difficult to solubilise.
	— NaOH	Disintegration of a large number of silicates (kaolins, clays, feldspars) and readily fusible products (glasses), of certain oxides (TiO2, SnO_2), phosphates (monazite) or sulphates and of various ores (Cr, Sn, Zn, Zr).	
	— KOH	More vigorous action than sodium hydroxide : allows to solubilise chromites. During the course of attacks by hydroxides, Sn, V, W, Mo, As, Sb, P, S, B and halogens produce sodium and potassium salts which are soluble in water in an alkaline medium.	

Table 2 — (*end*)

Fluxes		Applications	Disadvantages
Acids	Pyrosulphates	Alkaline metals, for certain alkaline refractories (chromium-magnesium oxide), complex alloys, Fe_2O_3, TiO_2, Nb_2O_5, alumina, numerous ores (Al, Sb,Cu, Cr, Co, Fe, Mn, Ni, Ta,...), steels, phosphates and slags. used whenever alkaline borate fluxes are inefficient.	Silicium oxide remains insoluble. Sulphate-based reagents are unfavourable for certain elements such as lead, barium and calcium on account of the low solubility of their sulphates.
	Alkaline fluorides	Disintegration of resistant silicates and of oxides of Be, Nb, Ta, Zr. Digestion temperature higher than with HF.	
	Boron oxide	Sands, aluminium silicates, tourmaline, corundum, enamels, ...	Difficulties for high magnesium and calcium content silicates, and for chromium ores which are not attacked.
	Boric acid + carbonate	Possibility of determining the major elements (Fe, Al, Ca, Mg, Na, K) and trace elements (Rb, Ba, Sr, Cu, Cr, V, Ni, Co, ...) insofar as their concentration is sufficient; possibility of determining silicium in the initial effluent solution. This method offers the advantage of separating the silicium oxide more rapidly than with the traditional methods.	
Oxidising agents	Sodium peroxide	Suitable for a large number of ores of Sb, As, Cr, Mo, Ni, V, U, Sn, for certain chromium alloys and steels and for chromium oxide or refractory oxide-based products (ZrO_2, Al_2O_3).	Violent reaction (also in presence of organic compounds), destruction of the bead.
	— mixed with NaOH	Allows the determination of rare elements.	
	— mixed with carbonates		
	Nitrates	Product not too refractory, chromites.	
Reducing agents	Molten sulphur and sodium carbonate	For major constituents producing a soluble sulphur in an alkaline medium, e.g. SnO_2.	

6 Comparison of different digestion techniques

Attacks by alkaline fusion are currently used for the disintegration of silicates in view of determining the major elements. These attacks are also much used for analysing Ti, Zr, W, and Cr, the latter elements very often being found in refractory minerals (chromite, ...). Traditional fluxes (sodium and potassium carbonates) are not recommended for analyses by AAS, ICP-AES or ICP-MS on account of the matrix effect. For these analytical techniques, where the samples are insoluble in acids, it is preferable to use as fluxes alkaline metal and alkaline earth borates and in particular lithium.

The obtained post fusion solutions can be analysed by AAS, ICP-AES or ICP-MS techniques, despite a high salt content. These high content solutions have however to be diluted in order to render them compatible with the measuring devices, which diminishes the sensitivity of the analyses for the elements present in trace state. Furthermore, the high quantity of dissolved salts can cause matrix effects when performing the analysis (examples: elements Na, K, Ca). Moreover, digestion by fusion is unsuitable for the most volatile elements (Hg, As, Pb, Sb, Sn, Zn, ...).

Totland et al. [20] give a comparison of the different digestion methods concerning nine reference geological samples. The three reference methods studied are:

- fusion by lithium metaborate: 0,25 g of test portion with 1,25 g of flux in a graphite crucible (1 050 °C during 20 min, dilution with 0,8 mol/l nitric acid);

- open system digestion: 0,5 g of test portion with a mixture of HF (29 mol/l) and of $HClO_4$ (12 mol/l) at a ratio of 10/4, heated at 200 °C, the residue being diluted with nitric acid (5 mol/l);

- microwave assisted digestion: 0,5 g of test portion with a mixture of HNO_3 (16 mol/l), HF (29 mol/l) and $HClO_4$ (12 mol/l) at a respective ratio of 4/2/1.

The elements analysed are:

- seven major elements : Si, Ti, Al, Fe, Mg, Mn, Ca;

- 24 trace elements : Ba, Cr, Cu, Ni, Sr, Y, Zn, Zr (ICP-AES and ICP-MS) Be, Co, Cs, Hf, Mo, Nb, Pb, Rb, Sb, Sc, Sn, Ta, Th, Tl, U, W (ICP-MS) and V (ICP-AES);

- 14 rare elements : La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu (ICP-MS).

The comparison of these three methods is given succinctly in Table 3.

Table 3 — Comparison of three digestion methods on geological samples, according to [20]

	Fusion with lithium metaborate	Open system digestion	Microwave assisted digestion
Advantages	— Allows the determination of all major elements, including Si	— Low dissolved salts concentration which allows the determination of numerous elements : Ba, Be, Co, Cs, Cu, Nb, Ni, Pb, Rb, Sb, Sn, Sr, Ta, Tl, Th, U, W, Y, Zn, rare elements	— Low dissolved salts concentration which allows the determination of numerous elements: Ba, Be, Co, Cs, Cu, Nb, Ni, Pb, Rb, Sb, Sn, Sr, Ta, Tl, Th, U, W, Y, Zn, rare elements
	— Digestion of refractory materials, allowing the determination of Cr, Hf, Zr		
	— Rapidity and low cost	— low blank tests level	— very low blank tests level
		— low investment cost	— better dissolution of refractory materials (allows the determination of Cr in certain samples)
			— rapidity
			— low operating costs
Disadvantages	— Loss of volatile elements (Pb, Sb, Sn, Zn)	— impossibility of determining Si ; incomplete digestion of certain refractory materials, limiting the determination of Cr, Hf, Zr	— impossibility of determining Si, Hf and Zr
	— high dissolved salts concentration which renders the detection of trace elements impossible	— slowness	— high investment cost
	— high blank test results level	— high operating costs	

Another study, carried out by CIRSEE [15] on four types of certified materials (sewage plant sludge, incineration ahes, river sediments, clay), allows to compare two fusion digestions and three by acid digestion

- fusion by the sodium and potassium carbonate mixture (see 5.3);
- fusion by the lithium metaborate and lithium tetraborate mixture (see 5.3);
- attack by the HCl/HNO3 mixture in a semi-open system;
- attack by hydrofluoric acid in a semi-open system;
- attack by the HCl/HNO3 mixture in a closed system.

On four types of certified materials (sewage plant sludge, incineration ashes, river sediments, clay). Table 4 indicates those elements for which the recovery rate is over 85 % depending on the digestion method.

Table 4 — Comparison of five digestion methods on diverse samples, according to [15]

Sample	Sewage plant sludge	Incineration ash	Sediment	Clay
Elements analysed	Cd, Mn, Pb, Fe, Cu, Ni, Zn, Mg	Cd, Cu, Mn, Ni, Pb, Zn, Fe, Mg, Al, Sb	Cd, Cu, Ni, As, Pb, Zn	Ba, Al, Fe, Mg, Co, Mn, Ca, Zn, Na, K, Li
Fusion with carbonates[a]	Cu, Ni, Zn	Mn, Ni, Zn, Fe, Al	Cu, As, Ni, Zn	Ba, Al, Ca, Li
Fusion with borates[a]	Cd, Mn, Fe, Cu, Zn	Sb, Mn, Fe, Al	Cd, Ni, Zn	Al, Fe, Mg, Mn, Na, K
HCl/HNO_3 semi-open[a]	Cd, Cu, Mn, Ni, Pb, Zn, Fe, Mg	Cd, Mn, Pb	Cu, Cd, Zn	Mn, Ca
HF semi-open[a]	Cd, Cu, Mn, Ni, Pb, Zn, Fe	Cd, Mn, Cu, Ni	Cu, As, Cd, Ni, Zn	Fe, Mn, Zn
HCl/HNO_3 closed[a]	Cd, Cu, Mn, Ni, Pb, Zn, Fe	Cd, Ni, Zn, Cu, Mn, Pb, Fe	Cu, Ni, As, Zn	Fe, Mn, Ca, Zn, Na

[a] Elements of which the recovery rate is greater than or equal to 85 %.

These results show that, depending on the type of material under study and on the sought after element, it can be preferable to conduct one method rather than another. Thus, fusion digestion methods seem to be the best adapted for the analysis of soils, whereas microwave digestion in semi-open or closed systems appear to be better suited for sludges. Often, digestions by fusion and by digestion can be complementary; it is the case for incineration ash.

In certain cases, it can be worthwhile associating an acid digestion then a fusion of the residue in order to better cover all of the elements. The acid digestion can enable in particular to solubilise with a good recovery rate the volatile elements, whereas the fusion will enable to better solubilise the most refractory elements. One can then either analyse the obtained solutions separately or combine them together before analysis.

7 Conclusion

The choice of the method for digestion of solid samples before analysis is determining for the accuracy of the quantitative results. Indeed, all dissolution processes can cause either a loss of the elements that one wishes to analyse (incomplete dissolution, volatilisation, reprecipitation), or a contamination of the obtained solutions (impurities of the reagents used, digestion of the receptacles used).

Fusions are generally used for the digestion of refractory materials and allow the analysis of elements like Cr, Hf and Zr. Relatively volatile elements (Pb, Sn, Zn, Sb, ...) do not give any valid results on account of the high temperatures required for the fusion, *a fortiori* Hg, As, Cd. Since the quantity of salts added to the sample at time of fusion is high, it is necessary to dilute the solutions obtained before analysis, which raises the quantification limits of the elements and can make the detection of trace elements impossible.

Acid attack techniques are therefore quite often currently preferred on account of a better compatibility of the solutions with the analytical techniques, of the lower quantification limits allowing the analysis of a larger number of elements and of a lower cost of the automatic appliances. However, acid attack does not always allow a complete solubilisation of the sample, and in this case, it can be necessary to dilute the attack residue by a fusion. This shows the need for combining several sample preparation techniques when quantitative data are being sought for all of the elements.

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