This book is in constant evolution; updated topics are added as research progresses. The reader is strongly invited to fax us for more information or to contribute his own findings or tricks; any valuable suggestion will be given credit in the reference list.

GLASS DISKS AND SOLUTIONS BY FUSION FOR USERS OF CLAISSE FLUXERS®

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Corporation Scientifique Claisse Inc.
350, rue Franquet, Suite 40, Sainte-Foy, Québec, Canada G1P 4P3
Tel.: (418)656-6453 – Fax.: (418)656-1169
www.claisse.com

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1.5 NOTE TO THE READER

Please note that in Claisse Fluxers®, time is entered as a 4-digit number; the first two represent the minutes and the last two represent the seconds. For instance, in the present document, a time value of 1025 would mean 10 minutes 25 seconds.

2 INTRODUCTION

2.1 OBJECTIVES

High accuracy in physical and chemical analytical methods, particularly X-ray fluorescence (XRF) analysis, can only be attained with homogeneous specimens, whatever the method used. A simple way to meet that requirement is by dissolving the sample into a solvent and a unique, universal and fast technique to do it is a fusion with alkaline borates.

In XRF analysis, borate fusion is particularly advantageous because the obtained result is a solid glass. In other physical-chemical methods – AA and ICP analyses – borate fusion competes with acid digestion techniques, and is frequently an easier and simpler way to make liquid solutions.

The main objective of this book is to show the analyst how simple and easy it is to make glass disks and solutions nowadays, and how he or she can select the proper parameters to make fusions short and efficient. Making glass disks for XRF is now the simplest thing to do if a few simple rules are followed.

Another objective is to clarify the situation for those who still have hesitations concerning the use of fusion, for its presumed complexity and limitations as a means of sample preparation.

This book is divided in two parts. Part I deals with the techniques for making glass disks for analysis of oxides and non-oxides by X-ray fluorescence. Borate fusion is described in simple terms, and instructions are given for its application to various materials such as rocks, ashes, residues, refractories, sulfides, metals, etc. The chemicals selection and the operations to perform for best results are described with details allowing the analyst to make justified technical modifications to improve the quality of his work.

Part II is built the same way as Part I but deals with procedures to transform the samples into liquid solutions instead of solid glass disks. The procedures for making solutions differ from those for making glass disks in only two aspects: the size of the samples, and how the last operation is done, that is, pouring the molten glass into a solvent instead of molds. For that reason, Part II contains only the differences in the procedures along with explanations on how to make solutions, assuming that the reader interested in solutions will read Part I first.

2.2 A WORD ON FUSION

Fusion is a general name for all kinds of chemical treatments on solid samples that transform them into new compounds that are easier to analyze. These compounds are an intermediate step between the original sample and the end solution that will be used in analysis. The final solution can be a conventional liquid solution, or a less conventional one, that is, a solid solution in glass.

Most fusion processes result in compounds that have the property of being soluble in one given solvent. These processes are regular chemical reactions and the products are crystalline.

Although borate fusion is also a chemical reaction in broad terms, its characteristics are different. At high temperatures, the borates melt and become solvents for oxides. Only one product is formed: a homogeneous molten glass. In one type of application, the molten glass may be cooled without crystallizing to yield an amorphous homogeneous solid glass. It is ideal for XRF work. Alternatively, the molten glass may be cooled rapidly by pouring it into a solvent to yield a solution. This is thus a quick and simple way to prepare samples for ICP or AA analyses.

The fusion then becomes a simple procedure: a sample is mixed with a flux (the borate) and heated at temperatures in the range of 800 to 1100°C. The flux melts, becoming a solvent for oxides in the sample. The product is an amorphous homogeneous solution of the positive ions of the sample and flux in a cloud of oxygen atoms. This solution may be poured into a mold and slowly cooled to yield an amorphous homogeneous solid glass required for accurate XRF work, or it may be cooled fast by pouring into an acid solvent where it shatters in fine particles that dissolve easily and yield a solution for analytical works other than XRF.

This description of the borate fusion helps to understand why high-temperature refractories can be fused as easily as other oxides, at temperatures as low as 1000°C, while their melting point is several hundred degrees higher. They simply *dissolve* in the molten borate, just like table salt dissolves in water.

The main features of the borate fusion are:

1. quick fusion in the order of 2 or 5 minutes only due to high temperatures;
2. possibility of quantitative transfer of the molten glass out of the crucible, without losing a residue in the crucible;
3. applicability to most oxides and sulfides, as well as several metals and alloys;
4. simple, fully automatic procedures that include pre-oxidation of non-oxidized materials when necessary;
5. possibility of making synthetic standards of any composition, starting from pure chemicals.

Other features are simplicity of the procedures, rapidity, cleanliness resulting in high analytical accuracy. These characteristics are so advantageous that more and more analytical laboratories adopt the fusion technique as a routine sample preparation method quality control as well as in precise chemical composition determination.

The fusion procedures are simpler than ever, since fusion is gradually becoming a science. Two general procedures covers the whole range of materials; one for oxide samples such as rocks and ceramics, and another for non-oxidized materials, usually metallic samples such as ferro-alloys, or sulfides from Cu, Pb, Zn ores and concentrates. In addition, these techniques can be used manually for occasional analyses, or with automatic multi-sample fusion instruments for greater loads of analyses. In the case of XRF analysis, the accuracy after a simple fusion matches that of the more refined and complex chemical analyses, while in the case of AA and ICP analyses, the time required to make solutions is considerably shorter than with other methods.

Peroxide fusion and its different advantages over other techniques for sample preparation will also be covered by this manual.

3 PART I

PREPARATION OF GLASS DISKS

3.1 GENERAL

3.1.1 Fusion – what for?

X-ray Fluorescence analysis is a powerful analytical tool: it is rapid, simple and applicable to most elements at all concentrations. Its potential accuracy can surpass that of any other physical analytical method, provided that the samples are homogeneous near the molecular level. In the early days of XRF (1948+), all samples were prepared as loose powders or as pressed pellets, but the analytical accuracy was no better than a few percent on account of the so-called "particle size effects" [Claisse 1962]. In order to improve accuracy, homogeneous specimens had to be prepared, and this was the motivation for the development of the borate fusion method [Claisse 1956]. It is still in use today and it has been considerably improved during the last few years. It now competes more than ever with the pressed pellet techniques and many other analytical techniques.

3.1.2 Are the problems with powder specimens so great?

The answer is Yes. The X-ray line intensities may vary by 10 %, 20% and sometimes more. The most important reasons for low accuracy are the following.

Particle size: a more accurate term would be heterogeneity. It represents any small volume of material that has a composition different from that of the surroundings. Examples of heterogeneities are any particle in a sample of sand, a layer of oxide on the surface of particles, small inclusions in a crystal, etc. When the particle (heterogeneity) size is large, the first layer of particles at the surface of a specimen contributes to most of the observed fluorescence intensity of any given element, and that intensity depends only on the composition of the particles in which that element is present. On the contrary, when the particles are very small, the intensity of the same element depends on the overall composition of the specimen.

Surface roughness: since the excitation and the fluorescence emissions are in two different directions, large particles can be excited on one side and their fluorescence can be totally or highly absorbed in the direction of the detector. This effect is very small if the specimen has been pressed at very high pressure but is strong in loose powders.

Preferred orientations: high pressure pressing tends to align the flat surface of a particle parallel to the specimen surface, which increases the measured intensities from particles with natural flat surfaces and decreases the intensities from particles with more irregular shapes.

Segregation: during shaking a powder specimen, the heavier and lighter particles sometimes tend to separate rather than mix; it is very difficult to obtain complete homogenization unless a binder is added in the powder.

Matrix effects: effects created by the varying XRF intensities when reading the same element bonded to different components. The higher the complexity of a component, the higher the apparent intensity is, even if the element is present at the same concentration.

Determination of composition: the only way to determine the concentration of elements in a powder specimen is by using regression analysis. That method is applicable to specimens that are similar only, i.e. that have similar overall composition, similar particle size distribution, similar compounds and that are prepared in a similar way. The accuracy can never match the accuracy of a similar but homogeneous specimen.

3.1.3 The original fusion procedure

Essentially, a fusion procedure for XRF analysis consists of:

1. heating a mixture of sample and borate flux until the flux melts;
2. continuing heating until the sample dissolves into the flux, and agitating to homogenize the melt;
3. pouring the molten glass into a hot mold;
4. cooling to obtain a solid glass disk, ready for X-ray measurement without any additional treatment.

To proceed with a fusion experiment, one must learn about the tools to use, the constituents of the mixture for fusion, the preparation before fusion, and the fusion procedure. All these will be considered, and for the reader unfamiliar with that subject, the original fusion procedure [Claisse 1955] that never fails is now described.

1. Make a ring from a 10-cm long bare electric wire and place it on a flat plate of aluminum or stainless steel.
2. Mix about 0.3g cement or sand with about 6g anhydrous sodium tetraborate (dehydrated borax) in a platinum crucible or dish.
3. Heat the crucible and its content over a gas burner until the mixture melts and the liquid is clear; occasional agitation of the container should be done to homogenize the melt.
4. Remove the crucible from the flame; while the crucible cools until the melt is a little viscous, heat the metal plate with the ring for a few seconds; then pour the melt into the ring and let it cool. The result should be a glass button with an irregular flat surface underneath and a smooth convex top surface.

The quality of this button does not compare with the quality that we can have now. For a long time, making better quality glass disks required a more complex fusion, because one wanted to get greater analytical accuracy and wanted to process a greater variety of samples. This used to mean more variables in the parameters involved such as composition of fluxes, temperature of fusion, cooling conditions, etc. Fortunately, recent research results make fusion actually easier than ever.

3.1.4 Limitations to the borate fusion

Molten alkali borates are good solvents for oxides, but *oxides only*. This includes hydrates, carbonates, sulfates and nitrates that are combinations of two oxides, one of which is volatile (H_2O, CO_2, N_2O_5, SO_2) or very little volatile (SO_3). The situation for halides is not clear; they are more or less soluble but very unstable as shown by their volatility that increases with the atomic number; fluorine is rather marginal, being slightly volatile. Metallics, carbides, nitrides and sulfides are insoluble *per se* but they can be fused after an oxidation treatment that fortunately can be included as an additional step at the beginning of a normal fusion process for oxides. Consequently, the fusion technique can now be described as if the sample were in their full oxidation state; and the modifications required when the sample is in a reduced condition will be described in chapter 3.6.

3.2 TOOLS FOR FUSION

3.2.1 Accessories

Most of the small accessories needed for fusion are already present in a laboratory. They consist of:

- ☐ an analytical balance for weighing the samples, the flux and other chemicals. A few milligrams accuracy is sufficient for the flux but one tenth of a milligram is sometimes preferable for the sample;
- ☐ a Teflon spatula for mixing and crushing the lumps;
- ☐ a suction cup* to remove the glass disks from the molds;
- ☐ steel wool pads for rough polishing of crucibles and molds;
- ☐ 800-grit abrasive paper for finer polishing of crucibles and molds;
- ☐ self-adhesive stickers for identification of glass disks.
  *available from Claisse

Platinum-5%gold (Pt-5%Au) alloy appears to be the best material for crucibles and molds; it is strong, stable, long lasting and is not wetted by glass (as compared to other metals). Graphite erodes in a gas flame and is not a good heat conductor. Zirconium oxidizes and dissolves in the flux at fusion temperatures. Iridium is difficult to work with, it oxidizes in air at high temperatures and forms a volatile oxide.

3.2.2 Crucibles and molds

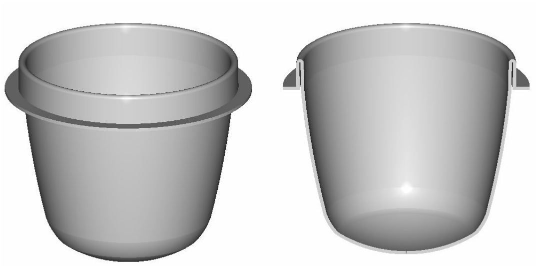

Figure 1 : Claisse crucible

Figure 2 : Claisse Bis!™ crucible

New, mirror-polished crucibles and molds are only slightly wet by molten glass and may not require the use of a non-wetting agent. As the number of fusions increases, the surface roughens on account of corrosion and aging. Then sticking increases and non-wetting agents are necessary to compensate for that. The surface of platinum ware can be improved by polishing as described in Chapter 3.7.

If granular flux is used, 20 to 25 ml capacity crucibles are sufficiently large to accommodate all the fusion mixture to make glass disks up to 40-mm diameter. Fine powder fluxes require much larger crucibles. If a fusion apparatus is used, the crucibles must be held safely in their holders and Claisse™ crucibles (with a flat rim at the top, Figure 1) or the equivalent are a must. With all fusion instruments, Bis!™ crucibles (with a mixing-enhancing hump in the bottom, Figure 2) enhance mixing and ensure fast homogeneity of the melt by producing strong convection currents around the hump (Figure 9). That is particularly necessary for samples that contain large particles of heavy minerals. Bis!™ crucibles can be obtained from Claisse and distributors only. Nominal capacity is 25 ml; other sizes are made on request.

Molds come in different sizes, between 30 and 40 mm diameter. Large-diameter molds (40 mm) are less rigid at the bottom and warp more easily, with consequent lower analytical accuracy; small diameter molds (30 mm) are tougher and have a longer life but some users may find it too small. Our experience favors the 32-mm size as the optimal one. This mold size is more economic in capital cost, in replacement cost, and in cost of flux.

3.2.3 Fusion Instruments

Only Claisse Fluxers® are described in this document. Information on other brands can be obtained from Corporation Scientifique Claisse Inc.

3.2.3.1 THE CLAISSE FLUXER-BIS!™

This instrument consists of two units: a Fluxer™ and its electronic controller. It is a fully automatic instrument with microprocessor. It is designed for the preparation of glass disks for analysis by X-ray fluorescence and for the preparation of solutions for analysis by ICP, AA or wet chemistry.

The main features of the Fluxer-Bis!™ are:

- ☐ six modified Fisher burners for processing 1 to 6 specimens;
- ☐ the same burners are used for heating the crucibles and the molds;
- ☐ seven fusion programs, each adaptable to all kinds of fusions; each program includes seven heating steps, casting, two-step cooling for disks or one-step stirring for solutions;
- ☐ each heating step has programmable heat (100 levels), agitation (100 levels), and time (up to 100 minutes, set by the second);
- ☐ the burners require propane or butane only; no compressed air nor oxygen;
- ☐ stable and reproducible gas flow, independent of the number of burners;
- ☐ uniform crucible temperature top to bottom;
- ☐ non-wetting agent injector for greater facility to release glass disks from molds, and to clean crucibles;

The automatic operation of the Fluxer-Bis!™ can be briefly described as follows: each crucible is held above a burner by means of a clip; a mold is held upside down above the crucible by a similar clip; the crucible and mold assemblies rock together in the flame during the heating steps for fusion and homogenization; at time of casting, the molds rotate forward to a horizontal position, and the crucibles pour their hot content into them; after a period of cooling in still air, the solidified glass is cooled to room temperature by means of fans underneath; the glass disks are picked up using a small suction cup and are ready for X-ray measurement without further treatment.

3.2.3.2 THE CLAISSE FLUXY™

This smaller instrument is designed for laboratories with smaller loads of samples, but by no means is a lower grade instrument than the Fluxer-Bis!™. It is also a microprocessor-controlled instrument and it has the same features with the following differences:

☐ processing of 1 to 3 samples instead of 1 to 6;

☐ 10 programs instead of 7;

☐ agitation is done by rotation of the crucible about its axis at an angle of 30° above the horizontal plane instead of rocking back and forth;

☐ exceptional uniform heating of crucibles top to bottom.

The automatic operation of the Claisse Fluxy™ can be described as follows: each pair of crucible and mold is held on a common holder by two clips that keep the mold inclined at 45° above the crucible; at the beginning of the fusion, the crucibles start with their axis almost in the vertical direction, then tilt forward about 20° while rotating slowly about their axis with the molds; when the fusion mixture has started to frit at the crucible wall, inclination increases to about 45°; rotation speed and flame increase; when one-half or two-thirds of the fusion mixture has melted, the crucible-mold assemblies tilt to about 60° from the vertical to complete the fusion and homogenization; when the fusion is ready for casting, the crucible-mold assemblies stop with the molds at a preset position. The arm that holds them is released and rotates rapidly, so that the molds end in the horizontal position with the crucible tilted at 45° over them, and the molten glass flows into the molds. After a short period of cooling in still air, the molds with glass disks in them are cooled to room temperature by means of fans underneath. The disks are ready for measurement without additional treatment.

Typical temperatures and fusion times (excluding cooling) to make glass disks for selected types of materials, with the two models of Claisse Fluxers® are illustrated in Figure 3.

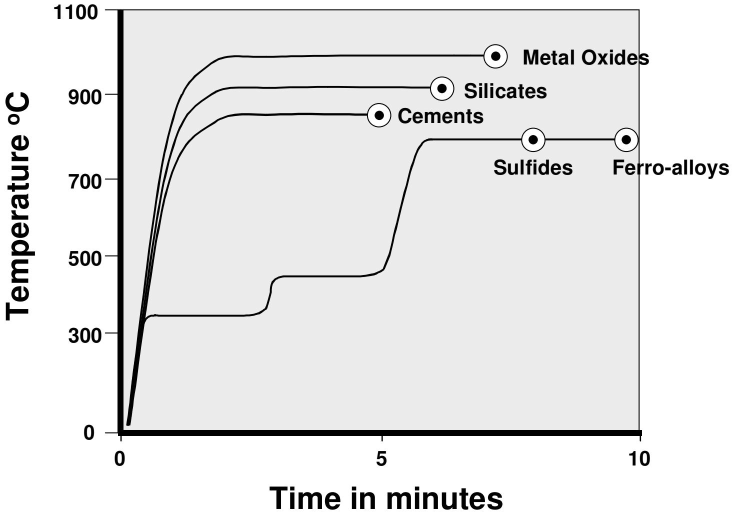

Figure 3 : Typical temperatures and times to make glass disks with Claisse Fluxers®

3.2.3.3 THE CLAISSE M4 FLUXER™

As it was the case with the Claisse Fluxy, the M4 fluxer is a three position fluxer. Specially developed for automation, the Claisse M4 is distinguished from the Claisse Fluxy™ due to the following characteristics:

- ☐ automatic ignition and flame watching system for increased safety and backfire control;
- ☐ newly developed burners for superior flame stability at low and high temperatures and for superior heating and oxidizing environments;
- ☐ separate arms for the molds and the crucibles, resulting in longer mold life;
- ☐ can be linked to a computer, equipped with an easy-to-use software allowing endless program memory;

The new burners, along with the axial rotation, assure the best oxidizing and fusing environment thus being the best choice for the fusion of non- or sub-oxidized components such as: alloys, iron ores, metals… It is also the best choice for the fusion of volatiles such as: sulfides, fluorides… This oxidizing environment can also be enhanced by the optional air/oxygen injector available with the M4 fluxer.

3.3 FLUX COMPONENTS

The three essential constituents of a fusion are a sample, a flux, and a non-wetting agent. Other chemicals may be added to ensure complete oxidation of the sample, or to change the chemical properties of the flux; they should be considered as flux components.

3.3.1 Stoechiometric fluxes

Lithium borate fluxes are the more commonly used in XRF analysis at the present time. They gained popularity from their high transparency for X-rays at long wavelengths making the sensitivity of light elements higher. The better known stoechiometric lithium borates from which current fluxes are made are the tetraborate and the metaborate. Sodium tetraborate is used occasionally, and sodium metaphosphate more rarely.

3.3.1.1 LITHIUM TETRABORATE

$Li_2B_4O_7$ has the highest melting point of all lithium borates, namely 920°C; it is the slowest to melt but that is not a problem. The crystals are slightly hygroscopic. Until now this chemical was, and is still, the most popular flux, but researches [Claisse 1997] have shown that the use of pure lithium tetraborate is responsible for most of the difficult and unsuccessful fusions. These difficult fusions were improved by fiddling with the cooling procedure, but still uncertain. This compound remains the best for pure alkaline oxides, and for them only (see section 3.3.2).

3.3.1.2 LITHIUM METABORATE

$LiBO_2$ has a melting point of 850°C. Fused alone, it always crystallizes on cooling. Fused with oxides, the fused disks also generally crystallize, except with a few acidic oxides at low dilution (see section 3.3.2). Lithium metaborate alone as a fusion flux is definitely not recommended for making glass disks. On the other hand, its high solubility for oxides in the molten state, together with its facility to crystallize make it the preferred flux for the preparation of solutions.

3.3.1.3 SODIUM TETRABORATE

$Na_2B_4O_7$ has a melting point of 741°C. It would be an excellent flux for glass disks if it were not for its high hygroscopicity. The glass disks made from it almost never crystallize or crack, but they must be kept in a desiccator to prevent the formation of a hydrate layer on the surface. Hydrated sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$ (borax) should never be used for fusion; it contains nearly 50% water that yields such a large volume of gas when heated, that part of the fusion mixture is sometimes blown out the crucible. Sodium tetraborate can be used as an additive to pure lithium borates to increase the stability of glasses.

3.3.1.4 SODIUM METAPHOSPHATE

$NaPO_3$ is a less-known flux that can be used in the same way as borate fluxes [Banerjee & Olsen 1978]. Its melting point is in the 600°C range, it fuses rapidly, the disks release easily from the molds, the crucibles and molds can be easily cleaned in water. The solubility of some oxides, for example chromium oxide, is higher than in lithium borates. Copper oxide disks that are difficult to make successfully with lithium borate fluxes are easy to make with sodium metaphosphate. The disadvantage is hygroscopicity; the disks become wet in humid conditions, and dry up when dryer conditions return.

3.3.2 *Mixtures of lithium borates*

A combination of lithium borates is definitely more efficient than pure tetraborate or metaborate for most oxides. As compared to pure lithium tetraborate, those fluxes have a lower melting point, are more fluid, lead to more stable glasses, stick less to crucibles and molds.

- Bennett & Oliver [1976, 1992] recommend a mixture of 1 part lithium tetraborate and 4 parts lithium metaborate, because that composition being close to the eutectic of the system, the preparation of glass disks should be easier.
- Norrish [1969] proposed the so-called 12-22 flux that contains 12 parts lithium tetraborate and 22 parts lithium metaborate and is also close to the eutectic composition.
- A more recent study [Claisse 1997] speaks of 50/50 lithium tetraborate/metaborate composition as the most universal flux, as shown by the following results. The glass disks were made by mixing various quantities of pure oxides with lithium tetraborate/ metaborate mixtures, and fusing. Some results are shown in Figure 4. The curves represent the greatest quantity of a given oxide mixed with 6g of flux that yields a perfect glass disk, i.e. one that contains no undissolved oxide and that is not crystallized. The best conditions to make good glass disks is obviously at the flux composition where the quantity of dissolved oxide is maximum, if no other factor must be taken into consideration.

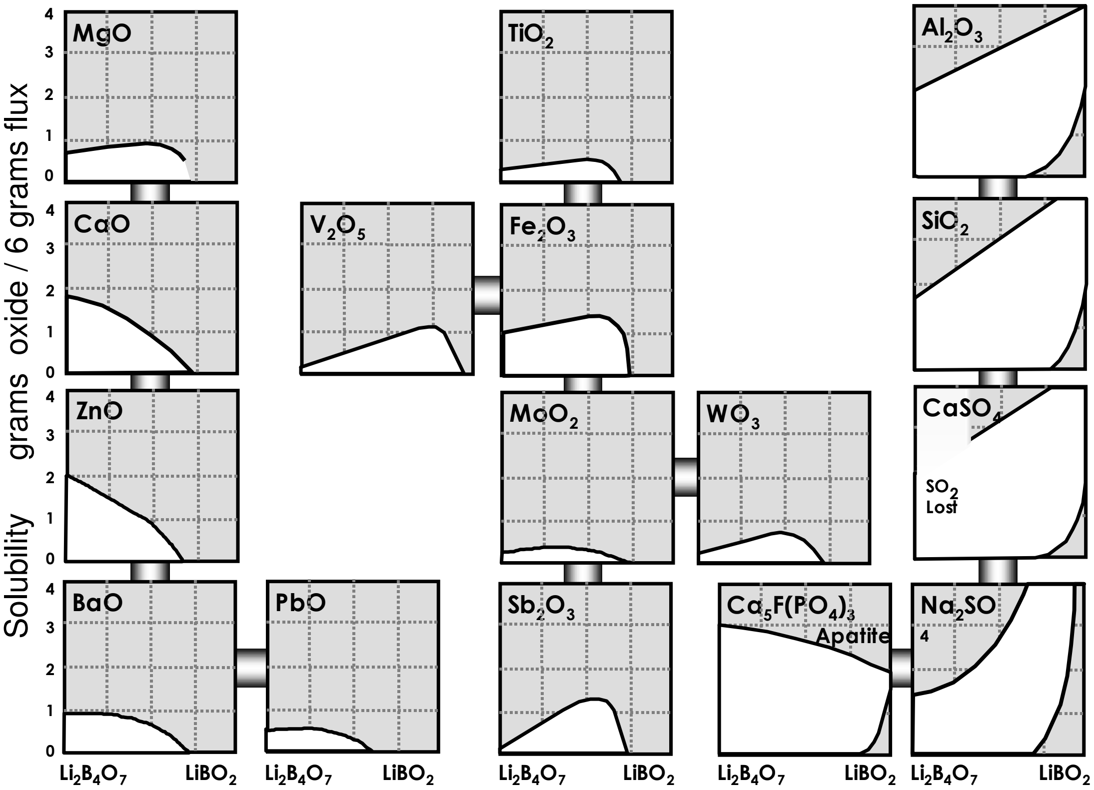

Figure 4 : Solubility of a few oxides in lithium borate disks

The diagrams on the far right have a common appearance: the maximum solubility is very high in lithium metaborate, and decreases when the latter is mixed with lithium tetraborate. At low concentrations of oxide, near pure metaborate, the disks always crystallize on cooling. This type of diagram is common to oxides of elements of the third group – Si, Al, P, and S – which are positive ions with very small atomic radii in the glass phase. Their oxides are acidic and the ratio of the number of oxygen atoms to the number of metal atoms in the molecule is larger than unity.

It is interesting to note that the maximum solubility is rather high at all flux compositions, and the optimal flux composition for these oxides would be pure lithium metaborate. But flux compositions above 80% lithium metaborate are not practical due to high risk of crystallization.

The diagrams on the far left are rather all similar and relate to oxides in which the oxygen/metal ratio is always equal or smaller than unity, which is the case of all basic oxides. For mixtures of those oxides, without any other oxide, lithium tetraborate appears to be the optimal flux to use if no other factor must be taken into consideration.

In the center of the illustration, we find all the other oxides, i.e. those that are not basic, and those that are not "acidic with small positive ions". These oxides are acidic since their oxygen/metal ratio is larger than unity, but their metal atom is bigger. Consequently, they should have diagrams that resemble those at the right, but since the metal atoms are large, the solubility is lower and drops to zero in the metaborate region. The highest solubility is near the 50/50 lithium tetraborate/metaborate composition.

Considering all three types of diagrams, the 50/50 lithium tetraborate/metaborate composition appears to be the most universal one because:

1. it seems to be the best for all non basic oxides;
2. this composition should also be the optimal for real samples, since the majority of samples are mixtures of two or more oxides, with an overall oxygen/metal ratio >1, like for single acidic oxides; two examples are shown in Figure 4: calcium phosphate and calcium sulfate, which contain a high concentration of basic CaO, but the 50/50 composition is good for them, due to the influence of their other acidic constituent;
3. comparatively, the 50/50 composition may not seem to be the best for pure basic oxides, but is not bad in absolute values; in addition, as the flux composition goes from lithium tetraborate towards the right, and the solubility decreases, other interesting advantages increase, such as non-wettability, sulfur retention, and lower fusion temperature.

3.3.3 Physical properties of borate fluxes

Physical properties of fluxes are almost as important as chemical properties. Lithium borate fluxes are available as

1. single-phase stoechiometric compounds;
2. mixtures;
3. fine powders;
4. agglomerates of fine powders
5. granular crystals;
6. more recently, spherical glass beads.

Physical mixtures of fluxes or addition of chemicals are not recommended because segregation may occur in the containers. The risk is obviously greater when the mixed components differ much in density or in particle size. Homogenizing them by agitation of the container usually leads to additional segregation. It is preferable to have pure components and weigh each of them separately for each sample unless high analytical accuracy does not count.

Loose powders and agglomerates of fluxes have a large specific surface area and since they are somewhat hygroscopic, the finer they are, the more they absorb humidity. As a result, the very fine powders contain a minimum of 1% H_2O after manufacturing and may reach a maximum of about 4 or 5% H_2O rapidly during use. A major inconvenience of the absorbed water is obviously a loss of analytical accuracy due to errors in the flux weight and to sudden volatilization of water during heating that sometimes blows a fraction of the flux and sample out of the crucible. Those fluxes should be kept in an oven at about 400°C for dehydration. Newly received flux can be checked for absorbed water by measuring L.O.I. (see section 3.11.3) at that same temperature.

Granular crystals of lithium borates usually contain 0.1% H_2O by weight when manufactured, but as compared to fine powders, the rate of further hydration is much lower. They do not require storing in an oven if the containers are not left open for long periods of time. Granular fluxes are ground during fabrication; consequently, they always contain some dust even after sieving.

Spherical vitreous lithium borate fluxes, the Claisse MiniBeads™, do not absorb more than about 0.03% H_2O. They are stable and hard glass particles that contain no dust, which are responsible for droplets that may appear near the top of crucibles during fusion, or that deposit on the fluxer during loading or heating. Their exceptional fluidity makes them ideal for automatic weighing. They have a high bulk density of 1.45, as compared to 1.0 for granular crystals and 0.2 or 0.3 for loose powders. For instance, the quantity of flux required to make a 40 mm glass disk is about 10g; a standard 25ml crucible filled to the top with fine flux would not make it; the same crucible would be 30% filled with granular flux, and only 20% filled with MiniBeads™. Additionally, these fluxes are made from such high purity materials, that all batches are suitable for analysis of trace elements. They are available in several standard lithium tetraborate/metaborate compositions.

3.3.4 Additives to fluxes

Chemicals are sometimes added to fluxes to modify their properties. The number of additives should be kept to a minimum to save time in the preparation procedure, to minimize human errors and to avoid impurities. Unfortunately, many additives cannot be added while manufacturing the flux because they lose their specific properties if they are fused. Since physical mixtures are not recommended, they must be added in each sample separately.

3.3.4.1 HEAVY ABSORBERS

For example, La_2O_3 or BaO_2 are added to decrease matrix effects by increasing the X-ray absorption of the flux. In principle, such additions also improve the analysis by absorbing the background intensity more than the line intensities, thus increasing the line contrast. The disadvantages are interferences between their emission lines and those of their impurities, plus additional preparation time of samples. Heavy absorbers should be used with moderation; it has been reported that La_2O_3 in lithium tetraborate at a concentration of the order of 16% (as it is often used) yields homogeneous melts that separate in two liquid phases during cooling. Since, by definition, these phases have different compositions, the glass disks are not homogeneous. In one particular instance, not consistent results of analyses on cements became reliable when no La_2O_3 was added in the flux.

3.3.4.2 OXIDIZERS

For example, nitrates of ammonium, sodium or lithium are added at a concentration of a few percent in the flux to oxidize small amounts of organic matter or partially oxidized elements, and to minimize the corrosion of crucibles. The same oxidizers are also used in larger amounts to oxidize specimens that contain high concentrations of sulfides or metallics. In the latter case, ammonium nitrate is not sufficiently efficient because its boiling point (210°C) is low, and its reaction with sulfides forms volatile SO_2 instead of stable SO_3. Carbonates of lithium and sodium are weak oxidants for sulfides but are excellent ones for oxidation of ferro-alloys. Other weaker oxidants that can be considered are BaO_2 and V_2O_5. Oxidants cannot be added during the manufacturing of fused fluxes.

3.3.4.3 FLUIDIZERS

Fluidizers and non-wetting agents are one and the same to a certain extent. All non-wetting agents ensure easy transfer of the molten glass into the mold, and consequently are excellent fluidizers, but their high volatility and their unknown concentration after fusion is a problem (see section 3.3.4.1.). Fortunately, volatile fluidizers like iodides and bromides, are so efficient that they can be used at low concentrations thus not affecting the analytical accuracy.

Alkali fluorides are efficient fluidizers, and are sufficiently stable to be used at larger concentrations for that purpose. In this case, though, the fusion temperature should be kept as low as possible to keep the loss of fluorine low and rather constant. Lithium carbonate added to lithium tetraborate acts as a real fluidizer by lowering its melting point.

3.3.4.4 STABILIZERS

Stabilizers, or glass-forming oxides, help prevent devitrification and cracking of the disks. The addition of silica, germanium or lanthanum oxides or sodium tetraborate at a concentration of a few percents is efficient. Most stabilizers fused in lithium borates during manufacturing are preferable to using pre-mixed fluxes (risk of segregation) or making individual mixtures for each sample (increase of preparation time).

3.3.4.5 INTERNAL STANDARDS

Internal standards are sometimes used in analytical techniques. Preferably, these elements would be better added as oxides during the manufacturing of fused fluxes if possible. Certainly, they should not be physically mixed with large quantities of fluxes, on account of their usually high density and tendency to segregate in containers. Incidentally, the internal standard technique used to correct for matrix effects requires measurements of two line/background intensities, which may not be more accurate than measuring only one line/background intensities in a more diluted fused disk.

3.3.5 Non-wetting (or releasing) agents

Depending on their composition, borate glasses have from much to almost no tendency to stick to the crucibles and molds in the liquid and solid states. In most cases though, the use of a non-wetting (or releasing) agent is beneficial or even essential.

3.3.5.1 COMMON NON-WETTING AGENTS

Halogens are the only elements that are known to be efficient as non-wetting agents, but iodine and bromine are the only two that are practical. They can be added as a salt or a solution into the mixture before the fusion, or as a salt only during the fusion. Most iodides and bromides can be used as a solution, but only those that are not hygroscopic can be used as solids, such as LiI, KI, NaI, CsI, NH_4I, and NaBr. Lithium bromide, LiBr, is an excellent non-wetting agent, but it can be used as a solution only because it is highly deliquescent. Pure iodine, I_2, and even bromidic acid, $HBrO_3$, have also been reported to be efficient. Ammonium iodide, NH_4I, is not recommended when sulfur is the analyte, because ammonium and sulfur react to form H_2S gas. Similarly, non-wetting agents must be used with caution when copper is present because the latter frequently forms volatile compounds with iodine or bromine, so that both Cu and the non-wetting agent are lost; in such case, the best time to inject the non-wetting agent is a few seconds before casting. Bromine has apparently the least volatility with copper.

3.3.5.2 VOLATILITY OF HALOGENS

Volatility of halogens is high and increases rapidly with the atomic number (Figure 5). Iodine is the most volatile – less than 5% of the original amount remains in the melt after a normal fusion, but this quantity is usually sufficient to ensure an essentially complete transfer of the melt into the mold and easy removal of the disk from the mold. Bromine is more stable. Fluorine has the lowest volatility and is not normally used as a non-wetting agent, but when its concentration is high, some releasing effect becomes noticeable. When it is used as a fluidizer, a concentration of 10% by weight in the flux seems to be a reasonable maximal concentration. Unless the temperature is kept reasonably low, the loss of fluorine may require correction for matrix effects.

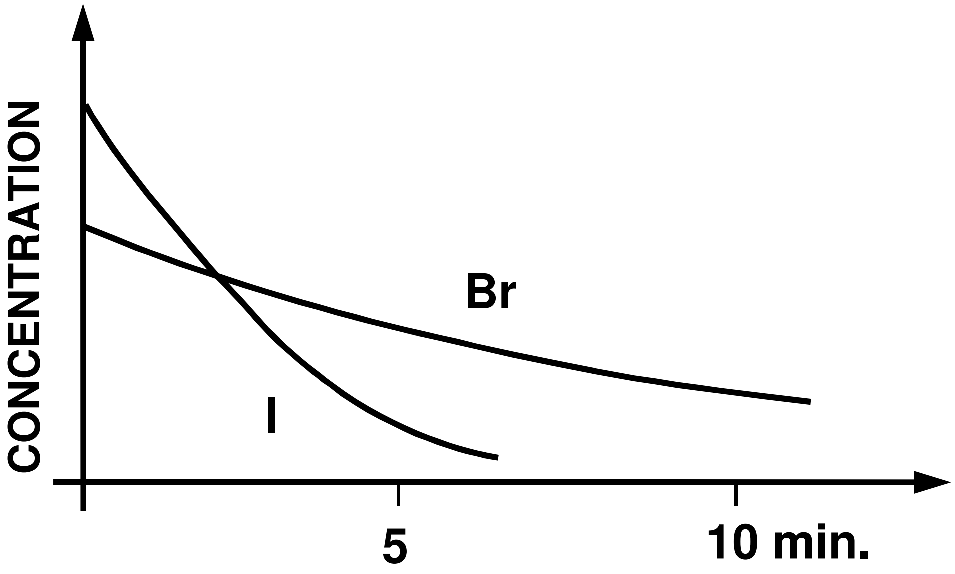

Figure 5 : Volatilization of I and Br from the melt as a function of time

3.3.5.3 QUANTITY OF NON-WETTING AGENT

Usually, the non-wetting agent is added in the crucible on top of the mixture to fuse before starting heating. To avoid weighing, it is prepared as an aqueous solution, and one or more drops are poured over the fusion mixture. A convenient concentration is about 250g of halide per liter. LiBr must be used that way because it is highly deliquescent. The usual quantity of non-wetting agent is about 0.2 to 0.4% of the flux weight, but the optimal quantity depends on the sample material, the flux composition, and the sample/flux ratio. A convenient way to determine the optimal quantity is to observe the shape of the disk in the molds after cooling (Figure 6): if the top surface is flat or slightly convex, the quantity is right; if it is concave at the edge, the quantity is too small; if the glass is reluctant to spread all over the surface of the mold, the quantity is definitely too large. Do not use a quantity larger than necessary because corrections for matrix effects might be found difficult to take into account.

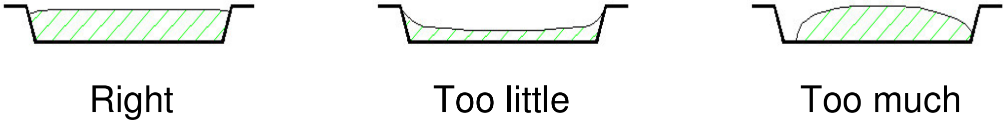

Figure 6 : Effect on non-wetting agent on shape of glass disks.

Fusion instruments that operate at or above 1200°C lose halogen elements by evaporation; also, certain elements of the sample increase the rate of volatilization of iodine and bromine. In both cases, a too large quantity of non-wetting agent at the beginning of fusion is necessary to avoid cleaning the crucibles after fusion. A better alternative is to use the usual or smaller amount of non-wetting agent before fusion and to inject an additional quantity just before pouring the melt into the molds. Cracking of disks in the molds during cooling is generally caused by the adherence of the glass to the molds; this can be prevented by a proper control of the non-wetting agent.

3.3.5.4 FLUXES WITH INTEGRATED NON-WETTING AGENT

A much better alternative to this manual non-wetting agent addition are the newly developed Claisse fluxes with integrated non-wetting agent. Since it is extremely important, for analytical accuracy, that the same concentration of NWA is consistently added to the fusion mixture, what better option than to have it pre-doped in the flux? Apart from contributing to higher reproducibility, this feature also eliminates a handling step during the preparation.

3.3.5.5 INTERFERENCES FROM NON-WETTING ELEMENTS

The emission lines of the elements of the non-wetting agent sometimes overlap those of the elements of interest in the specimen: the Br L_α line interferes with the Al K_α line and the Br K_α line interferes with the Rb K_α line; similarly, the I K_α line interferes with the Ba K_α line. However, these interferences are usually small; corrections can be made by mathematical methods (see section 3.11.1), or using analyzing crystals with a better line resolution. Other line interferences exist but they can be eliminated by pulse height discrimination.

3.4 THE FUSION OF OXIDES

This chapter and the next one deal with oxides only, because oxides constitute the majority of samples that are fused. The technique is as simple as ABC, now that we know that crystallization and cracking of disks are due to incorrect choice of flux composition and not to incorrect cooling procedures. Fusion of oxides will be used as a reference for other materials that require the somewhat more complex procedures described in chapter 3.6.

The preparation of the fusion mixture consists in:

1. Taking a representative sample from the bulk material to analyze. To ensure that the aliquot is representative, the material should be ground fine. Since a borate fusion is a dissolution, the finer the particles, the faster the fusion; grinding to -200 mesh (<75 µm) or finer is recommended.
2. Selecting the most appropriate flux for the sample. As shown in the figure 4 of section 3.3.2., one flux, the 50/50 lithium tetraborate/metaborate composition is capable to process all kinds of oxides. More specific flux compositions are not usually necessary, but may offer some additional advantages in specific cases. A few examples are:

- ☐ lithium tetraborate is recommended for samples that are made solely of basic oxides;
- ☐ when the samples contain essentially alumina and silica, a lithium tetraborate/metaborate flux containing 60 or 70% metaborate, or perhaps lithium metaborate alone, would allow making glass disks with higher sample/flux ratios, for higher sensitivity of trace elements;
- ☐ some users prefer adding about 3 to 5% lithium fluoride into lithium tetraborate, an acidic fluidizer that makes casting easier, for the analysis of cements and geological materials. The addition of a small amount of lithium nitrate or ammonium nitrate mixed with the sample is useful to eliminate graphite in shale and raw mix, or to minimize corrosion of crucibles by sulfide minerals. Refer to Table 1 for recommended flux compositions for selected materials. As far as physical properties of fluxes are concerned, Claisse fused MiniBeads™ are the most convenient fluxes; they are available in several standard and custom-blend compositions;

3. Set a convenient sample/flux weight ratio, taking into consideration the following observations:

- ☐ a very low ratio, for example 1/100, results in line intensities proportional to concentrations; calibration curves are nearly free of matrix effects (Figure 7). However, the contrast, line/background ratio, is low and the detection limit is relatively high;
- ☐ at high sample/flux ratios, for example 1/5, the matrix effects are relatively high; it is necessary to make matrix corrections;
- ☐ there is no lower limit on the sample/flux ratio except that some lithium fluxes tend to crystallize when the ratio is too low. There is however, an upper limit that should not be approached too close, on account of the slow dissolution rate and the increasing risk of disk cracking. Sample/flux ratios that are reasonably high yet sufficiently not too close to the solubility limits in Figure 4 are given in Table 1;
- ☐ any impurity in the flux appears as being in the specimen at a concentration equal to its concentration in the flux multiplied by the ratio of flux to sample. As an example, an impurity at about 50 PPM in the flux gives an XRF intensity that corresponds to 0.5% of the same element in the specimen if the flux-sample ratio is 100/1, and 0.02% if the ratio is 5/1. The purity of Claisse MiniBeads is outstanding.

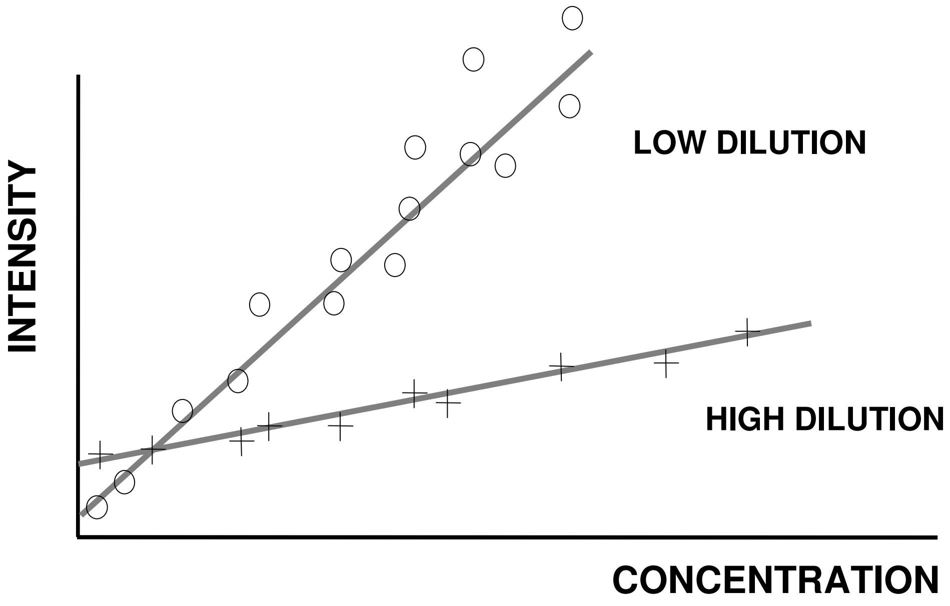

Figure 7 : Effect of dilution on fluorescence/background intensities and matrix effects

4. Weigh the sample to a precision of a milligram or better directly in the crucible. Weighing the flux to ±5mg is usually sufficient. It is correct to weigh close to a predetermined value (catch weight) and make corrections to compensate for weight differences.
5. Manually add 10 to 30 mg LiI or LiBr over the mixture (this step can be avoided if a flux with integrated non-wetting agent is used). These two non-wetting agents are excellent and add no interfering cation. After the above preparations are done, the last operation is the fusion of the samples. That subject is outlined in the next paragraph. The details of the execution of fusion depends on the fusion instrument that is used, and the experimental conditions required by the process are given in chapter 3.5.
6. Choose a fusion program appropriate to the type of sample. Although many substances accommodate to a simple program that contains one or two heating steps followed with casting and cooling, more complex programs are necessary for samples that require oxidation. Examples: a) samples that contain sulfide minerals, ferro-alloys or graphite are mixed with an oxidant, and must be heated at low temperature at the beginning to let oxidation take place, before the temperature is increased for fusion; b) gradual heating might be necessary when dealing with a carbonate-rich sample in combination with a finely ground flux. These special cases are considered in chapter 3.6.
7. Start the program. Remove the glass disk from the mold with the suction cup once the last cooling step has completed.

Sample Material	Flux (LiT/LiM)**		Sample / flux / (C or N) C = carbonate N = nitrate
	50/50	Other	
Cement		67/33	2-3 / 6 / 0-0,5 N*
Raw mix		67/33	2-3 / 6 / 0-1 N*
Silicate rocks	X		0.5-1 / 6 / 0
Bauxite	X		0.5-1 / 6 / 0
Copper concentrates*		LiT	0.2 / 6 / 2 N*
Slags	X		0.5-1 / 6 / 0-0.5
Sulfide ores*		LiT	0.3-.5 / 6 / 2 N*
Sulfide concentrates*		LiT	0.3 / 6 / 2 N*
Coal ash	X		0.6 / 6 / 1 N*
Ca sulfate	X		2 /6 / 0
Alumina	X		1 / 6 / 0
Silica	X		1 / 6 / 0
Magnesia		LiT	0.4/ 6 / 0
Iron ores*	X		0.45/ 6/ 1 N*
Titania	X		0.3-0.5 / 6 / 0
Zirconia	X		0.3-0.5 / 6 / 0
Ferric oxide	X		0.5-1 / 6 / 0
Ferro-alloys		LiT	0.2-0.4 / 6 / 1 C*
Chrome oxide	X		0.1 / 6-10 / 0

* Special sample and flux arrangement in crucible (see chapter 3.6)

** LiT = lithium tetraborate; LiM = lithium metaborate

Table 1 : Typical sample-flux ratio and flux composition for the preparation of glass disks

3.5 FUSION OPERATIONS

The fusion process consists in four operations: heating the sample-flux mixture, homogenization of the melt, pouring the molten glass into molds, and solidification of the glass.

3.5.1 Heating

3.5.1.1 REQUIREMENTS FOR HEATING AND HOMOGENIZATION

Basically, any means of heating can be used to bring the flux above its melting point to dissolve the sample, but practically, some means are better suited to meet the requirements of a good fusion. Whether heating is manual or automatic, these requirements are:

- ☐ a temperature range from a minimum in the 300°C for oxidation of sulfides and metallics, and preferably not exceeding 1000°C for fusion. Higher temperatures may cause excessive volatilization of flux and of some elements such as sulfur (Figure 8). When the temperature is low enough to avoid volatilization, a stable temperature is desirable but not necessary;
- ☐ easy access and adjustment to any level of heat;
- ☐ day-to-day reproducibility of the heating conditions;
- ☐ oxidizing conditions to minimize the reduction of elements to a lower oxidation state;
- ☐ a mechanism for agitation of the melt to accelerate the dissolution of the specimen into the flux and for homogenization;
- ☐ availability of non-wetting agent injection at time of pouring, for easy transfer to the molds, and to avoid cleaning the crucibles.

Fusion times longer than the minimum time for complete fusion are not important for elements that are not volatile; Kodama et al. (1967) fused the samples for various periods of times up to 50 minutes, and found no X-ray intensity differences other than statistical deviations. We found that if heating is done at temperatures where lithium is volatile, all the calculated concentrations in the sample increase with fusion time.

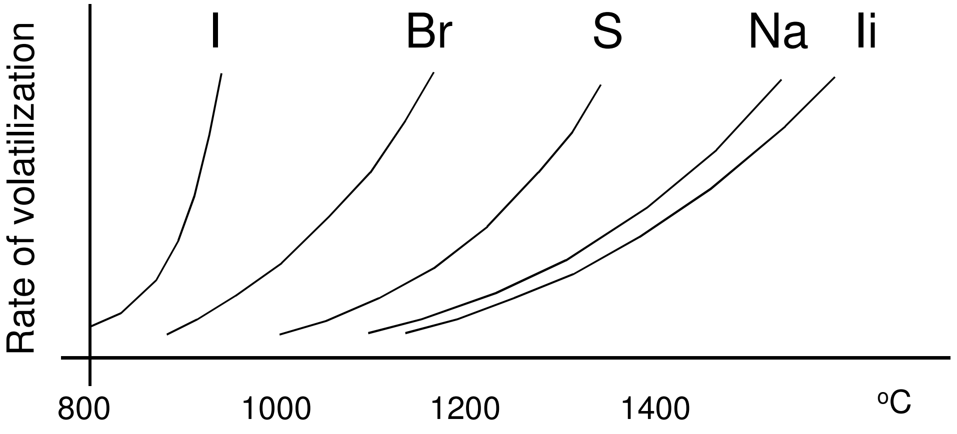

Figure 8 : Volatilization of a few elements in function of the temperature (not to scale)

i - Heating with propane gas burners

Fisher burners, modified by Claisse, have been selected for Claisse fluxers® on account of their simplicity and efficiency.

- ☐ The heat range is optimal and very low temperatures are attainable. The maximum temperature is more than sufficient for any type of sample, so there are no risks of damaging empty crucibles;
- ☐ control of gas flow is easy and ensures reproducible and stable heating conditions that are independent of the number of burners used;
- ☐ temperatures can be changed rapidly and set independently for each heating step, which is particularly important when dealing with sulfides and ferro-alloys;
- ☐ oxidizing conditions are obtained with the burner's base air inlets wide open, and avoiding excessive temperatures;
- ☐ several samples can be processed at the same time in identical heat conditions;
- ☐ heating is fast: typical complete fusion/homogenization times for silicates, ceramics and similar specimens is 2 to 3 minutes for 2g fusion mixtures (for solutions) and 5 to 7 minutes for 6 to 8g fusion mixtures (for glass disks);
- ☐ modified Fisher burners need only occasional and rare cleaning of the gas orifice;
- ☐ costs for burners, gas and control system are low;
- ☐ specially designed burners for the M4 fluxer which are built in a way to avoid flame backfires.
- ☐ the symmetrical arrangement of the orifices on the M4 burners allow very stable flames at high and low temperatures

ii - Heating with propane-oxygen gas burners

This particular kind of burners reaches a slightly higher range of temperatures than with propane gas only, which is not adequate for borate fusions and is a serious risk for damaging crucibles. Gas and oxygen are difficult to adjust when more than one burner is connected to the same gas line, and individual regulation is required.

iii - Muffle furnace heating

This method is fairly good, but slow. Frequent manual agitation of crucibles is needed to ensure homogenization. More than one furnace is needed when more than one level of heat is required in the process.

iv - Induction heating

Heating using electric induction is good; its main disadvantages are its high cost, its limitation to process one specimen only at a time, and its unequal heating of the side and bottom of the crucible.

v - Temperature measurement

Exact temperature measurement during fusion is not necessary. As a matter of fact, such measurements have very limited significance when one observes that the color of a hot crucible does vary considerably from top to bottom in some fusion apparatuses. In practice, what counts is to ensure that the temperature in the molten mixture does not exceed a level at which the elements of interest (essentially sulfur, halogens and alkalis) volatilize at a non-acceptable rate. There is no such a thing as a critical temperature, because volatilization varies exponentially with temperature, so that volatilization takes place at all temperatures, but is negligible in certain conditions (Figure 8). A temperature inferior to 1000°C is safe for flux elements, rather safe for sulfur, and too high for fluorine; all temperatures are too high for iodine and bromine. A practical way to make sure the desired temperature is not exceeded is to calibrate the gas control of the instrument once and for all. Dip a thermocouple in the molten glass, and make a curve of the temperature as a function of gas setting. A motto to keep in mind: a long fusion at low temperature is preferable to a short fusion at high temperature. Apart from the lower loss of sample and flux elements at low temperatures, the halogen element of the non-wetting agent evaporates less, which leads to cleaner crucibles after casting and easier releasing of the disks from the molds.

Fusion may involve several heating steps that versatile programmable fusion instruments can cope with. The heating steps in a complex fusion procedure are now described.

3.5.1.2 HEATING STEPS FOR OXIDATION

Oxidants are added to the flux to oxidize the reduced sample components, for example carbon-bearing samples, metal sulfides, or sub-oxides such as Cu_2O and FeO. Usually, the oxidant is a salt, such as $NaNO_3$ or $LiNO_3$, that melts at a lower temperature than the flux; it is mixed with the sample and a small part of the flux at the bottom of the crucible; the rest of the flux is laid over this layer in the crucible (see chapter 3.6). If the temperature at the beginning of the process is slowly increased, the oxidant melts first, wets the reduced component and reacts with it to yield oxides that dissolve into the flux. The temperature should be increased slowly enough to allow the reaction to reach the center of each reduced particle, so that oxidation is complete. Depending on the concentration of the compounds to oxidize, two, or occasionally three, heating steps might be considered. During oxidation, the crucible should only be slightly agitated to avoid mixing the two layers in the crucible.

3.5.1.3 HEATING STEPS FOR FUSION AND HOMOGENIZATION

When no oxidation step is required, the fusion consists of two steps only. The first one occurs with very little agitation, so that no particle of the flux is projected onto the wall of the crucibles to form fine droplets that never mix with the rest of the fusion mixture. This first step lasts until about two thirds of the flux has melted; it must occur at a temperature lower than that of the main fusion step. This step is obviously not necessary when fusion is preceded by oxidation as described in 3.5.1.2 above.

In the second step, heating is done at the "cruising temperature" for fusion. When the flux has melted, the sample should dissolve very slowly because the convection currents from thermal gradients during fusion are not sufficient to lead to fast homogenization. The fusion mixture must be shaken vigorously. All kinds of agitation that produce friction between adjacent layers in the melt are efficient. Those that produce a mere rotation or displacement of the molten mass as a whole are not efficient. Here are two examples.

The effect of rocking a standard crucible (Figure 1) containing a fluid can be described as follows: changing the inclination of the crucible from one side to the other, and considering that molten fluxes are rather viscous, the fluid mass rotates about its center instead of flowing, and almost no mixing occurs. The situation is different when a Bis!™ crucible (Figure 2) is used: when changing the inclination of the crucible from one side to the other, the hump in the bottom of the crucible is an obstruction that prevents the liquid mass from moving as a whole; instead, the fluid is divided by the hump and must flow on both sides and above the hump; these forced currents are strong and very efficient for mixing.

A similar situation arises in systems where the motion of the crucibles is a rotation about its axis (Figure 9) as in the Claisse Fluxy™ and Claisse M4 fluxer™. In a regular flat bottom crucible, the fluid mass rolls about its center of gravity and little mixing occurs, but in a Bis!™ crucible, the liquid glass is squeezed between the hump and the wall of the crucible, and the tendency to roll now produces strong countercurrents in a narrow space, and mixing is strong.

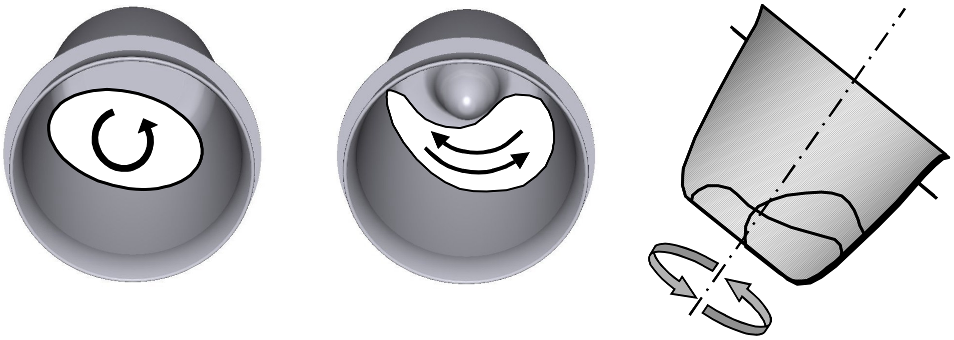

Figure 9 : Mixing efficiencies in flat bottom crucibles and Bis!™ crucibles.

Continuous agitation, from the beginning of the fusion program, leads to faster mixing as compared to short occasional agitation periods. It also contributes to faster dissolution of the samples. In addition, if the samples eventually contain particles that are susceptible to corrode the crucibles, keeping them moving minimizes their reaction with platinum. Another reason for vigorous agitation is the elimination of bubbles that sometimes form at the beginning of fusion. However, tiny bubbles on the surface of the melt and large bubbles that form continuously in the bottom of the crucible are due to graphite (see section 3.6.6) or sulfides (see section 3.6.3), and are not completely eliminated by agitation.

3.5.1.4 HEATING STEP FOR CONDITIONING BEFORE CASTING

In the Claisse Fluxy™ and the Claisse Fluxer Bis! ™, the molds are above the crucibles and are partly shielded from the flame. On casting, the lower temperature of the molds may produce a thermal shock that induces crystallization of the disks. To prevent that, the temperature of the molds should be raised by heating for 10 to 20 second at a higher temperature immediately before casting; the molds heat up fast because they are thin and the heat conductivity is high, while the molten glass in the crucibles heats up just a little because the mass is larger.

In the Claisse M4 fluxer, before the casting step, the mold arm is automatically raised in the flame for about 25 seconds thus insuring that the mold is at the adequate temperature when casting is done.

3.5.2 Casting into molds

When the hot glass is ready for casting, it is merely poured into the molds. To prevent crystallization associated with cooling, a few conditions must be met:

- ☐ the molds should contain no solid residue from a fusion; any material on a mold that is still solid at the time of casting is a seed for crystallization;

- ☐ the molds should be hot enough to avoid too great a thermal shock.

3.5.3 Solidification

This operation is an important step in the production of glass disks on account of its great influence on the final state of the disks. Never forget that glass is a supercooled liquid; therefore it is an unstable material that tends to crystallize, and it will do if it is given the slightest chance.

A typical crystallization curve (A) and a typical cooling curve (B) vs. temperature are shown in Figure 10. At temperatures above the melting point of the stable crystalline state of the molten material, the latter is and indefinitely remains a liquid. Just below the melting point, the tendency to crystallize is low and the viscosity of the molten glass is an obstacle to the atoms trying to form crystals. As the temperature decreases both the viscosity and the tendency to crystallize increase, but the latter predominates so that the time for crystallization is shorter. Eventually a temperature is reached where the viscosity becomes so high that the atoms have no possibility to form crystals and the glass remains in the amorphous metastable state. The metastable state is usually indefinitely stable near room temperature.

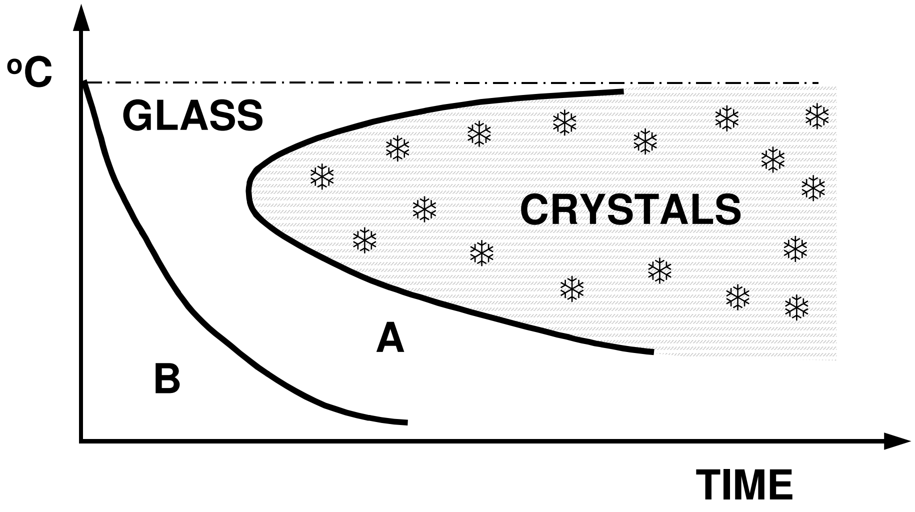

Figure 10 : The crystallization curve (A) and cooling curve (B) of the same glass

In simple terms, the secret of a successful glass disk lies in working out a crystallization curve (A) and a cooling curve (B) that do not cross. At first sight, the situation might look complex. The crystallization curve varies a great deal with the overall composition of the glass (flux and sample). Moreover, the analyst has only limited means to change the shape of a cooling curve, and he must take into account that forced cooling induces stresses that may lead to cracking, particularly when the glass sticks to the molds. That is where the correct selection of flux composition becomes important; as discussed in section 3.3.2, there is a range of flux compositions in which the glass phase is particularly stable. If we refer to Figure 10 again, those fluxes have crystallization curves (A) that are far to the right. Consequently, cooling can be slow, and without risk of crystallization or cracking of the disks. Doing this is the opposite of what has been done in the past and is still done. unfortunately: choosing a non appropriate flux (lithium tetraborate generally) that has a crystallization curve close to the temperature axis, and trying to cool the glass in a certain way to avoid the two curves from crossing, with all the undesirable difficulties and uncertainties with such cooling. It is obvious that there are great advantages in spending a little energy to learn how to choose a right flux composition, and not fiddle with highly susceptible cooling curves that are so sensitive to sample variations.

The following observations should be of interest to all analysts, and may be helpful when the flux composition is "accidentally" not the optimal composition of the sample:

- ☐ after the hot molten glass has been poured into molds, immediately cooling the latter by means of an air jet is certainly efficient to avoid crossing the crystallization curve, but that leaves the glass disks under stress; such disks have been observed to shatter in the hands of analysts and are a hazard for eyes. However, cooling with an air jet immediately after pouring can be done if it is short; then the disks should be left cooling slowly in still air so that annealing takes place at medium temperatures;

☐ annealing the glass disks after cooling is normally not necessary if the initial period of solidification in still air has lasted at least one minute. Annealing for a minute or perhaps two in the 200 to 400°C range is not wrong but long annealing may lead to a beginning of crystallization with consequent shattering of the disks;

☐ during cooling, while the temperature is still above about 100°C, no cool object such as a pair of tongs should come in contact with a glass disk; the disk will crack;

☐ a freshly made glass disk needs no polishing. If streaks or scratches are found on the surface, it is the mold that should be polished. Polishing a disk is a risk of contamination with Si or Al, two commonly used abrasives.

3.6 TYPICAL FUSION PROCEDURES

As was previously mentioned, only oxides dissolve into molten borates. All other compounds must be oxidized prior to fusion. Ideally, the oxidation and the fusion operations should be combined in a single procedure. That combination has been an objective in the research program at Corporation Scientifique Claisse Inc., and has now become a routine procedure in the analysis of formerly impossible-to-fuse materials.

Fusion of oxides has been described in chapter 3.4, but more specific details are given here. Procedures for other materials include fusion of carbonates, sulfides, ferro-alloys, graphite-bearing materials, copper-bearing ores, and organic materials. Trace elements may require a special technique because the loss of intensity due to dilution in the flux becomes critical when the X-ray intensities are already very low.

3.6.1 Oxides

The following procedure is applicable to most silicate rocks, cements, and other oxides. In these cases, it is presumed that 32 mm glass disks are made. All given values are approximate and may have to be adjusted for a particular sample.

The Claisse Fluxy™ and fluxer Bis!™ programs each include ten functions. Function 0 is reserved for ignition of the gas. Functions 1-3 are used for oxidation; functions 3-5 for fusion; functions 6-7 for casting; functions 8-9 for cooling.

The Claisse M4™ fluxer has thirteen fusions. The additional functions are attributed to the possibility of adjusting the cooling fans strength. Therefore, it is possible to gradually increase the fan strength for better chances of controlling disk cracking and crystallizations.

Before fusion: mix about 0.5g sample with 6.5g 50/50 lithium borate flux, and load into a Bis!™ crucible on a Claisse fluxer®; if the sample contains alkalis only, use lithium tetraborate flux. Add two drops of LiBr solution (250 g/l) over the mixture (or use 6,5g 49.75% / 49.75% / 0,5% LiBr). Use the program below.

Function	F:	1	2	3	4	5	6	7	8	9
Agit. speed	S:	10	–	30	–	50	20	35	–	–
Gas	G:	10	–	30	–	45	60	60	–	–
Time	T:	0020	0000	0130	0000	0500	0020	0001	0200	0200

Table 2 : Fusion program for oxides

When fusion is complete, remove the disks from the molds by means of a suction cup and examine them; if defective, refer to the troubleshooting Chapter 3.10. If found correct, they can be inserted in the X-ray spectrometer for measurement, or store them in a dessicator. Do not polish or give them any other treatment.

3.6.2 Carbonates

Carbonates behave as oxides after they have lost their carbon dioxide; they are processed in the same way. Samples that contain large amounts of carbonates are often reported to foam and run over the crucible during fusion because the decomposition of the carbonates takes place in a viscous environment. To avoid that, the carbon dioxide gas must have a way to escape easily with a minimum of effervescence. One way is to place the samples above the flux in the crucibles instead of mixing them together. Another way is to use a coarse flux that offers large open spaces for carbon dioxide to escape. Last alternatives are to use smaller samples or to heat more slowly at the beginning of fusion.

3.6.3 Sulfide ores and concentrates, sulfide-bearing cements

3.6.3.1 GENERALITIES

As mentioned before, sulfides are insoluble in borate fluxes without first being oxydized. After a long fusion, a few particles may seem to have dissolved without an oxidant, but in fact, some particles came into contact with air, oxidized, then dissolved. Such fusions are far from safe, because the insoluble particles have so many opportunities to come into contact with the crucibles that corrosion problems can be serious. Consequently, sulfide-bearing materials, especially concentrates, were considered too risky to process in platinum crucibles because no reliable, simple and safe fusion technique was available. A simple and safe fusion technique that includes an oxidation step in the process has now been developed [Claisse 1994]. It is now routinely used in some mining laboratories.

Three conditions must be strictly met to successfully process sulfides with retention of sulfur:

☐ oxidation must be complete before the fusion itself starts;

☐ the oxidation reaction must produce SO_3 and not SO_2 ;

☐ precautions to retain SO_3 must be taken because it is slightly volatile.

Oxidation when heating sulfides in air is not sufficient; the reaction usually yields mixtures of oxides, sulfates and sulfur dioxide gas SO_2 that is lost. A much better oxidation procedure is to heat the sample with a low melting point oxidant; only sulfates are formed. This method is found to be the best at the present time. The most convenient oxidants are lithium and sodium nitrates. Potassium pyrosulfate is also good when sulfur is not an analyte. Ammonium nitrate cannot be used when sulfur must be retained, because it forms SO_2 and SO_3 . The oxidizing efficiencies of lithium, sodium and ammonium nitrates were compared by Eastell and Willis [1990] who found $LiNO_3$ to be the most efficient. In our lab, we did not find lithium and sodium carbonates to be efficient for oxidation of sulfides. For complete retention of sulfur, oxidation with nitrates must be done at the lowest temperature possible, as long as required for each sulfide particle to react. To minimize the evaporation of SO_3 during fusion, the overall composition of the flux/oxidant must be equivalent to a flux containing about 40 to 65% lithium tetraborate, with lithium metaborate as the rest; the temperature should not exceed 1050℃.

3.6.3.2 FUSION TECHNIQUE

The technique for the fusion of sulfides that meets all the above conditions and that is as straightforward as in the usual fusion of oxides is now described. Sulfide concentrates about 0.3g in weight are mixed with 2g lithium nitrate and 1g lithium tetraborate. The mixture is thoroughly mixed to make sure the contact between the sample, flux and nitrate is good; the mixture is loaded into the crucible on the fusion instrument and about 5 or 6g of lithium tetraborate is added over it (see Figure 11). A part of the lithium tetraborate can be replaced by sodium tetraborate to increase the stability of the disks. The fusion program (below) must start with a low-temperature heating step to completely oxidize the sulfides, followed by a regular fusion like for oxide materials. Sulfide ores and cements contain much smaller amounts of sulfides than concentrates, and the sample weight can be increased. But the weights of oxidant and flux should not change, because each sulfide particle must still have the same probability of reaction as in the case of concentrates.

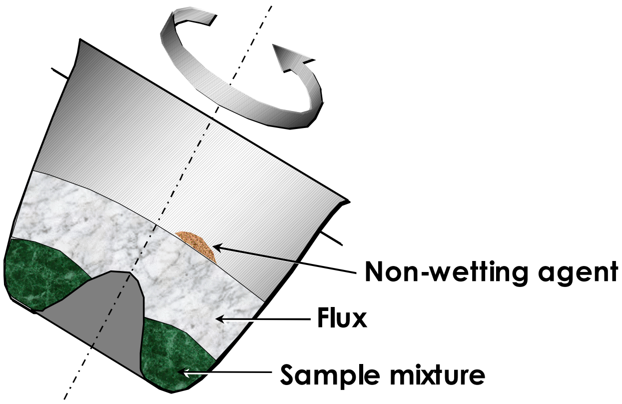

Figure 11 : Arrangement of the crucible content for sulfide-bearing samples

A typical program for fusion of sulfide ores and concentrates, as well as other sulfide-bearing materials follows. Again, it is presumed that 32 mm glass disks are prepared. All given values are approximate and may have to be adjusted for a particular sample. In oxidation functions 1 to 3, make sure that effervescence (quite intense with lithium nitrate) does not project particles onto the molds above. Functions 3-5 are used for fusion; functions 6-7 for casting; functions 8-9 for cooling.

Function	F:	1	2	3	4	5	6	7	8	9
Agit. speed	S:	10	10	30	40	50	20	35	-	-
Gas	G:	05	10	20	30	45	60	60	-	-
Time	T:	0200	0200	0030	0000	0400	0020	0001	0200	0200

Table 3 : Fusion program for sulfides

The process includes the addition of about 30 mg LiBr or LiI (as a solution) before beginning heating if the specimen weight does not exceed about 0.3g. It includes the injection of a pellet containing about 15 milligrams of a non-wetting agent 5 to 10 seconds before casting if the specimen contains more than 0.3g of sulfides. Total time is not significantly longer than for fusion of oxides. There is no crystallization problem, no sticking in the mold or cracking of the disks except when the specimen is composed of copper sulfide (see section 3.6.5). When the disks are cold, they should be removed from their molds by means of a suction cup and examined carefully; if found defective, refer to the troubleshooting Chapter 3.10. On the other hand, should the disks be found adequate, they can be directly inserted into the X-ray spectrometer for further measurements. They need no polishing nor any other treatment. After pouring, the crucibles should be clean and ready for another fusion; if not, more non-wetting agent should be used. Some corrosion of crucibles is unavoidable in fusing any reduced material, but in the case of sulfides, it should be very mild. Refer to chapter 3.7 for occasional refreshing of the crucible's inner surface.

An alternative method of sulfides fusion that deserves consideration was proposed by Norrish [1990]. It consists in mixing together the sample, 12/22 lithium tetraborate/metaborate flux and sodium nitrate in the crucible, then heating in a muffle furnace at 700°C for 10 minutes for oxidation; then carrying the crucible to the fusion machine, and fusing like for oxides.

3.6.4 Ferro-alloys and other alloys

Ferro-alloys are successfully fused with a procedure similar to the sulfide one. There are differences, though, due to some particularities of these alloys.

☐ Ferro-alloy particles are dense and hard, and not porous like sulfides; oxidation is slower and more difficult. Adding more oxidant is not the way to go since the oxygen / metal ratio would confer an overall composition resembling that of 100% lithium metaborate; the disks would then crystallize.

☐ Lithium carbonate is definitely a better oxidant than lithium nitrate. For the same oxidation power, there is less generated gas and effervescence. The melting point is higher, though, and a smaller quantity is lost in a reaction with the flux in the low temperature range where metals oxidize slowly. Lithium carbonate is also preferable to sodium carbonate because it allows for the determination of sodium.

☐ Ferro-silicon can be a crucible killer if fusion is not done very carefully; this material reacts violently with oxidants and the reaction is strongly exothermic. This material is heavy and tends to cluster after mixing with flux; if oxidation starts at one point in a large cluster, the heat is so intense that the whole cluster and sometimes all other clusters ignite at the same time; the parts of the crucible close to the hot clusters usually crack or even melt. A means to prevent that is using lithium carbonate flour in the sample/oxidant/flux mixture, so that ferro-silicon particles will have more difficulty to cluster. But the best protection is making a flux coating on the crucible wall as described in section 3.6.4.1. Such coatings are highly recommended for fusion of all ferro-alloys.

☐ Ferro-chrome is not more difficult to fuse than other ferro-alloys, but the solubility of chromium is very low. In an average fusion, the maximum weight of ferro-chrome is about 100 mg, which is small as compared to 0.5 g with most other ferro-alloys. There is hope, however, to increase the solubility of chromium in a near future.

☐ Graphite is more than often present in ferro-alloys. It is readily detected by looking at the fusion, either at the beginning of melting if the concentration of graphite is a few percent, or near the end of fusion if the concentration is very low. When the concentration is high, black graphite particles float on the surface of the melt, and the melt does not wet the crucible; then, the whole melt takes the shape of a ball and rolls in the crucible during agitation. When the concentration is very low, graphite is observed as a black spot, sometimes not larger than one millimeter; it floats on the molten glass and looks as it is not going to disappear by heating longer. Even if graphite is in such small quantity, and even if it does not absorb X-rays significantly, it should be removed; otherwise the glass disks will have bubbles on the surface. Refer to section 3.6.6 for elimination of graphite.

The procedure for fusing ferro-alloys was developed from the new "universal flux composition concept" described in section 3.3.2. The weights of lithium and boron components are chosen so as to oxidize up to 0.5g of ferro-alloys without corroding the crucible, without spattering during fusion, and without risk of crystallization of the bead. Do not change these proportions of lithium and boron compounds.

3.6.4.1 MAKING THE PROTECTION COATING

When fusing ferro-alloys, a protection coating (Figure 12) should be made first, by melting 5g of lithium tetraborate (no other flux composition) in the crucible and swirling the crucible during cooling. Coatings made manually are often crystallized and cracked. Transparent and uncracked coatings can be made automatically with the Claisse M4™ and semi-automatically with the Claisse Fluxy™.

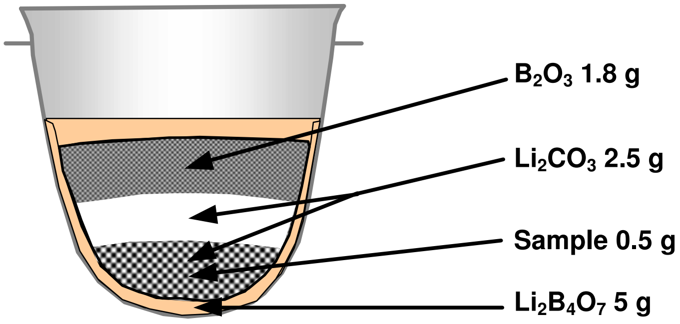

Figure 12 : Fusion of ferro-alloys using a protective coating.

The procedure to make a coating semi-automatically with a Fluxy™ is the following:

- Pour 5 g lithium tetraborate into the crucible and start the following program to make the coating.

Function	F :	1	2	3	4	5	6	7	8	9
Agit. speed	S:	10	–	–	–	50	20	–		
Gas	G:	30	–	–	–	50	0	–		
Time	T:	0030	0000	0000	0000	0300	0500	0000	0000	0000

Table 4 : Fusion program to make a protection coating

- After the flux has completely melted during F5, the gas is turned off in F6 and the rotation is kept on; when the flux becomes rather thick and the crucible is covered with a uniform coating of flux, manually raise the arm (holder) until the crucible is vertical. Some of the viscous flux should now cover the bottom of the crucible. Let the coating continue cooling with rotation on. Once cooled, the coating is usually vitreous, but it doesn't matter if it crystallizes once in a while. Rotation stops after F6;

- A flat or round bottom crucible must be used to ensure complete protection of the crucible. Unfortunately, one can therefore not benefit from the high agitation efficiency of Bis! crucibles, and that must be compensated by increasing the fusion time.

3.6.4.2 PREPARATION BEFORE FUSION

Weighing the sample mixture is more easily done by using two weighing pans.

- Weigh approximately 1.25g lithium carbonate in one pan and continue adding lithium carbonate in the second pan to make a total of 2.5g. Add the sample in any of the pans; up to 0.5g can be used if the solubility of the material permits (ferro-molybdenum and particularly ferro-chromium have a low solubility);

- Mix well the sample and the lithium carbonate, pour into the crucible and spread;

- Pour the lithium carbonate of the second pan over the sample mixture and spread it;

- Weigh 1.8g boron oxide (never use boric acid) and spread over the carbonate layer. Boron oxide is hygroscopic; keep the container closed at all times and store in a cool and dry area;

- Add about 20mg of a non-wetting agent (crystals or solution) on top. Or, preferably use flux with integrated non-wetting agent for utmost control over volatilization;

Function	F:	1	2	3	4	5	6	7	8	9
Agit. speed	S:	10	10	10	–	50	20	01	–	–
Gas	G:	03	10	25	–	50	60	60	–	–
Time	T:	0700	0100	0030	0000	0500	0020	0001	0200	0200

Table 5 : Fusion program for ferro-alloys

If graphite is not totally consumed early during fusion, a fine jet of air can be used during F5 (on the M4™ fluxer) until all graphite is eliminated; time in F5 might have to be increased accordingly. Injecting additional non-wetting agent can be done in F6.

The most important settings in this program are:

a) the very low temperature and rather long heating in F1 for more efficient oxidation

b) the slow agitation in F1, F2 and F3, to allow uniform heating of he crucible without mixing the layers in the crucible.

After fusion, the glass disks are ready for measurement without further treatment.

3.6.5 Copper-bearing materials

These materials are difficult to process at high concentrations, and it is important to know what the risks are when insufficient precautions are taken. Let us see some facts about copper:

- ☐ A coating of metallic Cu forms on the crucibles when copper oxide is fused with lithium tetraborate;
- ☐ The Cu coating is responsible for the strong adherence of glass to crucibles. After fusion and casting, the crucibles are covered with a layer of fused glass all over, and the solidified disks break into small pieces that are impossible to remove from the molds, except if dissolved or re-melted;
- ☐ Cu oxide fused with lithium borates reacts with the halogen ion of non-wetting agents to form volatile compounds; the reaction is faster with iodine than bromine;
- ☐ As the composition of the flux changes from the tetraborate to the metaborate, the Cu coating gradually disappears, the formation of volatile iodides and bromides diminishes, and sticking to crucibles and molds decreases;

The following observations seem realistic, but additional experimentation would be necessary to definitively accept these observations as conclusions:

- ☐ The optimal lithium borate flux for Cu-rich specimens should contain as much metaborate as possible. The 50/50 lithium tetra/meta composition, recommended for general use with oxides, should be enriched with lithium metaborate just below the composition where crystallization starts, i.e. about 75% metaborate;
- ☐ Bromides should be preferred to iodides as non-wetting agents; addition can be done at the beginning of fusion with samples of low Cu content; when the concentration is high, addition of a tablet of bromide (NaBr) must be done 5 seconds before casting;
- ☐ Sodium tetraborate may retain Cu more than lithium tetraborate;
- ☐ Flared molds with an angle of about 20° help release the disks more easily;

The most difficult case in making glass disks used to be copper sulfide concentrates, which caused problems with copper and problems with sulfur. With the recent technique for fusion of sulfides described in section 3.6.3, copper sulfide has become less difficult to fuse than copper oxide on account of the presence of sulfur.

3.6.6 Graphite-bearing materials

Carbon is often found in small concentrations in raw mix cements, ashes and limestone, and at higher concentrations in ferro-alloys. Graphite is insoluble in borate glasses; when its concentration is very low, particles of about 1- to 2-mm size float on the surface of the melt and absorb gases that are released on the surface of the disk during cooling, which induces bubbles or cracking in the disk. Then, the addition of a fraction of a gram of sodium or lithium nitrate in the fusion mixture is often sufficient to eliminate graphite. Ammonium nitrate can be used instead in larger amounts, because the excess volatilizes completely on heating. That is not the case with lithium and sodium nitrates that leave a residue of Li_2O or Na_2O in the glass. With addition of nitrates, heat at the lowest temperature possible (ammonium nitrate volatilizes at 210°C) for a short time to allow oxidation to take place. If the concentration of graphite cannot be eliminated by the addition of a nitrate in the flux, do just like for sulfides: increase the efficiency of the oxidant by mixing it with the sample and a little flux, and put the rest of the flux over the mixture. When lithium or sodium nitrates are used, do not forget that the Li_2O or Na_2O residue becomes part of the flux and must be taken into account, which means that the combined composition of the flux/residue has moved towards lithium metaborate, and that matrix effects are now different.

If the amount of graphite is still too high, an injection of air into the crucible is necessary and very efficient. A very small flow of air for a short time is enough to yield clear glass disks from samples highly contaminated with graphite. The air injection should start after the fusion mixture has molten, and should stop at least half a minute before casting. This automatic option is available on the Claisse M4 fluxer only. Other wise, manual air injection is required.

3.6.7 Organic materials

Examples of fusion of organic materials in borates are rare but a case is known of a customer who makes fusions to prepare solutions from polymers for further analysis by ICP. A similar procedure could be used to make glass disks. The fusion mixture contains 5g sample, 1g 50/50 lithium tetraborate/metaborate and 0.1g KI. The operating conditions are: heating at the lowest possible temperature until all the combustible material has burnt, then proceeding to fusion like for oxides, pouring the melt into a 10% HCl solution, and stirring for dissolution. The process is done with an automatic Claisse Fluxy™ modified for operation by a Zymark robot. The user claims that accuracy has increased over the more conventional dissolution technique previously used. Claisse has also made a few successful fusion trials from paper and leaf samples. Further researches must be done on these applications before developing a typical fusion procedure.

3.6.8 Low dilution fusion for trace elements

The dilution of the sample in the flux results in a decrease of fluorescence intensities. Usually, this loss of intensity is less than expected (see section 3.8.2.3) from direct proportionality with the dilution, and is not too inconvenient, because the efficiency of modern spectrometers is high. It is different when one deals with trace elements: the flux being a material made of light elements only, scattered radiation are higher than usual, which results in higher background and lower line/background ratio or contrast. It is then obvious that the sample/flux ratio should be made as high as possible; the advantage would be twofold: line intensities would increase and background noise would decrease.

Low dilution techniques and application to the analysis of trace elements were described by Haukka and Thomas [1977], Eastell and Willis [1990], Lee and McConchie [1982]. In those techniques, the sample/flux ratio is about 1/2 and the flux is generally lithium metaborate. At such concentrations, the loss on intensities is very small for most elements except for light elements; matrix effects are high, but can be adequately corrected. The major problems arise in making glass disks: solubility in glass is limited and crystallization is fast (lithium metaborate crystallizes easily and silica is needed to stabilize it). Both problems can be avoided by freezing the glass very rapidly, casting into a mold and pressing immediately with a plunger [Claisse 1956, Norrish and Hutton 1968]. Specimens that devitrify can be ground and pressed with no significant loss of accuracy because the particles are small and rather homogeneous.

The new information that we now have on the solubility/stability of lithium borate glasses (see chapter 3.3) can be exploited in combination with the low dilution techniques mentioned above. For example, most oxides are 1½ to 2 times more soluble in lithium borate fluxes containing 50 to 60% lithium metaborate than in lithium tetraborate alone, and are even more soluble if the sample contains acid elements. Another example: fused disks of silica or alumina can be made from a mixture of 1 part sample and 1½ part lithium metaborate, using conventional fusion techniques and a Claisse Fluxy™ or M4™. Trace elements in such samples should be easily measurable.

3.7 CARE OF PLATINUM WARE

3.7.1 Crucibles

3.7.1.1 MINIMIZING CORROSION

Partially oxidized materials heated in Pt-Au crucibles always cause some corrosion. The most frequent corrosive materials are sulfide minerals, sub-oxides – such as FeO, MnO, Cu_2O – ferro-alloys and metallics. Corrosion is minimized by using low melting point oxidants mixed with the corrosive material and slowly heated at a low temperature until the non-oxidized material is completely oxidized. When sulfides are present in very low concentrations, mixing the sample with a few tenths of a gram of lithium or sodium nitrate with the flux and heating at low temperatures for one minute before continuing fusion is recommended. If the concentration of sulfides is higher, heating as described in section 3.6.3 (fusion of sulfides) is recommended. The reaction of sulfides with platinum produces platinum sulfide that makes the crucibles brittle.

When metallic particles are present, refer to section 3.6.4. Take note that oxidation of metals is very slow and that the reaction is done through the formation of Li_2O_2 from the oxidizer. That compound is highly corrosive, much more than the metallic particles. The latter can only alloy superficially with the platinum and do not generally make the platinum brittle. The best protection is making a coating of flux inside the crucible and making it last until the oxidation reaction has finished.

An alternative way to minimize the effect of corrosive materials on crucibles consists in placing the sample so that it is not in contact with the crucible. The flux is placed into the crucible; then a funnel is lowered into it and moved so that there is flux under and outside, and none inside; pour the sample/oxidant mixture into the funnel, then pull up the funnel and fuse.

3.7.1.2 CLEANING

On the first hand, the best attitude is to prevent residues by using the right amount of non-wetting agent.

Crucibles should not be scraped by means of hard tools, for example screwdrivers. Scratches in the crucible cannot be removed, and retain more residue in subsequent fusions.

There are easier ways to remove solid residues from crucibles. A simple way is to make a blank fusion as follows: put about 2g flux or more (purity is not important, a chip of broken disk is acceptable) and 0.2g of KI in the crucible, heat until fused, swirl, then pour. A similar fusion with potassium pyrosulfate can also be used; this strong oxidant also dissolves metallic coatings on crucibles after Fe or Cu oxides have been fused in lithium tetraborate. An alternative way is to let the crucibles stand in 1% or 2% nitric acid or hydrochloric acid in water overnight. Never use both hydrochloric and nitric acids together. If a residue is still present after trying these alternatives of cleaning, it is likely that a reaction has taken place between platinum and the sample, and the crucible is probably damaged permanently. As a last trial, let the crucible stand 3 to 5 days in 20% nitric acid and 80% water. If that does not work, do not try to remove the residue by mechanical means; instead, one can continue using the crucible as if there was no residue; there is no risk of contaminating the next fusion. The last alternative is to declare the crucible as scrap and sell it for its precious metal value.

3.7.1.3 POLISHING

When crucibles have lost their luster, glass sticks more to them. For sure, working with well-polished crucibles at all times is more pleasant, analytical results are more reliable, and perhaps overall analytical costs are lower, but if that is not the case, crucibles can often be re-polished sufficiently well in the lab if small imperfections are acceptable. First, make sure the crucible is clean. To polish, use steel wool pads, and rub for a minute or two. Usually that should be sufficient. If fine scratches are present, start with wet fine abrasive paper (800 grits if possible) before using the steel wool pads. If scratches or corrosion are greater, start with a coarser abrasive, then switch to finer ones, then to the steel wool pads. Some customers have also succeeded polishing their platinum ware with a felt pad mounted on a rotary tool, along with an very fine abrasive alumina or diamond polishing paste.

3.7.2 Molds

3.7.2.1 RELEASING DISKS

Be very careful with molds; take note that damaged molds are generally unusable molds. Molds should never be hit hard to release a stuck glass disk. If a disk sticks, heat the mold over a low flame for half a minute; the mold will expand and the glass disk will not; the disk should then separate easily by turning it upside down.. If that is not successful, put some KI on the disk, heat until the KI and the disk melt, and pour the molten glass; then clean the mold in 10% nitric acid.

3.7.2.2 CLEANING

If a glass disk consistently cracks at the same position in a mold, examine the mold for a possible residue in the corner next to the flat surface. Then, it is sometimes sufficient to wipe the mold with a humid cloth or to let it stand overnight in water. Very dirty molds should be cleaned in an acid bath like the crucibles.

3.7.2.3 POLISHING

The surface of glass disks is an exact replica of the surface of the molds, so molds should be kept well polished. Polish the molds in the same manner as the crucibles. Of course, polishing with steel wool pads is not perfect and leaves the platinum with a dull surface. The surface of the glass disks will also be dull, and the resultant analytical accuracy of light elements might be affected slightly. Some customers have also succeeded polishing their platinum ware with a felt pad mounted on a rotary tool, along with an very fine abrasive alumina or diamond polishing paste.

3.7.2.4 DEFORMATION OF MOLDS BY CYCLIC HEATING

In normal fusions, the solidified disk starts releasing at the edge of the mold, and gradually towards the center. Thus, for a short time, the mold is pulled up at the center, and pushed down at the rim. The deformation at the bottom is elastic and the mold takes back its flat shape. However, the temperature is not low when that occurs, and in reality, a very small permanent deformation remains, too small to be observed. After a large number of fusions, this deformation becomes visible and X-ray intensities begin to change. Reshaping a mold flat is not easy, but before returning a mold for its metal value, it is worth trying reshaping: make a hardwood rod with a diameter equal to that of the mold and with a flat end; protect the surface of the mold with a thick piece of paper; place the mold on a flat hard surface, and hit with the rod and hammer. A stainless steel mold reshaper is also available from Claisse.

3.8 ADVANTAGES AND LIMITATIONS OF BORATE FUSIONS

3.8.1 Advantages

The fusion technique has several advantages over most of the other sample preparation techniques. Apart from the elimination of particle size and mineralogical effects, the following advantages are worth mentioning.

3.8.1.1 REPRODUCIBILITY

Being that a quality glass disk is as close to perfection as a specimen can be – flat surface, no porosity and good homogeneity – the fluorescence intensities should be constant from sample to sample. Tertian reported the following fluorescence intensities (Table 6) and maximum deviations from the mean value for six identical glass disks obtained by fusing a granodiorite (a silicate) in a mixture of 3 parts sodium tetraborate and 2 parts lithium tetraborate; these early fusions were manually prepared.

Element	X-ray intensity total counts	Max. deviation from average in %
Al	251507	0.06
Si	462682	0.08
K	470066	0.23
Ca	497847	0.17
Ti	155903	0.28
Fe	411551	0.30

Table 6 : Reproducibility of a few elements in glass disks (Tertian)

This next example speaks of an user who compared his 5-year old induction heating fusion instrument with a rather poor condition demo Claisse Fluxy™. The results obtained from ten glass disks prepared from a single cement sample are shown in Table 7. The calibration that was made for the induction-heating instrument was used to determine the concentration in the fused disks made with the Fluxy™. The results obtained from the Fluxy were all 2.3% lower than those of disks made with the induction-heating instrument. The difference is due to the evaporation of flux in the latter because of higher temperatures. When this correction is applied, the two sets of concentrations agree, but the maximum deviation from the average is smaller with the Fluxy than with the induction-heating instrument.

Oxide	Calculated Concentration (%)			Max. Observed Deviation (%)	
	Fluxy™		Competitor	Fluxy™	Competitor
	Uncorrected *	Corrected	Corrected		
CaO	42.57	43.55	43.57	0.33	0.48
SiO_2	12.03	12.31	12.34	0.11	0.17
Al_2O_3	3.18	3.25	3.30	0.08	0.18
Fe_2O_3	1.48	1.51	1.52	0.04	0.02
MgO	0.92	0.94	0.92	0.01	0.02
K_2O	0.50	0.51	0.52	0.03	0.04

Table 7 : Reproducibility observed on fused glass disks of cement

- uncorrected values were obtained using the calibration for the induction heating unit; a correction of 2.3% is applied to account for flux lost by volatilization in the high frequency induction unit.

As a third example, a customer interested in purchasing a Claisse Fluxer-Bis!™ first tested its reproducibility. He did so by making 16 identical glass disks, four disks at a time on four burners. The observed results, listed in Table 8, include errors due to weighing, flame reproducibility, instrument stability, fusion reproducibility and counting statistics. The glass disks were composed of 0.4g slag, 6g sodium tetraborate, 0.2g $NaNO_3$ and 30mg $NaIO_3$.

Burner	Ca (%)	Si (%)
#1	41.53 ± 0.05	37.22 ± 0.15
#2	41.49 ± 0.06	37.13 ± 0.08
#3	41.54 ± 0.09	37.17 ± 0.09
#4	41.56 ± 0.09	37.17 ± 0.05

Table 8 : Reproducibility test with the Fluxer-Bis!™

3.8.1.2 ACCURACY

On account of their high homogeneity and ideal shape, glass disks meet the requirements of the hypotheses made in the development of X-ray fluorescence emission theory. As a consequence, the application of software packages based on fundamental parameter calculations should yield the most accurate analytical results that XRF analysis can reach. Many such software packages are available commercially.

3.8.1.3 PREPARATION OF STANDARDS

Borate fusions can benefit much from the possibility of making synthetic standards. Pure oxides can be mixed in any desired combinations and proportions to make standards that contain all and only the desired elements [Kodama et al. 1967]. The preparation of glass disks must be the same as for the unknown samples to ensure full reliability of calibration.

Making standards for trace elements is also easy. The preparation is done in two or three steps. A first fusion is made with quantities of oxides large enough to be weighed accurately. Then, an aliquot of this disk is mixed with more flux to make a second disk with much lower concentrations. The procedure can be repeated.

The analyst sometimes has to face the problem of making new standards when he wishes to change the composition of the flux. Fundamental parameter calculations indicate that the total substitution of lithium tetraborate by lithium metaborate in a disk made of 1 part of cement and 5 parts of flux results in an increase of intensity of the K_α line of about 2.5% for Si, 0.5% for Ca, 0.3% for Fe, and less for heavier elements. For lower sample/flux ratios and for more absorbent samples, the change in intensities should be still lower. Consequently, if substitution of flux is made, a simple mathematical correction can be acceptable until new standards are made.

3.8.1.4 VERSATILITY

Although the more reliable method of analysis is using a few standards in combination with a fundamental parameter software package, all the other analytical techniques applicable to powder samples are still applicable to glass disks: internal standard, spiking, double dilution, etc. Since particle size effects are absent in fused disks and since matrix effects are smaller than in powders, the techniques using fusion give better results.

3.8.1.5 COST

The purchase of a fusion apparatus with platinum crucibles and molds may seem expensive, but there are several other aspects to consider when total costs are compared with other techniques:

- ☐ crucibles and molds are consumables but the scrap value should be subtracted from the cost of new pieces; the average net cost of platinum crucible and mold can be less than about US$0.50 per glass disk (1999);
- ☐ the only other consumables are essentially fluxes (6-7g), gas (30g propane) and electricity (5 W-hr); cost is about US$0.50 per sample;
- ☐ installation costs for the Claisse fluxers® are negligible since a fume hood and a propane line are normally already available;
- ☐ no highly skilled personnel is required to operate a fusion instrument after the operating conditions have been set;
- ☐ with an automatic fluxer, the analyst can weigh the next batch of samples while one is being fused;
- ☐ the reliability and success in making disks is high, and samples do not have to be made in duplicate.

3.8.1.6 ENVIRONMENT

The discovery of the borate fusion technique has a significant impact on the environment. This technique is gradually replacing many conventional chemical methods that pollute the air we breathe, the water we drink and the food we eat, on account of the acids and corrosive substances that are used. Oppositely, the fusion technique yields analyses with all the accuracy desired using essentially no harmful product and producing essentially no reject. Numerous laboratories have adopted this new technique and even more do, when they learn that Corporation Scientifique Claisse Inc. makes it easy to introduce that technique in their laboratories.

Indirect effects on the environment are important. The combination of fast fusion and fast XRF analysis makes accurate analysis immediate, resulting in production of goods of constant high quality, savings of raw materials, and reduction of dumps for waste.

3.8.2 Limitations

3.8.2.1 LIMITATIONS ON ELEMENTS

The materials that cannot be processed easily are those that are explosive, radioactive, or poisonous (As, Hg). The elements that cannot be fused are those insoluble in glass (Pt, Ag, Au), or too volatile (Br, I, Se). It is interesting to note that none of them belongs to the usual industrial elements.

3.8.2.2 CONTAMINATION

Contamination essentially comes from the flux, where the impurities appear as if they were present in the sample at a concentration equal to that in the flux multiplied by the dilution factor expressed as flux/sample. In the new Claisse MiniBeads™ fluxes, the impurity concentrations are exceptionally low, and trace elements can be determined accurately without difficulty. With other common fluxes, the problem is important in the analysis of trace elements, particularly because the impurity concentrations vary from batch to batch; then, it is necessary to buy large quantities of a given batch of flux, or to make new calibrations frequently.

Contamination may also arise from polishing the disks after they are made. In this case, the contamination is important because the impurities are on the surface of the specimen and are strongly excited by the incident radiation. It is preferable to polish the molds once in a while rather than polish each glass disk and risk contamination.

3.8.2.3 LOWER X-RAY INTENSITIES

The fact that fusion implies the addition of a flux to the sample means that fluorescence intensities decrease. In borate fusions, the diluent is made of light elements that are highly transparent to X-rays. Consequently, the dilution has little effect on short wavelengths. In the case of light elements such as Mg and Al, the presence of the diluent is more important, but the loss of intensities is still lower than proportionally with the dilution ratio. Figure 13 shows how the X-ray intensity of Fe changes in mixtures of Fe_2O_3 and lithium tetraborate (upper curve), which is typical of a strong absorber (Fe_2O_3) mixed with a light absorber ($Li_2B_4O_7$). The straight line is the Fe intensity that would be observed if it were proportional to the concentration in the mixture. At a higher-than-usual dilution ratio of 9 (i.e. 10% Fe_2O_3), we observe that the intensity of Fe is nearly 50% that of pure solid Fe_2O_3, as compared to only 10% if calculated from dilution. Bourgault et al. [1977] observed that the intensity of Ni (as trace element) was 50% higher only in pellets than in glass disks; the pellets were made by mixing 1g sample with 0.1g wax, and the glass disks were made by fusing 1g sample with 5g lithium tetraborate. That is equivalent to say that "the intensity of Ni in the (diluted) disk is about 65% of the intensity in the undiluted sample".

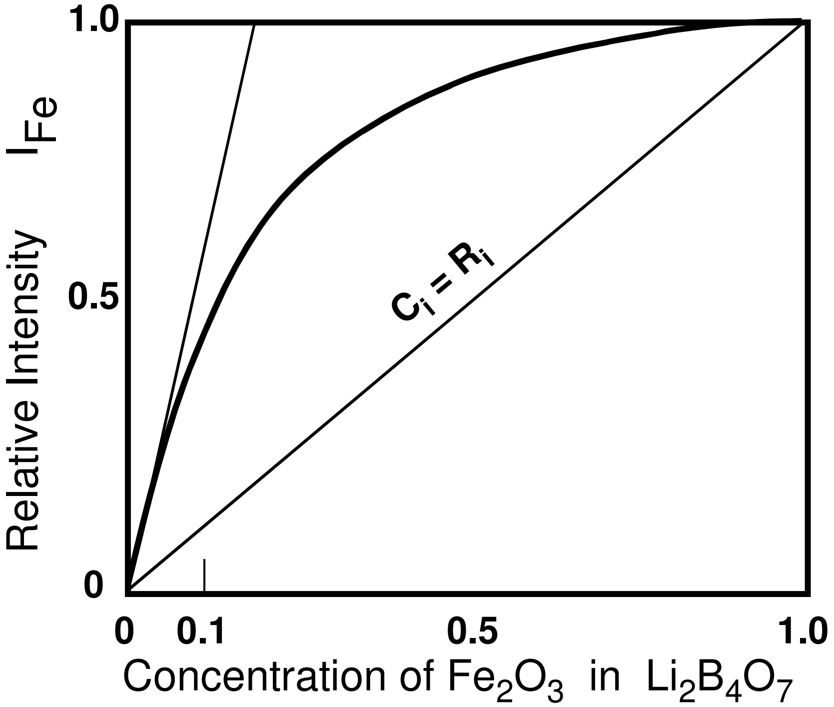

Figure 13 : Effect of dilution on X-ray intensities of Fe after dilution in flux.

3.9 MISCELLANEOUS

3.9.1 Crucible maintenance

3.9.1.1 GLASS RESIDUES

Residues from a previous fusion left in a crucible will contaminate the following fusion. However, the contamination is often so small that it is not necessary to clean the crucible after each fusion, in which case it is better not to remove the crucible from the Fluxer as long as that is possible. Handling crucibles is one of the two efficient ways to shorten the life of a crucible; the other is corrosion.

The amount of contamination brought to a fusion by not cleaning a crucible can be estimated by the following relation:

$$\mathbf{Contamination(\%)} = \frac{\mathbf{m_{residue}}}{\mathbf{m_{total}}} \cdot (\mathbf{C_{sample1}} - \mathbf{C_{sample2}})$$

Equation 1 : Contamination by unclean crucibles

where: $m_{residue}$ is the mass of the glass remaining in the crucible after a fusion

m_{total} is the total mass of glass after a fusion (disk and residue)

$C_{sample1}$ is the concentration of the element in the first sample

$C_{sample2}$ is the concentration of the element in the second sample

Example: a sample with a calculated concentration of 26.35% Fe is fused *after* another that contains 17.84% Fe. The residue in the crucible from the first sample is estimated to be 10 mg; total weight of the fusion is 7.5g.

The contamination is: 10 mg ÷ 7500 mg × (17.84% - 26.35%) = -0.01%

This means that the calculated concentration is 0.01% *too low* and the corrected concentration is 26.36%. Cleaning is obviously not necessary.

3.9.1.2 METAL COATINGS

Metal coatings on platinum crucibles are produced during fusion of samples that contain elements with multiple valences, such as Fe or Cu, when reducing conditions exist. That generally occurs when oxides of those elements are fused with lithium tetraborate. At the optimal flux composition for those elements, 50/50 lithium tetraborate/ metaborate, coatings do not form. Coatings are soluble in dilute nitric acid. Coatings affect analytical accuracy.

3.9.2 Blanks

It is often difficult to make a blank disk from lithium tetraborate, because this material in the pure form crystallizes easily. The addition of just a few milligrams of any non-wetting agent stabilizes the vitreous state.

3.9.3 Storage of glass disks

Most glass disks are somewhat hygroscopic. The worse case is that of disks made with sodium tetraborate; the disks become covered with a layer of white hydrate. Lithium borate fluxes are much less affected by moisture. Whatever the case, analysts do not feel comfortable in analyzing disks that look tarnished. Keeping standards in a dessicator is necessary.

3.9.4 Examination of highly colored disks for homogeneity

Glass disks containing high concentrations of colored elements (Fe, Co, Ni, Mn, etc…) appear opaque and consequently might be considered unsuitable for accurate analysis. In fact, they are probably transparent and homogeneous, but the color is so dark that ordinary light does not go through them. A simple way to verify if those disks contain undissolved particles is using a halogen flashlight, placing a sheet of black paper with a 2-cm diameter hole in it on the flashlight lens, and laying the disk over the hole.

3.10 TROUBLESHOOTING (GLASS DISKS)

The right choice of flux in a fusion is the best assurance that the fusion will be successful. In case of difficulties, calculate the Li_2O content of the "overall flux", which includes the flux itself, and the lithium nitrate or carbonate added; the Li_2O content should be about 24% as in the so-called optimal flux composition, the 50/50 lithium tetraborate/metaborate.

The more frequent problems and their correction are the following.

3.10.1 Cracking of disks

Cracking of disks can be attributed to many factors:

☐ insufficient non-wetting agent; add some before fusion; add before casting if problem continues, particularly with Fe, Cu, Ni... samples;

☐ glass residue or foreign particles in molds;

☐ incompletely dissolved sample;

☐ beginning of crystallization; if small white spots appear during cooling, the flux composition is a little off the optimal composition;

☐ residual graphite from the sample (if small bubbles also are observed on the flat side of the disks);

☐ cooling fans started too early;

☐ air drafts around the molds during cooling;

☐ molds are too cold.

3.10.2 Bursting of disks

Disks with internal stresses sometimes explode spontaneously, usually during handling – and sometimes long after cooling.

☐ Insufficient amount of non-wetting agent;

☐ time of cooling in still air before starting forced cooling is too short;

☐ non-optimal flux composition;

The user can increase the stability of glass by adding a small quantity of SiO_2 or sodium tetraborate in the fusion mixture.

3.10.3 Disks crystallizing slowly during cooling

☐ Check if the composition of the flux is optimal;

☐ molds are too cold for casting: add a conditioning heating step;

☐ flux particles have been projected onto molds; use dust-free flux;
☐ nitrate or carbonate particles have been projected unto the molds; lower heating during oxidation.

If none of the above seems responsible for the consistent devitrification of a disk, clean the mold well; invisible dirt particles in the corner of the mold may induce crystallization; that is characterized by crystals appearing at a constant position in the mold when repeated fusions are made.

3.10.4 Disks crystallizing quickly during cooling

☐ Non-optimal flux composition.

3.10.5 Fusion mixture puffing out of the crucible

This problem is due to moisture, hydrates or carbonates and can be corrected as follows:

☐ Use coarse, dehydrated flux;

☐ carbonates are heated too fast;

☐ do not mix the sample with the flux; spray it on top of the flux.

3.10.6 Black spot floating on melt, apparently insoluble

Graphite is present.

☐ Mix the sample with an oxidizer; put the flux on top;

☐ inject air inside the crucible.

3.10.7 Bubbles continuously forming on the bottom of the crucible

Due to the decomposition of SO_3 (dissolved) into SO_2 (gas).

☐ If sulfates are present, use 50/50 lithium tetraborate/metaborate flux;

☐ if sulfides are present, process like sulfides (see section 3.6.3.).

3.10.8 Bubbles appearing on the surface of the disk

☐ Refer to "black spot floating on melt" above (see section 3.10.6.);

☐ projection of nitrate or carbonate particles on molds during oxidation step: lower heat;

☐ add more non-wetting agent;increase fusion time or fusion temperature if acceptable.

3.11 ANALYTICAL PROCEDURES

This chapter contains analytical procedures that are pertinent to the use of fusion as a sample preparation technique.

3.11.1 Correction for line overlap from elements in the non-wetting agent

Non-wetting agents cannot be avoided completely. A frequent case of line overlap is that of LiBr and other bromides, where the L_α line of Br at 8.37Å overlaps the K_α line of Al at 8.34Å. Since the amount of LiBr added is not usually measured exactly and since the loss of Br depends on several factors such as fusion temperature, fusion time, sample composition etc., a small correction on the Al line might be necessary for each specimen. The correction is always small and variable, because the concentration of residual Br in the glass is always low, but it might become relatively important when the concentration of Al is also low. In the simplest case, the correction procedure described in Lachance-Claisse [1995] is:

1. select an Al-free sample and make a glass disk, using two or three times the usual amount of non-wetting agent;
2. measure the net intensity of the L_α line of Br at the peak position of the Al line at 8.34Å, and the net peak intensity of the L_β line of Br at 8.12Å;
3. calculate the ratio of these two intensities, the L_α line over the L_β line, and keep that value on file;
4. in actual analysis, measure the peak intensity of the L_β line of Br at 8.12Å and multiply it by the above ratio;
5. subtract that value from the peak intensity of the Al line at 8.34 to obtain the correct intensity for Al.

Another alternative that is applicable to overlapping lines that are not too close is as follows, for the same example as above:

1. select an Al-free specimen that contains some Br, and measure the Br net intensities at the peak position of both the Br L_α line at 8.37Å and the Al K_α line at 8.34Å. The ratio of the 8.34Å reading to that of the 8.37Å reading is called "a";
2. select a specimen containing Al and no Br, measure the net intensities at the same two peak positions; the ratio of the 8.37Å intensity to that of the 8.34Å intensity is called "b";
3. then, in an actual analysis when the two lines overlap, the true Al line intensity is given by

$$I_{Al,corrected} = \frac{I_{Al,measured} - a \cdot I_{Br,measured}}{1 - a \cdot b}$$

Equation 2 : Corrected Al intensity

The Br corrected intensity can also be obtained by the same relation, after substitution of "Al" by "Br" and "a" by "b".

3.11.2 Correction for matrix effects

The residual matrix effects after dilution with the flux are small when the dilution is high, but may be rather important when the dilution is low, for example at sample/flux ratios of 1/5 or higher. When the dilution is high, the simple Lachance-Traill algorithm should be sufficient when the concentrations in the unknown and reference specimens do not differ by more than 10%:

$$C_i = R_i\,(1 + \alpha_{ij}C_j + \alpha_{ik}C_k + \ldots)$$

Equation 3 : Lachance-Traill algorithm

where the α coefficients are constants that can be determined theoretically for a specimen with an average composition.

The more accurate Claisse-Quintin algorithm can be used with an accuracy of about 0.5% in fused disks of all compositions:

$$C_i = R_i\,(1 + \alpha_{ij}C_j + \alpha_{ik}C_k + \alpha_{ijj}C_jC_j + \alpha_{ikk}C_kC_k + \alpha_{ijk}C_jC_k + \ldots\ldots)$$

Equation 4 : The Claisse-Quintin algorithm

where the α coefficients are constants that can be determined theoretically.

A better choice is the Lachance algorithm that is applicable to all homogeneous specimens, including non-diluted specimens:

$$C_i = R_i\,(1 + m_{ij}C_j + m_{ik}C_k + \ldots)$$

Equation 5 : The Lachance algorithm

where the m coefficients are variables; they can be determined theoretically for a composition very close to that of the unknown if that composition is first calculated by means of another less accurate algorithm. The final accuracy is the highest that can be reached at the present time.

3.11.3 Correction for loss on ignition (L.O.I. and L.O.F.)

Loss of sample by volatilization changes the total weight of a fusion mixture and yields apparent concentrations that are too high. L.O.F. is the loss of weight during fusion and includes L.O.I. (loss of sample) and loss of flux (alkalis, absorbed water). The following methods apply when there is no gain of weight from oxidation and when loss of flux is the same in the standards and in the unknown samples.

Method 1. If loss on ignition has been measured by heating the sample alone and comparing its weight before and after heating, a correction on concentrations after fusion can be made by using any of the algorithms listed in section 3.11.2. Each of them has a term for L.O.I.; the correction is calculated in the same way as for elements. As a matter of fact, L.O.I. can be considered as an element with a zero absorption coefficient. When all the elements are included in the summation, the result of the analysis totals 100% including the L.O.I. concentration.

Method 2. If L.O.I. is known, a slightly larger quantity of sample can be used in the fusion; the quantity must be such that the sample weight after fusion will be equal to the nominal weight of sample with no L.O.I. Then, the sum of concentrations of all the elements will add to 100%, which does not include L.O.I.

Method 3. If L.O.I. is unknown, one procedure is to fuse with the nominal weight of sample. In the first calculations, a value of zero is assumed for the concentration of L.O.I., leading to a sum of concentrations of elements lower than 100%. The difference with 100% is a first approximation of the L.O.I. concentration. A second calculation using that first value of L.O.I. in the algorithm will lead to a better sum of concentrations and a better approximation of L.O.I. Repeated calculations (iteration) will eventually lead to stable values for the concentrations of elements and L.O.I.

Method 4. If L.O.I. is unknown, and the nominal sample weight is used in fusion, it is possible to apply a variant of any of the algorithms referred to in Method 1. In such variants, the term for L.O.I. is combined with the other terms so that each α or m coefficient takes a new value. The result of the calculations is now the concentration of each element in the original sample before L.O.I.. Refer to Lachance and Claisse [1995] for details.

3.11.4 Correction for gain on ignition (G.O.I.)

Gain on Ignition usually results from the oxidation of elements, particularly sulfides in which both elements oxidize. Gain on ignition cannot be taken as negative L.O.I.. In the case of G.O.I., when

L.O.I. is zero, the calculations are similar to L.O.I. except that the α or m coefficient values are different. Refer to Lachance and Claisse [1995] for details.

3.11.5 Correction for L.O.I. and G.O.I. together

That is the most complex case. When L.O.I. and G.O.I. are present together and relate to several compounds, the total change of weight during fusion has no meaning, because the effect of L.O.I. and G.O.I. are of opposite sign but are not simply additive. For example, in the determination of L.O.I. by heating the sample in air or oxygen, sulfur is partially lost as SO_2, but after fusion, sulfur can be anywhere between totally lost and totally retained.

To make exact corrections, one must know the compounds that lose weight (for example, $CaCO_3$ becomes CaO) and those that gain weight (for example, ZnS becomes $ZnSO_4$). A method of calculation using modified influence coefficients [Lachance and Claisse, 1995] is available and leads to the concentration of each compound originally present in the sample before fusion. The calculations are rather complex, though. A new algorithm for matrix corrections [Claisse 1998] is able to solve that problem of simultaneous L.O.I. and G.O.I. in a simple and direct way without using influence coefficients; the software is in development.

4 PART II

PREPARATION OF SOLUTIONS

The preparation of solutions for use in analysis by AA, ICP or wet chemistry can be done in a manner similar to that for glass disks described in Part I of this book. The reader is referred to Part I as a prerequisite for this additional application. What follows are only the differences with the procedures for making glass disks; for easier reference, the Chapter number for a given subject is the same in both Part I and Part II.

4.1 GENERAL

4.1.1 Typical simplified fusion procedure

Essentially, a fusion procedure to make solutions consists in:

1. heating a mixture of sample, flux and non-wetting agent until the flux melts;
2. continuing heating until the sample is completely dissolved in the molten flux, and agitating to mix the melt;
3. pouring the hot molten glass into a diluted acid in such a way that the glass shatters into small flakes;
4. mixing the particles in the acid until they are dissolved.

4.1.2 Features of the procedure

The main features of the borate fusion for solutions are:

1. quick reaction in the range of 1 or 2 minutes only, due to high temperatures;
2. production of a molten glass that does not stick to the crucible;
3. complete transfer of the molten glass from the crucible to a solvent, leaving no residue in the crucible;
4. applicable to oxides, sulfides and metals;
5. simple, fully automatic procedure that includes oxidation (in case of non-oxidized materials), fusion, transfer into a solvent and dissolution;
6. silica is soluble in borate solutions;
7. synthetic standards of any composition can be prepared from pure chemicals.

4.2 TOOLS FOR FUSION

4.2.1 Crucibles

Like for glass disks, platinum-5% gold alloy is the best material for crucibles; it is probably the only satisfactory material to use for the preparation of solutions.

A mirror-polished crucible is rather non-wetted by the molten glass, which is a necessity for making solutions, because complete transfer of the melt into the acid is a must. If a fusion apparatus is used, the crucibles must he held safely in their holders and Claisse™ crucibles or equivalent (Figure 1) are necessary. With all fusion instruments, Bis!™ crucibles – Claisse crucibles with a mixing-enhancing hump in the bottom (Figure 2) – enhance mixing and ensure homogeneity of the melt in a short time by forcing the molten glass to flow around and over the hump (Figure 9), thus producing strong convection currents. Bis!™ crucibles made of all kinds of materials can be obtained from Corporation Scientifique Claisse Inc. and distributors.

The crucibles should never need cleaning between fusions; if they do, the transfer into the solvent (acid) was not complete, and thus, quantitative analyses can not be accurate. The probable cause for residues left in crucibles is insufficient amount or excessive loss of non-wetting agent.

4.2.2 Fusion instruments

4.2.2.1 THE CLAISSE FLUXER-BIS!™ FOR SOLUTIONS

This instrument is the same as that for making glass disks except that it has the following additional parts: beakers for acids and magnetic agitators for dissolution. Note that unbreakable Teflon beakers are included with the Claisse fluxers® designed for solutions.

The main features of the instrument are:

- ☐ simultaneous processing of 1 to 6 specimens;
- ☐ seven programs adaptable to all kinds of fusion; each program has up to seven heating steps, one pouring step and one stirring step for solutions;
- ☐ programmable heat settings (100 levels), agitation (100 levels) and time (up to 100 minutes, set by the second);
- ☐ needs propane only; oxygen is taken from the surroundings;
- ☐ stable gas flow, independent of the number of burners used;
- ☐ very low temperatures obtainable for oxidation;
- ☐ rather uniform top to bottom temperature of crucibles;

4.2.2.2 THE CLAISSE FLUXY™ FOR SOLUTIONS

Like for the Fluxer-Bis!™, this smaller instrument is a standard Claisse Fluxy™ with the same kind of additional accessories for making solutions, that is, unbreakable beakers and a magnetic agitation plate.

4.2.2.3 THE CLAISSE M4 FLUXER™ FOR SOLUTIONS

Identical to the standard M4™, this fluxer comes equipped with the Teflon beakers, stirring bars and the magnetic stirring plate. The computer can also be used when preparing solutions.

4.2.2.4 THE CLAISSE PEROXIDE™ FLUXER

Built from a Fluxer-Bis! ™ frame, the Claisse Peroxide™ fluxer is specially designed to prepare 1 to 6 solutions only. Unlike the other fluxers, the Claisse! Peroxide™ fluxer does not accommodate borate fusions. It is specially built to make sodium peroxide, sodium carbonate, sodium metaphosphate and potassium pyrosulfate fusions. These reagents, having lower melting points than borates, are fused in Zirconium crucibles. The back and forth rocking motion assures a fast and efficient fusion thus replacing long and tedious acid and microwave digestions.

The Claisse Peroxide™ fluxer presents the following characteristics:

- ☐ six modified Fisher Burners;
- ☐ two fusion programs; a shorter one when five grams of flux are used and a longer one when 10 grams of flux are used;
- ☐ all parameters can be modified: heating, cooling, gas flow, mixing speed and amplitude;

The automatic operation of the Claisse Peroxide™ fluxer is very similar to that of the Fluxer-Bis!™. The Zirconium crucibles are agitated in a back and forth rocking motion until everything has melted. Once the fusion is complete, the crucibles are cooled by means of fans. Once cooled to room temperature, manually remove the crucible from the clips and dunk it in a predetermined volume of diluted acid for subsequent dilutions and analyses by AA or ICP spectrometry.

4.3 FUSION COMPONENTS

4.3.1 Fluxes

All lithium and sodium borate fluxes are acceptable to prepare solutions but lithium metaborate is the best on account of the higher solubility of most oxides, its tendency to crystallize faster during cooling, and consequent facility to dissolve.

4.3.2 Physical properties of fluxes

The MiniBeads™ fluxes supplied by Corporation Scientifique Claisse Inc. are recommended for their exceptional high purity, ease of handling, no water content and total absence of dust. Refer to section 3.3.3 in Part I.

4.3.3 Additives

The only additives to flux that might be necessary in the preparation of solutions are oxidizers that are required when sulfides or metals are present, particularly when the concentration of sulfur must be determined. Alkali nitrates are excellent oxidizers for sulfides, and alkali carbonates for metals.

4.3.4 Non-wetting (or releasing) agents

When preparing solutions, a complete transfer of the fused sample from the crucible into the solvent is imperative; no residue must remain in the crucible. The use of a non-wetting agent is essential. Iodine and bromine are the only two elements that are known to be efficient for that purpose. They are added into the mixture before the fusion, usually in the form of one of their salts, for example, NaBr, LiBr, KI, LiI, CsI, etc.

Usually, these salts are added in the crucible with the mixture to fuse in a quantity of about 100mg for a fusion mixture not exceeding 2 grams. Most iodine has left the melt after a normal fusion (Figure 5), but the quantity that remains is sufficient to ensure a complete transfer of the melt into the beaker. Bromine is slightly less efficient than iodine, but it volatilizes at a slower rate.

4.3.5 Solvents

The selection of solvent depends on the elements in the sample. Usually, nitric and hydrochloric acids are used. The latter has been reported to be better than nitric acid when the major element of the sample is Fe. Usual concentrations are 4 to 10%. When solutions containing silica are not analyzed immediately after having been prepared, a stabilizer is sometimes required to prevent eventual silica precipitation. In these cases, the perfect solvent is made from 10% nitric and 0,5% hydrochloric acid.

4.4 PREPARATION OF THE FUSION MIXTURE

The following procedure applies to fully oxidized specimens only; differences in procedures for other materials will be considered in chapter 4.6.

1. Take a representative sample of the material to analyze. To ensure representativity, the material should be finely ground. Since borate fusion is a dissolution, the finer the particles the faster the fusion grinding to < 200 mesh (<75 µm) or finer is recommended.
2. Determine a convenient sample/flux weight ratio, taking into consideration the following facts:

- ☐ any impurity in the flux looks as belonging to the sample at a concentration equal to its concentration in the flux multiplied by the ratio of flux to sample. As an example, an impurity of about 50 PPM in the flux is equivalent to 0.02% in the sample if the ratio is 5/1.
- ☐ there is a limit to the quantity of a given sample that can be dissolved in a given flux; in a first test, a convenient sample/flux ratio to start with is 1/10; in subsequent fusions, it can be increased to 1/5 or even 1/2 for some materials. In a few cases when the dissolution into the flux appeared to be incomplete, it was observed that the particles were fine enough to eventually dissolve in the acid solvent; that may not be the general behavior, though. Table 1 in Part I lists typical sample-flux ratios for some materials; those ratios can be increased by a factor of about 1.5 when solutions are made using lithium metaborate as flux.
- ☐ the total weight of sample and flux should be about 1.5 to 2 grams. A weight larger than about 2.5g is not recommended because the large amount of heat that is brought into the solvent on pouring might be excessive and cause a violent reaction in the beaker, with possible spilling of the acid solution in the instrument.

3. Weigh the sample to the nearest milligram or better. Accuracy on the weight of flux is less critical.
4. Transfer the mixture to fuse into a crucible on the fusion instrument.
5. Add about 100 mg of a non-wetting agent (iodide or bromide of lithium, sodium). This can be added on top of the mixture to fuse, as crystals or as an aqueous solution. Accurate weighing is necessary only if these elements have a significant effect on the analytes. This quantity of non-wetting agent is a large excess so as to make sure that the total quantity of molten glass will pour into the beaker as a single drop of glass, and that no residue remains in the crucible. Thus, the analytical accuracy is assured and the crucibles will never need to be removed from the instrument for cleaning.
6. Pour about 100 ml of an acid solution (for example, 10% concentrated nitric acid and 90% water) and put a magnetic bar (Spinbar™) into the beakers on the Fluxer.
7. Start the automatic fusion process.

Perfect homogenization of the melt is not important in the preparation of solutions, since the whole fused material will transfer into the solvent and no residue will be lost in the crucible. As soon as the sample/flux mixture has completely melted, it is ready to pour.

4.5 BORATE FUSION PROCEDURE

A standard borate fusion process for solutions consists in three operations: melting the sample/flux mixture, pouring the molten glass into an acid solvent and dissolution of the glass particles in the solvent.

4.5.1 Melting the fusion mixture

Small amounts of material in a crucible heat faster and reach higher temperatures than larger amounts such as the ones used to make glass disks. For that reason, heating the fusion mixture should start at low temperature without agitation, so that none of the particle is projected onto the wall of the crucible. Refer to section 3.5.1 of Part **I**, for additional details on heating.

4.5.2 Pouring

When the fusion is complete, the hot fused glass is poured into a beaker containing an acid originally at room temperature when the fusion process started. Just before pouring, it is a good practice to adjust the temperature of the glass to an optimal value estimated to be about 200°C lower than the fusion temperature; a pre-casting step is programmable in the Claisse fluxers® to lower the temperature before pouring. At the optimal temperature, the hot drop of liquid glass shatters into fine flakes of glass when it comes in contact with the colder solvent. If the temperature of the liquid glass is too high, a layer of water vapor forms around the drop of glass and prevents it from cooling fast; then the drop keeps its shape and sinks to the bottom of the beaker where it may stick and slightly damage the beaker. It is absolutely necessary to have the solvent in motion before pouring so that any contact between the molten glass and the beaker is short. This condition is met in the Fluxer-Bis!™ , Fluxy™ and M4 fluxer™ in the automatic mode. Teflon™ beakers, like the ones included with Claisse® fluxers, stand thermal shocks much better than glass beakers.

4.5.3 Dissolution

Dissolution of the glass flakes takes place when the latter are agitated in the acid solvent. Typical time for dissolution is generally about 3 to 5 minutes. The conditions that influence the rate of dissolution are:

- ☐ the size of glass particles: as mentioned in the preceding paragraph, the size of the glass flakes depends on the temperature of the molten glass at time of pouring. It also depends on the temperature of the solvent. When these two temperatures are not correct and the glass drop does not shatter when it comes in contact with the solvent, then it may take hours before the glass dissolves. There is a maximum temperature of the solvent above which no flakes are formed (Figure 14). The radiation from the burners during fusion increases the temperature of the solvent during a normal fusion, but usually not to a level at which the glass will not shatter, so that one can use a solvent stored at room temperature. On the other hand, if the solvent has been cooled before fusion is started, the dissolution rate obviously might be slow.

- ☐ the concentration of acid in the solvent (Figure 15); at less than 3 or 4% nitric acid in water, the dissolution is very slow; at 6 to 10%, it can be as short as 2 to 5 minutes.

- ☐ the agitation of the solvent; in the Claisse Fluxers®, the solvent is kept swirling by means of magnetic bars (Spinbar™) in the beakers in combination with magnetic coils under the beakers' tray.

- ☐ the solubility of the material in acid (Figure 15); after the concentration in the solvent has reached a certain level (saturation), the dissolution stops whatever the time or the agitation.

When the dissolution is complete, the solution is ready for dilution and analysis. It contains all the atoms in the original solid specimen except the few that are volatile at the fusion temperatures such as Hg, Br, I, etc.

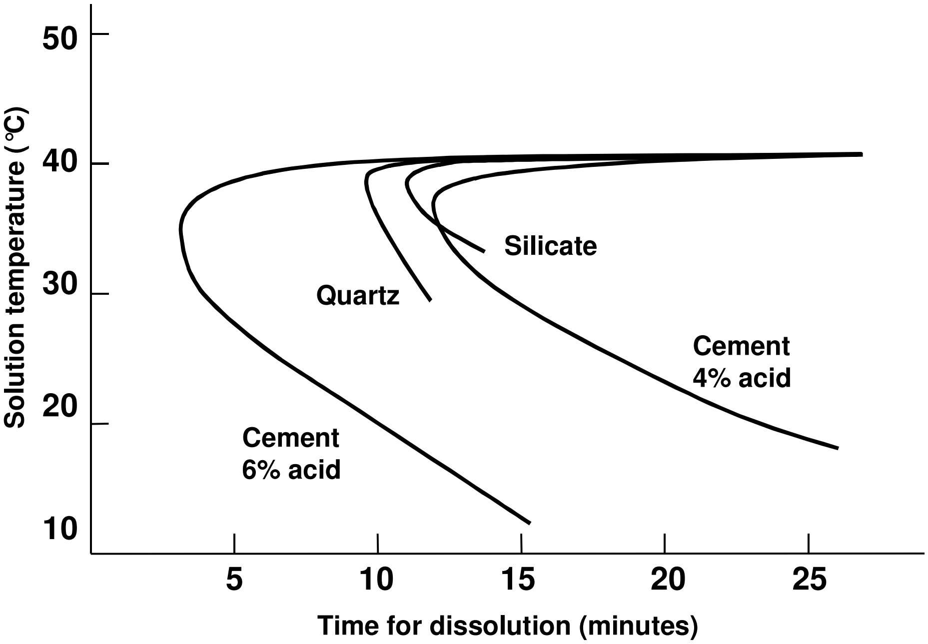

Figure 14 : Absence of shattering when glass is quenched in acid above 40ºC

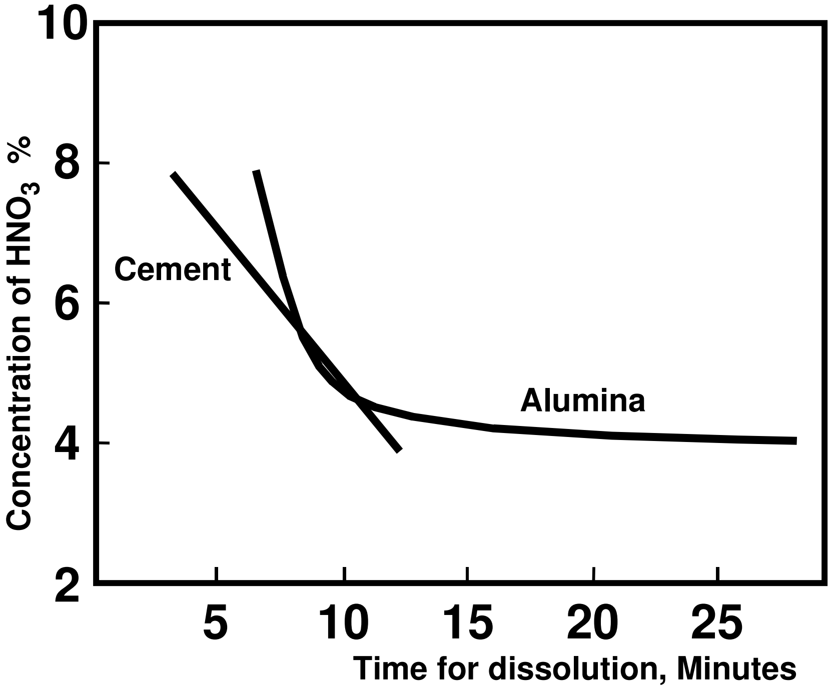

Figure 15 : Incomplete dissolution of alumina in 4% nitric acid

4.6 TYPICAL EXAMPLES OF BORATE FUSIONS FOR SOLUTIONS

As mentioned before, only oxides can be dissolved in molten borates. All other compounds must be oxidized prior to fusion. Ideally, the oxidation and the fusion operations should be combined in a single procedure. The following examples include specimens that require particular treatments, the so-called special cases: sulfides, graphite-bearing materials, metallic materials, copper-bearing samples and organic materials.

4.6.1 Oxides

The following procedure is applicable to all compounds that contain metallic ions and oxygen only, such as silicates, cements, refractories, glasses, to name only a few.

1. Mix together about 0.2g of finely ground sample and lithium metaborate to make a total of about 1.5g; do not exceed 2.5g. The sample weight can be increased after observing that the solubility is higher than estimated. Add about 100 mg of a non-wetting agent. Load the mixture into a crucible on the Claisse fluxer®.
2. Start the automatic program previously set at the following conditions:

Function	F:	0	1	2	3	4	5	6	7	8	9
Agit. speed	S:	---	5	10	30	40	50	15	---	---	---
Gas	G:	15	10	20	25	30	35	20	25	---	---
Time	T:	0005	0000	0010	0030	0100	0200	0005	0001	0200	0300

Table 9: Typical fusion program for the preparation of solutions by borate fusion

4.6.2 Sulfide minerals and concentrates

The method is the same as for oxides except for the following: mix together about 0.2g sample, 1g lithium or sodium nitrate, 1.5 to 2g lithium metaborate and 100 mg non-wetting agent; load that mixture into the crucible. Do a first heating step at the lowest temperature possible for about 1 minute, and then continue with step 1 as in section 4.6.1.

If problems arise from the decomposition of the nitrate and the process is found unpractical, an alternative is to make a normal glass disk first, using the regular fusion procedure for sulfides; then taking a 2-g aliquot of the disk (do not grind) and 100 mg of non-wetting agent, start the fusion program as if making a solution from oxides.

4.6.3 Metals and alloys

Refer to section 3.6.4 of Part I. The aliquot technique described for dissolution of sulfides in section 4.6.2 above should work with metals also.

4.6.4 Copper-bearing specimens

Fusions that contain copper strongly tend to stick to crucibles. LiBr as non-wetting agent has been found to prevent copper glasses to stick, usually without losing copper by evaporation. If a problem of copper loss arises, the non-wetting agent may be added about 2 to 5 seconds only before pouring, but LiBr is difficult to add as a solid because it is very deliquescent. NaBr can be used instead.

4.6.5 Graphite-bearing materials

Refer to section 3.6.6 of Part I.

4.6.6 Organic materials

Examples of fusion of organic materials in borates are difficult to find, but a customer who analyses polymers is known. The fusion mixture contains 5g specimen, 0.5g lithium tetraborate and 0.5g lithium metaborate. The operating conditions are: a period of heating at very low temperature for ashing the organic matter, followed by normal fusion, pouring in 10% HCl solvent. The process is done with a Claisse M4™ fluxer. The user claims that the analytical accuracy is better than with their previous manual technique. Claisse has also made a few successful fusion trials from paper and leaf samples. Further researches must be done on these applications before developing a typical fusion procedure.

4.7 TYPICAL EXAMPLES OF PEROXIDE FUSIONS

Highly refractory compounds such as chromite, magnetite, ilmenite, rutile, silicon and silicon carbide are difficult to process even with borate fusions. Sodium peroxide, sodium carbonate and potassium pyrosulfate can easily and quickly fuse these samples. They can also easily process materials with high sulfide content and noble metals. The lower melting temperatures of these fluxes insure the retention of volatile elements. A typical fusion lasts five minutes when the mixture weighs five grams. A ten grams content fuses in about 10 minutes. The fusion program is very simple and all its parameters can easily be modified.

For example, you mix 0,5 grams of a chromite sample with 5 grams of sodium peroxide and fuse with the following fusion program on the Claisse Peroxide fluxer:

Function	F:	0	1	2	3	4
Agit. speed	S:	---	02	10	30	30
Gas	G:	08	04	07	10	06
Time	T:	0005	0100	0200	0020	0100

Table 10: Typical peroxide fusion program for a chromite sample

4.8 CARE OF PLATINUM CRUCIBLES

The main requirement in making solutions by borate fusion is that the molten contents of the crucible must be completely transferred from the crucible into the solvent. Consequently, crucibles should be kept polished, and should not need to be cleaned. If cleaning is occasionally needed, refer to section 3.7.1 of Part I.

4.9 ADVANTAGES AND LIMITATIONS OF BORATE FUSION

4.9.1 Productivity

The main advantage of the borate fusion technique in the preparation of solutions is productivity. The total time for fusion and dissolution varies between 3 and 5 minutes generally, depending on sample-flux ratio, acidity of the solvent and temperature of the melt at time of pouring. Taking into consideration that Claisse fluxers® process 3 or 6 samples at a time, and assuming that the time to load the crucibles and to pick up the solutions is about 2 minutes per batch, the productivity can easily reach 25 samples per hour. Close to 90 samples per hour can be made with a Fluxer-Bis!™ combined with a separate accessory for dissolution (supplied by Corporation Scientifique Claisse Inc.). These figures compare advantageously with acid digestion that takes several hours.

4.9.2 Preparation of standards

Borate fusions benefit from the possibility of making synthetic standards. Pure oxides can be mixed in any combinations and proportions to make standards that contain all the required elements and none of those that are not desired. Their preparation as solutions must be the same as for the unknown samples.

4.9.3 Environment

Borate fusion is one of the cleanest techniques for the preparation of solutions: no use of corrosive gas, no waste materials accumulated, and acid is used as solvent only. The only undesirable product is NO_2 gas when sulfides and metallics are processed, but the quantities are very small.

4.9.4 Cost

Despite the higher cost of Claisse fluxers® as compared to glassware, the average cost per analysis is lower when cost of materials and labor are taken into account. Cost of platinum crucible is approximately 15 cents US per sample and cost of flux is about 20 cents US per sample. Refer to section 3.8.1.5 of Part I for more details on costs.

4.10 ADVANTAGES AND LIMITATIONS OF PEROXIDE FUSION

4.10.1 Productivity

When compared to acid and microwave digestions, it is easy to notice that significant time saved. When using the shorter program, 60 solutions can be prepared within one hour while 40 can be prepared in one hour when using the longer program.

4.10.2 Simplicity

The entire fusion process takes only one step, microwave and acid digestions require several steps and an array of different acids thus reducing acid impurities and risks of losing volatile elements.

4.10.3 Cost

Even though the Claisse Peroxide fluxer may be of higher cost than a microwave bomb or simple glassware, in the long run, its cost per analysis is much lower when the value of material and labor are taken into account.

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