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A COMPARISON OF **WEIGHING METHODS** PRIOR TO FUSION

Preparing iron samples for XRF analysis

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Introduction

Major investments are often made in state-of-the-art XRF equipment without knowing that the whole analytical chain, including the weighing step in sample preparation prior to fusion, is of crucial importance to get precise and accurate analytical results and consequently obtain estimated financial pay-offs. In fact, precision and accuracy of results enable the manufacturer to decrease the level of uncertainty associated with the concentrations of its products, and therefore avoid huge losses in revenue.

The weighing step in sample preparation by fusion for XRF analysis is all about knowing the exact weights of the sample and the flux (sample-to-flux ratio). Consequently, the weighing method, the tolerance accepted as well as the analytical method to obtain this ratio will affect the quality of analytical results given by the spectrometer.

There are many ways to weigh the sample and the flux prior to fusion:

- Manual weighing (most widespread technique)
- Automated weighing (with Claisse® LeDoser™ or LeDoser-12™ for example)
- Weighing the sample and the flux directly in the platinum (Pt) crucible
- Weighing the sample or the flux in another container, reusable or not, before transferring it into the Pt crucible
- Pre-weighed flux vials
- Weight correction on the XRF instrument (exact weight needs to be known)

All these weighing methods affect the precision of the sample-to-flux ratio and consequently impact the final analytical results. The description of each weighing methods tested in this study is found in ***Table 1*** with the corresponding abbreviation used in the text . In this application note, the effect of the different weighing methods on the precision (RSD) of the obtained XRF results are compared.

Instrumentation

LeDoser and LeDoser-12 automatic instruments were used to perform the weighing step with high precision prior to fusion (when applicable). The different modes on both dispensing balances allow fast and accurate weighing, thus facilitating sample preparation before the fusion step.

LeNeo® fusion instrument was used to create 40 mm lithium borate glass disks. Its resistance-based electric system, excellent insulation properties and preset fusion programs allow uniform heating, thus providing repeatable fusion conditions as well as excellent retention of volatile elements. The same mold was used throughout the whole sample preparation process to eliminate potential sources of error induced by the mold surface in XRF analysis.

A PANalytical 4 kW WDXRF spectrometer with a 37 mm collimator mask was used to analyse the glass disks.

LeDoser-12™ is a 12-position dispensing balance that makes a huge difference in the preparation of samples for XRF analysis. In fact, this instrument saves tremendous labor time and costs since it weighs samples and dispenses borate flux automatically while leading to highly repeatable results.

LeDoser™ instrument is more than a weighing device: it is an essential instrument to achieve constant, on-target results and efficient laboratory management. It is specifically designed to weigh and dispense borate flux with high precision for the preparation of glass disks for XRF and solutions for ICP.

Table 1. Description of the different weighing methods

Test name	Abbreviation	Description	Flux tolerance (g)	Sample tolerance (g)	No XRF correction	XRF correction (sample and flux)
Claisse pre-weighed	PW1	Sample weighed in a Pt crucible (lab balance) Claisse pre-weighed flux used directly in a Pt crucible	0.02	0.045	✓	✓
LeDoser catch weight 1*	D_CW1	Sample weighed in a Pt crucible (lab balance); Automatic flux weighing by LeDoser in a Pt crucible	0.02	0.045	✓	✓
Manual 1	Manu 1	Sample weighed in a Pt crucible (lab balance); Flux weighed in a Pt crucible (lab balance)	0.02	0.045	✓	✓
Manual 4	Manu 4	Sample weighed in a Pt crucible (lab balance); Flux weighed in a Pt crucible (lab balance)	0.0003	0.0001	✓	
LeDoser ratio 1**	D_R1	Sample weighed in a Pt crucible (lab balance); Automatic flux weighing by LeDoser in a Pt crucible	0.02	N/A***	✓	
LeDoser ratio 2**	D_R2	Sample weighed in a Pt crucible (lab balance); Automatic flux weighing by LeDoser in a Pt crucible	0.01	N/A***	✓	
LeDoser ratio 3**	D_R3	Sample weighed in a Pt crucible (lab balance); Automatic flux weighing by LeDoser in a Pt crucible	0.005	N/A***	✓	
LeDoser ratio 4**	D_R4	Sample weighed in a Pt crucible (lab balance); Automatic flux weighing by LeDoser in a Pt crucible	0.001	N/A***	✓	
Plastic container	PC1	Sample weighed in a plastic container (lab balance); Flux weighed in a plastic container (lab balance); Transferred into a Pt crucible	0.02	N/A***	✓	
LeDoser-12 ratio 4 scooping¥	D12_R4S	Sample scooped into a Pt crucible; Automatic flux weighing by LeDoser-12 in a Pt crucible	0.001	N/A***	✓	
LeDoser-12 ratio 4 metal container**¥¥	D12_R4MC	Sample weighed in a metal container (lab balance); Automatic flux weighing by LeDoser-12 in a metal container; Transferred into a Pt crucible	0.001	N/A***	✓	
LeDoser-12 ratio 4 plastic container**¥¥	D12_R4PC	Sample weighed in a plastic container (lab balance); Automatic flux weighing by LeDoser-12 into a plastic container; Transferred into a Pt crucible	0.001	N/A***	✓	

** The catch weight mode on LeDoser and LeDoser-12 records the weight of sample and flux in the Pt crucible. The flux is dispensed according to the tolerance required by the operator when setting up the method.*

*** The ratio mode on LeDoser and LeDoser-12 records the weight of sample and flux in the Pt crucible. The flux is dispensed according to the sample/flux ratio required by the operator when setting up the method. The tolerance on the flux is determined by the operator.*

**** Since the ratio mode is selected with the automatic weighing instrument (LeDoser, LeDoser-12), no tolerance is required for the sample. The instruments calculate the amount of flux to be dispensed to obtain a constant ratio.*

¥ A volumetic spoon is used.

¥¥ The plastic and metal container used with LeDoser-12 were coated to reduce static.

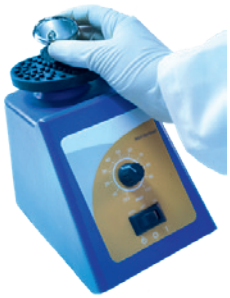
Global Sample Preparation and Analysis

One (1) certified reference material (CRM), ECRM 683-1 (see ***Table 2*** for composition (major oxides only)) was used throughout all experiments. The sample was prepared using a 1/10.3 dilution ratio with a LiT/LiM 50/50 pre-fused flux, pure grade (99.98+%). The flux was weighed using various methods with different levels of precision (see ***Table 1***). The sample was mixed with a VortexMixer™ agitator.

Table 2. ECRM 683-1(>2%)

Fe_2O_3 (%)	SiO_2 (%)	Al_2O_3 (%)	CaO (%)
Fe	0.06	0.01	7.98

Claisse Accurate Total Solution (CATS™) iron ore fusion procedure was used to fuse the samples. The fusion procedure was performed without an oxidizer in order to really focus on the impact of weighing. Once the sample was dissolved in the molten borate flux, it was automatically poured into a 40 mm Pt/Au mold. Each weighing method was used to produce twenty (20) glass disks. Each glass disk was analysed three (3) times with the XRF instrument. An average of each reading was calculated to reduce the XRF instrumental error. A global average was then calculated on twenty (20) averages. The RSD of the global average was used in this comparison.



Results and Discussion

1. Impact of the tolerance during the weighing

The first important factor to consider when developing a sample preparation methodology in fusion (or in any other sample preparation technique) is the accepted tolerance when it comes to weigh the sample, flux, additive, etc. As shown in ***Figure 1***, the tolerance accepted during weighing directly affects the precision obtained during the analysis by XRF. The methods with high tolerance (PW1, D_CW1 and Manu 1) give the highest RSDs for the major elements compared to the methods that require a much tighter tolerance during the sample preparation (Manu 4, D_R4). This can be explained by a much smaller variation in the sample-to-flux ratio in the final disks which has a direct impact on the precision of results.

The effect of the tolerance when using an automatic weighing instrument (LeDoser, LeDoser-12) in ratio mode is shown in ***Figure 2***. As demonstrated in the high tolerance methods (PW1, D_CW1 and Manu 1), a high tolerance on the flux leads to a high RSD. In fact, the obtained RSDs follow the trend of the tolerance accepted on the flux during the sample preparation which is D_R1 ≥ D_R2 ≥ D_R3 ≥ D_R4. It is simple to explain the results observed since the ratio mode on LeDoser or LeDoser-12 calculates the exact amount of flux required to be dispensed in order to keep a constant ratio according to the weight of the sample actually weighed by the operator. The results are comparable to or even better than the manual weighing method with the highest precision (Manu 4) since the ratio is kept constant by the automatic instrument. The capacity to calculate the exact amount of flux required also explains the high precision obtained with the scooping method (with a volumetric spoon) (D12_R4S). In this case, the weighing device dispenses the amount of flux needed according to the weight of sample transferred into the Pt crucible. Furthermore, even if scooping can induce errors during the transfer (the amount of sample transferred into the Pt crucible can vary), Claisse automatic weighing instruments allow an easy control and traceability on the sample-to-flux ratio.

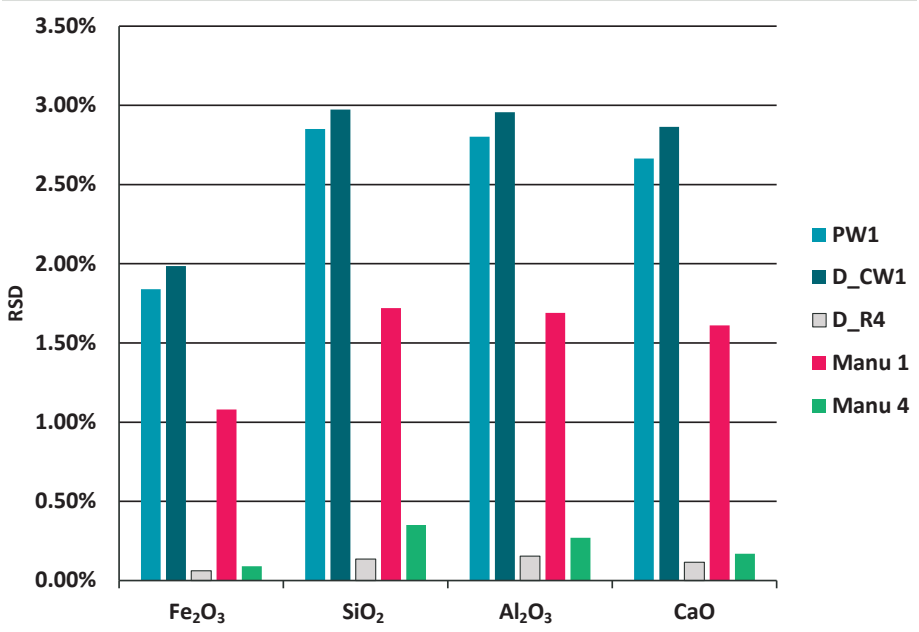


Figure 1. RSD (%) on major elements by XRF analysis of ECRM 683-1 (iron ore) prepared by LeNeo fusion instrument using different weighing methods.

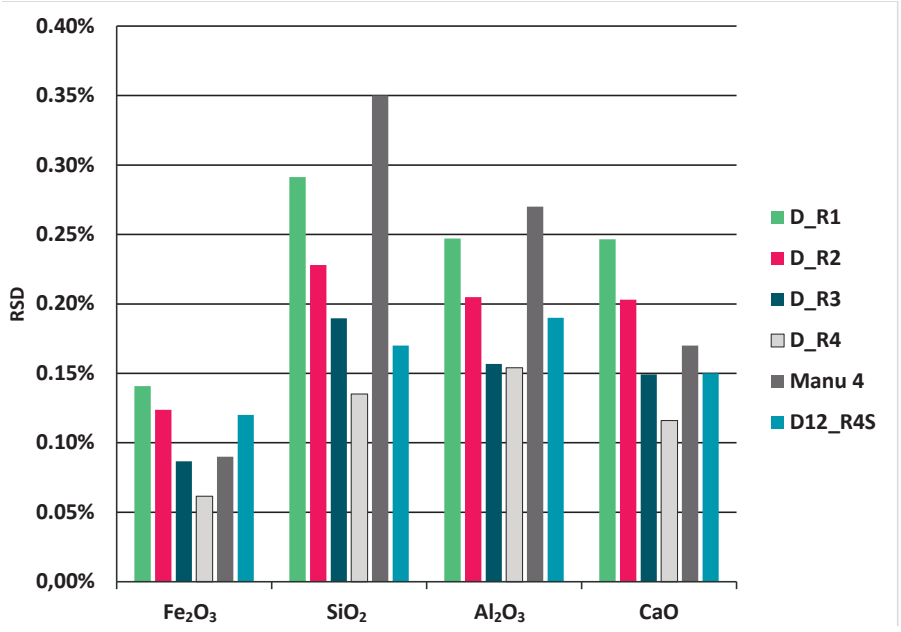


Figure 2. RSD (%) on major elements by XRF analysis of ECRM 683-1 (iron ore) prepared by LeNeo fusion instrument using different weighing methods.

2. Impact of the correction by the XRF instrument

It has been determined that the tolerance of the weighing influences the quality of results. However, Malvern Panalytical XRF instruments allow the operator to correct for the real weight used during the production of glass disks. Obviously, to do so, the exact weights used during sample preparation must be known and the traceability of the data is essential. As shown in ***Figure 3***, the precision obtained in the results is significantly improved after weight correction by the XRF instrument for PW1, D_CW1 and Manu 1 weighing methods (more than 20 times better for iron oxide). Indeed, the RSDs obtained after correction (PW1(corr.), D_CW1 (corr.) and Manu 1 (corr.)) are comparable to the method with the tightest tolerance for the weighing during the sample preparation (D_R4 and Manu 4). Entering the exact weights in the XRF instrument before

the analysis allows the XRF instrument to correct the ratio for each disk and have a much higher tolerance on the weighing during the sample preparation. However, as mentioned previously, a good traceability is essential to achieve this. Automatic instruments such as LeDoser and LeDoser-12 used in catch weight or ratio mode (D_CW1, D_R1 to 4) allow easy traceability since they will save each weight used for the sample and flux for each disk. It is still possible to have good traceability with manual methods (PW1 and Manu 1), but the risk of human errors is increased. That risk is much lower with an automatic weighing instrument that can be connected to a spectrometer with a Laboratory Information Management System (LIMS ready).

3. Impact of the transfer

Another widely used method for sample preparation by fusion consists of pre-mixing the sample and the flux in a container (reusable or not) before transferring the mix into the Pt crucible. However, as shown in ***Figure 4***, the methods including a transfer (PC1, D12_R4MC and D12_R4PC) increase the RSD of the XRF analysis. The method that leads to the worst RSD is the one that consists of mixing the sample and the flux in a plastic container before the fusion (PC1). In each of these methods, a part of sample or flux is lost either because of static (particularly true for PC1 method) or simply because not all the mix was transferred. Since it is impossible to know exactly how much of the sample or flux was lost during the transfer, it is not possible to accurately correct for the exact weight the XRF instrument like in the previous cases. In all the methods that include pre-mix and a transfer into the Pt crucible, the traceability of the real mass in the final disk is lost. Consequently, a higher RSD is observed in the results and it's impossible to use XRF correction.

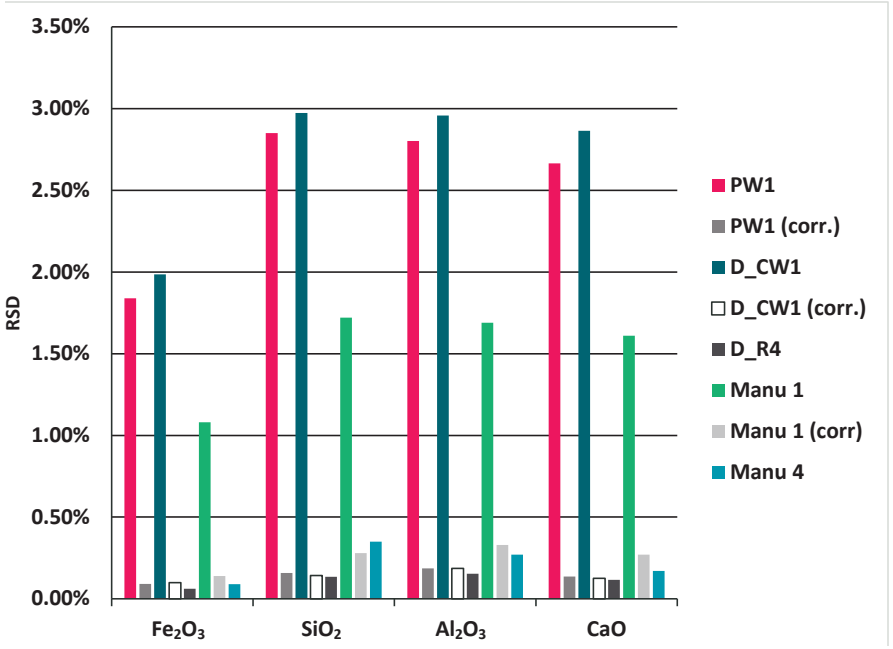


Figure 3. RSD (%) on major elements by XRF analysis of ECRM 683-1 (iron ore) prepared by LeNeo fusion instrument using different weighing methods.

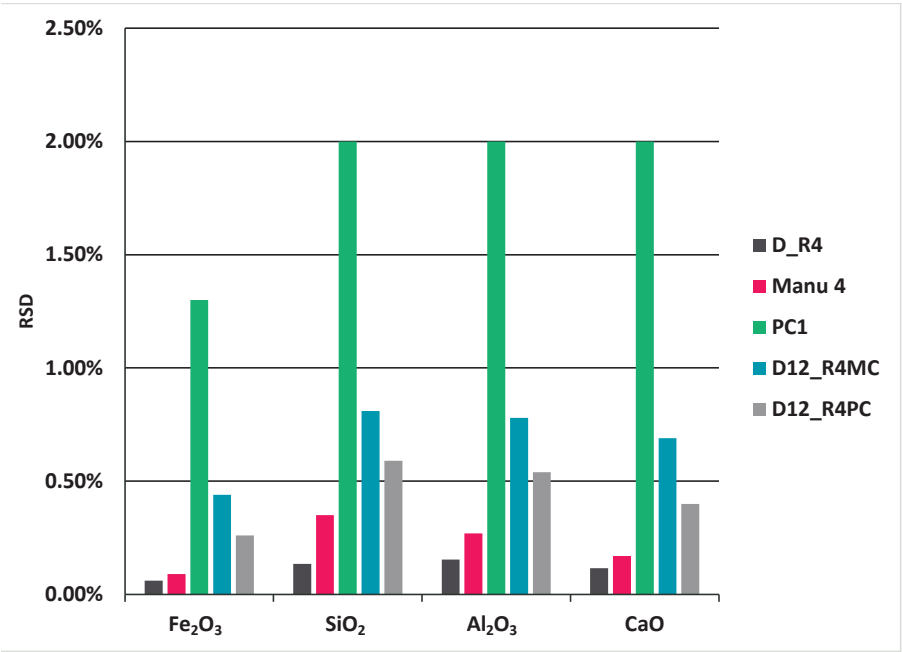


Figure 4. RSD (%) on major elements by XRF analysis of ECRM 683-1 (iron ore) prepared by LeNeo fusion instrument using different weighing methods.

4. Best methods: advantages and limitations

Based on the results obtained in ***Figures 1 to 4***, here are the methods that achieve the best analytical results in terms of comparable precisions in the XRF results (see ***Figure 5*** for the comparison):

- **Manual weighing, low tolerance weighing**
  A low tolerance in the weighing step of sample preparation allows a good control of the sample-to-flux ratio in the glass disk (Manu 4). A constant ratio in the glass disk reduces the error in a significative way and results in a lower RSD. This method is the most widespread and is often used as a reference to compare each method. However, since it requires human intervention during all the preparation, there is a high risk of error.

- **High tolerance, XRF corrected**
  As mentioned in section 2, it is possible to obtain high-quality results in XRF even when allowing high tolerances in the weighing step. Sample preparation is then much faster and easier for the operator. However, a good traceability of each mass (sample, flux and additive) must be kept to allow weight corrections in the XRF. Claisse automatic weighing instruments greatly reduce the risk of human error and can even be coupled with a LIMS for fast and easy transfer of the data to the XRF instrument.

- **Automatic instruments (LeDoser, LeDoser-12) in ratio mode**
  LeDoser and LeDoser-12 instruments used in ratio mode allow high precision measurements since the flux is always calculated to obtain a constant sample-to-flux ratio. It is not necessary to precisely weigh the sample since the instrument calculates and dispenses the exact amount of flux to obtain a constant ratio. Since most of the weighing and traceability of the data is done automatically, there is a low risk of human error, which in turns leads to low RSDs and easy correction in the XRF (if required).

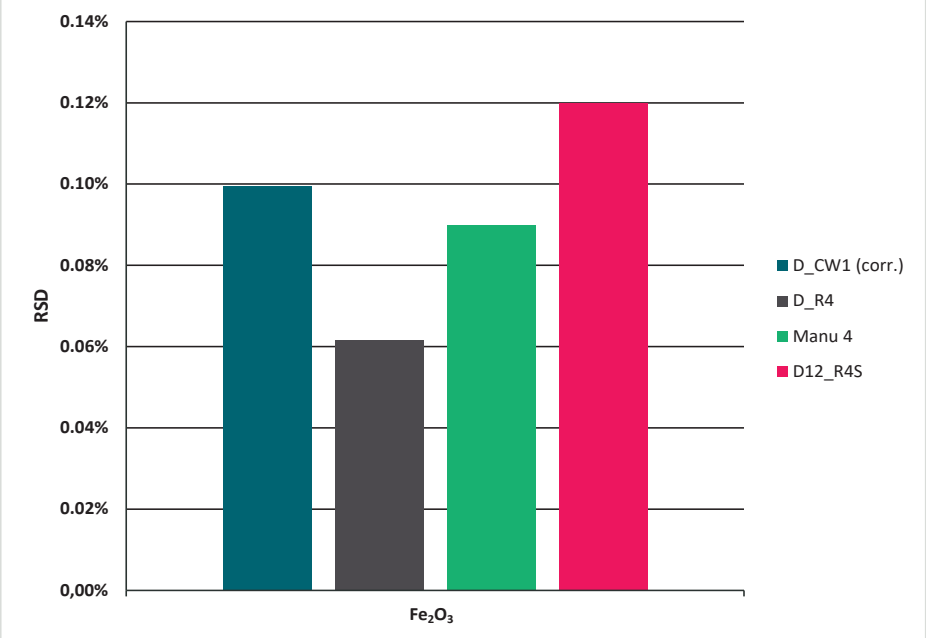


Figure 5. RSD (%) on Fe_2O_3 by XRF analysis of ECRM 683-1 (iron ore) prepared by LeNeo fusion instrument using different weighing methods.

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Conclusion: To conclude, the results of this study clearly show that the weighing method used during sample preparation will affect the precision of the final XRF analysis. It also highlights the importance of traceability during sample preparation to obtain the best analytical results. Finally, each method has limitations that must be taken into consideration. The weighing method must be carefully selected at the application development stage depending on the minimal precision required during the analysis of the glass disk.

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