

Analytical Determination of Total Carbon and Sulphur in Solid Samples by Full Combustion and Integrated NDIR Detection

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Abstract

In the framework of the chemical characterisation of low alloy steels, we carry out the analytical determination of C and S by total combustion, followed by a **Non Dispersive Infra Red** (NDIR) quantitative detection. Accurately weighed samples are fully oxidised under a controlled flow of pure oxygen passing through a tubular furnace heated up to 1350 °C. The combustion gases are filtered and dried by flowing through adequate chemical traps. Next, the gases pass along two detection chambers mounted in series where the IR absorbance of carbon dioxide (at $\lambda = 4.26 \mu\text{m}$) and sulphur dioxide (at $\lambda = 7.3 \mu\text{m}$) are measured and integrated with respect to time. The present report describes the detailed analytical procedures and the validation of the method. Several practical aspects related to the technique are being highlighted as well.

Keywords: low alloy steel, carbon, sulphur, combustion, NDIR

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1 Introduction

The determination of C and S in metals can be achieved by different methods. Most of them rely on one or another variant (depending on the type of energy source applied to vaporize, atomise and excite the sample material) of Optical Emission Spectrophotometry (OES) or Absorption Spectrometry (AS). For instance, the steel industry uses spark (or arc) emission spectroscopy as a very common method for the semi-quantitative determination of C and S (as well as many other elements) in routine ^[1]. This technique gained recently some benefits from developments in the fields of new detectors, data acquisition and data treatment, thereby allowing it to compete with combustion analysis for the determination of low C and N contents in steels ^[2]. Even more modern OES or AS related techniques like ICP-AES, ICP-MS or the recent Laser Induced Breakdown Spectroscopy (LIBS ^[3, 4, 5]) can also be used for these elements ^[6], but in all cases, these techniques require expensive instruments. For C and S measurements, they suffer also either from a poor detection limit or from interferences resulting from the complexity of the matrix. Generally, they are better adapted to the analysis of liquid samples, unless use is made of laser ablation¹. However, whenever wet chemistry is being used, S can be easily converted quantitatively into sulphate, but the case of C is more problematic. Indeed, the dissolution (or the digestion) of the sample is carried out very often under oxidative conditions. In many cases, C residues cannot be easily and quantitatively dissolved. Even when an adequate quantitative dissolution technique is found, C is being converted into carbon dioxide, which escapes in the gas phase as a consequence of the often acidic character of the dissolution medium. This means that carbon dioxide has either to be trapped quantitatively for further analysis (e.g. by gas chromatography), or has to be quantified by integration of a response signal under well-defined flow conditions (e.g. infra red absorption under controlled mass flow at constant T and P). These facts were probably incentives for developing dedicated analysers based on the full combustion of the sample under high temperature, using high purity oxygen both as oxidant and carrier gas.

In 2004, the RMR department of the SCK•CEN considered several techniques for the quantitative analysis of C and S in low alloy steels, namely:

- The total conversion of C into CO₂ and eventually of S into H₂S, followed by the determination of these gases by gas chromatography: the main conclusion of the related works is that a quantitative conversion of C into carbon dioxide can only be ensured by a carefully controlled combustion at high temperature. All other chemical methods that were considered lacked from applicability to all possible cases;
- The full conversion of S into sulphate, followed by Ion Chromatography detection: this approach appears to be viable, but it requires quite a lot of development works to circumvent all matrix effects. In particular, the elimination of the matrix by cationic exchange followed by ebullition suffers from adsorption of anions on the resins. The same approach was considered for P after full conversion into phosphate, but this raised similar challenging questions;
- The full conversion of C into CO₂ and S into SO₂, followed by the quantitative determination of these gases by Non Dispersive InfraRed (NDIR) absorption: we finally selected this approach for the following reasons:

¹ As is the case for LIBS.

- The technique is well-recognized, especially by certification authorities (e.g. ASTM);
- Fully dedicated C – S analysers relying on this technique are commonly found on the market.

In the first quarter of 2005, the RMR department acquired a tubular furnace equipped with temperature, pressure and gas flow controllers, chemical traps and dedicated NDIR detectors. The present document describes the detailed experimental procedures and discusses essential practical aspects related to the technique. It discusses also the validation of the measurements, using ASTM standard steels.

2 Overview of the method

2.1 Range of application of the method

The method described here addresses solid samples only. It is not applicable to liquids. Moreover, care must be taken to avoid analysing substances that are likely to explode. Organic as well as inorganic samples (or mixed samples) may be treated, but in the given configuration, only the total carbon content (TC) can be determined. Making the distinction between total organic carbon (TOC) and total inorganic carbon (TIC) is possible, but this normally requires an extension² that is not available at present.

The analytical range reported by the manufacturer is 10 ppm to 100 % for C and 10 ppm to 10 % for S, depending on the weight of the sample. A slightly better detection limit (5 ppm) for both C and S can be achieved with extreme care. According to the manufacturer, the accuracy is better than 2 % for contents below 100 ppm and better than 1.5 % for contents higher than 100 ppm.

2.2 General overview of the basic equipment

The left part of figure 1 shows the consumable materials to be used during the analysis. One can see the so-called “boats”, which are the sample holders to be introduced in the furnace. The boats on the front of the picture have been loaded with weighed samples. Note that the samples are located in the back end of the holders. At the front end, one can distinguish a perforation whose function is to help in unloading the boats from the furnace. Note also the presence of a desiccator and a plastic bottle containing Sn pellets as accelerator (see further).

The right part of figure 1 shows the front opening through which samples are loaded into and unloaded from the furnace. This end of the tubular furnace must always remain open.

² The said extension allows converting the inorganic carbon quantitatively into carbon dioxide by reaction with an acid. CO₂ is being released in the gas phase and can be measured using the corresponding NDIR detector.

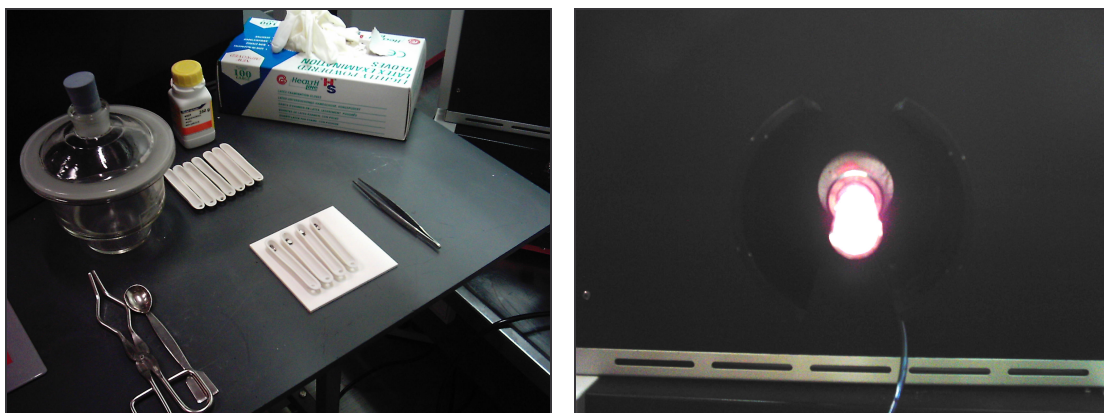


Figure 1: Consumables (left) and input port of the tubular furnace (right)



Figure 2: Detectors (left) and furnace with integrated controllers (right)

The detectors are represented on the left part of figure 2. They are mounted in series in the gas stream, the upper one (CO_2 measurement) being the first. The furnace is located above the flow and temperature control units as is shown on the right part of figure 2. Note the presence of a metallic stick posed on its support on the left side of the furnace. This stick is used to load and unload the boats.

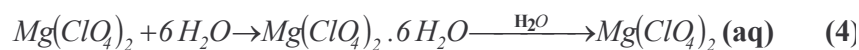
A simplified description of the operating features may be given as follows:

- A gas cylinder provides oxygen as oxidant and carrier gas to the device;
- The incoming oxygen passes through a chemical trap to remove both water vapour and carbon dioxide. Next, the gas enters the furnace where the combustion of the sample takes place;
- The combustion gases leave the furnace through a dust filter located in the back of the device;
- After having passed through a second filter containing quartz wool, the gases are cooled down and dried by flowing through chemical traps;
- Finally, they are directed to the detectors where CO_2 and SO_2 are being quantified. They leave the SO_2 detector under atmospheric pressure. The exhaust pipe must end-up in a fume hood.

Further information concerning a/o the correct assembly of all parts is given in the user's manual of the equipment ^[11]. In the following paragraphs, we will restrict our comments to practical tips directly related to the know-how acquired through several hours of operation. These tips may not be derived on a straightforward manner from the user's manual. They require hands-on work to get familiar with them.

2.3 Oxygen circuits

Flexible connections provided by the device manufacturer are used for all gas circuits, except for the outlet of the pressure regulator mounted on the gas cylinder. The outlet pressure of the two stages regulator should be adjusted between min. 1.5 bar and max. 2 bar. Oxygen leaving the cylinder passes first through two chemical cartridges. The first one contains NaOH on a silica carrier³. The purpose of this cartridge is to catch traces of both CO₂ and water vapours according to equations 1 and 2. Whatever the quality of the oxygen, it contains normally no SO₂, but if it was the case, the first cartridge would also eliminate this species from the incoming stream, according to equation 3.



The second cartridge is filled with anhydrous magnesium perchlorate⁴ as desiccant. The capture of water vapour by magnesium perchlorate is illustrated by equation 4.

In order to lengthen the lifetime of the chemical cartridges (especially the first one) and to limit the production of waste, we recommend using high purity oxygen in all cases.

2.4 Constrains related to combustion

In order to ensure a correct combustion of the sample, the following points should be observed:

- Metallic samples should be divided as finely as possible. Powders or fine granules (~ 1 mm diameter) are preferred, but chips may also be used. Metal sampling should be carefully carried out, using a tungsten carbide drill;
- The sample should be located in the back end of the boat. In the case of low alloy steels, we advise to add tin pellets as combustion accelerator. Tin pellets are anyway necessary

³ Also known as Ascarite[®]. See the annex for a detailed description of the products.

⁴ Also known as Anhydrone[®].

when some alloying elements (like V, Mo, Ni, Mn or Cr) are present in the sample at levels above 1 wt. %. The practice demonstrated that 1 tin pellet (i.e. ~ 120 mg) per 150 to 200 mg of sample is sufficient. Alternate combustion accelerators exist (e.g. tungsten or a mixture of tungsten and tin, the latter being recommended in the case of Ni alloys^[12]). Choosing the right accelerator is a matter of experience. Adequate experimental investigation of the influence of the accelerator should be carried out each time new materials are to be measured^[12]. For low alloy ferritic steels, we used tin as recommended by the manufacturer. This choice appears to be correct;

- The sample weight should normally range between 0 and 500 mg. The upper limit may eventually be increased (up to max. 1000 mg), but in this case, particular attention has to be paid for complete combustion;
- A visual inspection of the boat after unloading allows checking for proper combustion: there should be only one zone where the molten metals and oxides gathered apparently homogeneously. Ideally, the size of this zone should not exceed one third of the total boat length.

Boats should be pre-treated before being used for C analyses: the carbon dioxide adsorbed on the boats has to be evacuated. This can be done according to one of the two following methods:

- Method 1: Put the boats in a separate furnace at 500 °C during at least 35 minutes;
- Method 2: if a separate furnace is not available, the tubular furnace running at 1350 °C may be used. In this case, the boats should be treated one after another by putting them into the furnace, the oxygen flow being turned on. The front panel of the C detector will register the out gassed CO₂, thereby allowing the operator to assess the completion of the degassing process. Generally, 45 – 60 s are sufficient⁵ to observe a return of the detector signal to zero, but we recommend waiting at least 10 minutes for ensuring complete degassing, especially when dealing with low carbon contents. See also the discussion related to the calibration curves for further details.

Boats that have been treated should be used within 24 hours if they are stored in normal atmospheric conditions. Keeping them under inert atmosphere in a dessicator allows maintaining their condition for at least three days. However, for the determination of very low levels, it is highly recommended to use the boats within 2 hours after degassing.

According to Behr, no pre-treatment is necessary when only S is measured, but LECO reports that degassing is also necessary for S when dealing with ultra-low levels (< 1 ppm)^[12].

2.5 Post-combustion chemical treatment

Two cartridges containing magnesium perchlorate are used to dry the combustion gases before they enter the detectors. Note that perchlorates may give rise to explosion risks when they are brought in contact with organic materials, especially at high temperatures. The use of magnesium perchlorate should be re-considered each time the sample is organic in nature. Particularly, one has to ensure that the combustion is complete.

Care must be taken not to fill these cartridges with Ascarite[®], otherwise the measurement will unavoidably fail (see equations 1 and 3).

⁵ Some alternate manufacturers (LECO) recommend at least 15 minutes for determining very low levels of C.

A visual check of the status of all filters and cartridges should be made daily. Once two thirds of any cartridge have been used⁶, the full content of the cartridge should be replaced. Filters should be cleaned or replaced according to the recommendations given by the manufacturer of the instrument.

2.6 Detection of the gases

2.6.1 Spectral data of the targeted gases

The IR transmission spectrum of carbon dioxide in the gas phase is given on figure 3. One can see that absorption occurs between 2300 and 2400 cm^{-1} , which corresponds to a wavelength located between 4.17 and 4.35 μm . The centre of this interval is precisely the wavelength at which the instrument carries out the detection of CO_2 , namely 4.26 μm .

The IR transmission spectrum of sulphur dioxide in the gas phase is given on figure 4. Absorption occurs between 1300 and 1400 cm^{-1} , as well as between 1100 and 1250 cm^{-1} . These wave numbers correspond to 7.14 – 7.69 μm and 8.0 – 9.09 μm respectively. The instrument is tuned in the first region at 7.3 μm ⁷.

The IR transmission spectrum of water vapour is given on figure 5. Absorption occurs between 1200 and 2200 cm^{-1} (4.54 – 8.33 μm). This is the incentive to dry the gases before sending them to the detectors.

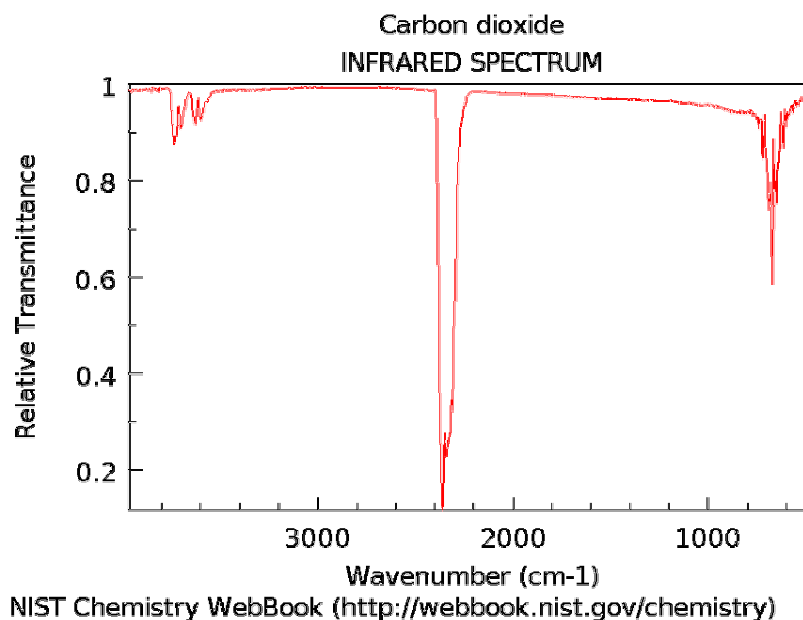


Figure 3: Infrared transmittance spectrum of gaseous carbon dioxide. The spectrum was recorded under a partial CO_2 pressure of 200 mm Hg (26.68 kPa), diluted to a total pressure of 600 mm Hg (80.05 kPa) with N_2 ; Dow KBr foreprism; 4 cm^{-1} resolution^[7]

⁶ Typical colour changes can easily be observed when the products are exhausted. The final colour may vary, depending on the type of sample, but typically, Ascarite[®] turns from grey brownish to white as a result of carbonate formation.

⁷ In the user's manuals ^[11], a value of 7.89 μm is incorrectly reported. After inquiry, the manufacturer confirmed that the wave length on which the S detector is tuned is effectively 7.3 μm .

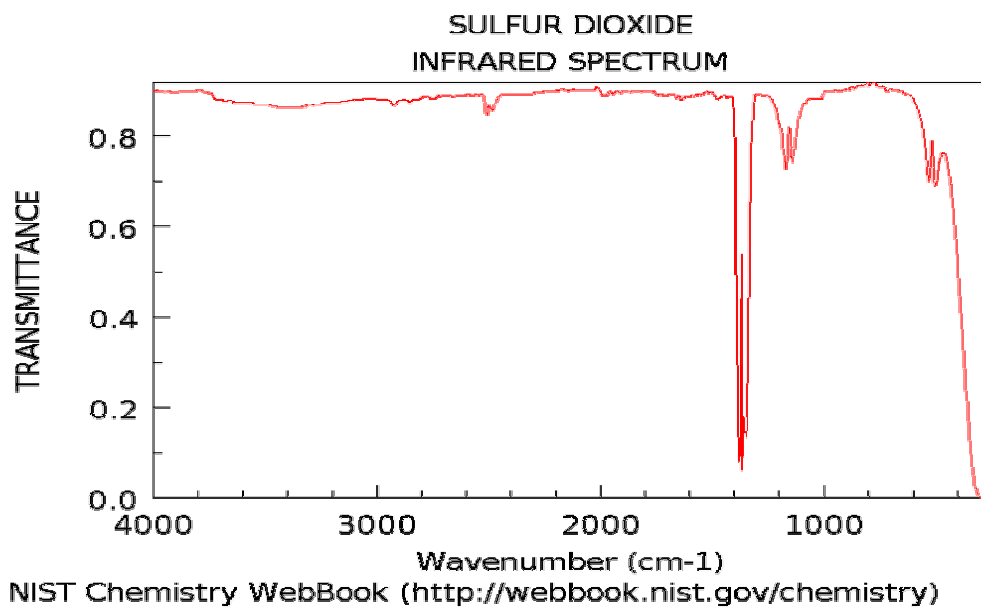


Figure 4: Infrared transmittance spectrum of gaseous sulphur dioxide. The spectrum was recorded under a partial SO₂ pressure of 100 mm Hg (13.34 kPa), diluted to a total pressure of 600 mm Hg (80.05 kPa) with N₂; 4 cm⁻¹ resolution ^[7]

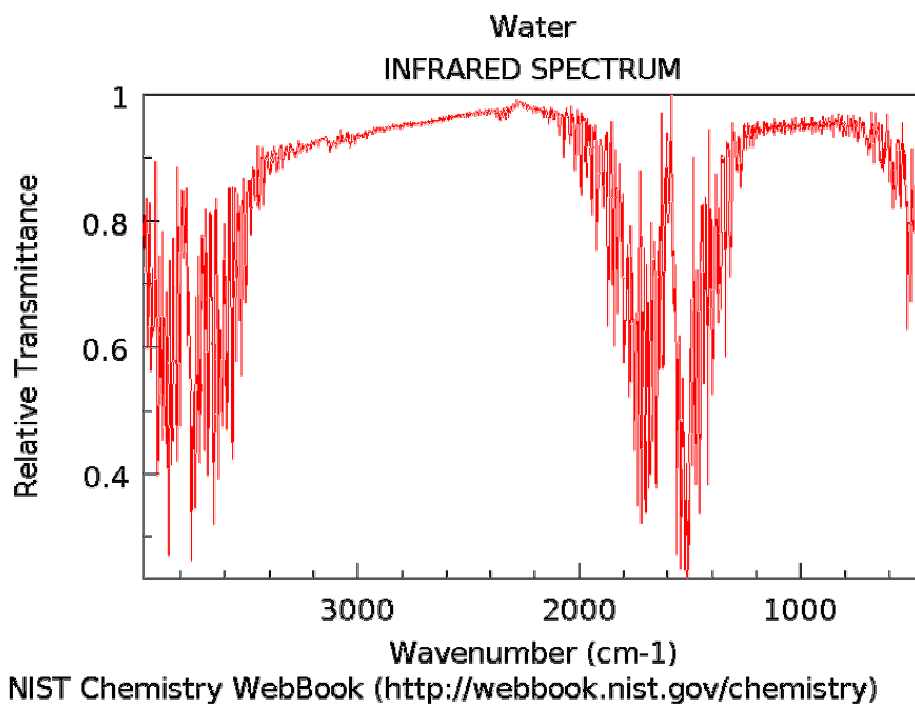


Figure 5: Infrared transmittance spectrum of water vapour ^[7]

2.6.2 *Mass flow, pressure and temperature controls*

IR absorbance is proportional to the concentration of absorbing species. For gases, the concentrations are closely related to the pressure and the temperature (for a given volume). Moreover, the absorption coefficients in the IR region depend heavily on the temperature. Therefore, the temperatures in the detectors are closely controlled by Peltier elements. According to the manufacturer, both detector temperatures are adjusted at $-15\text{ }^{\circ}\text{C}$. Note that there is no liquid coolant circuit for the Peltier elements. We conclude that the hot side of the elements are cooled by forced convection of air (probably by ventilators). This may explain some drift of the instrument observed when the ambient temperature is high. Ideally, the instrument should be operated in a lab equipped with air conditioning.

Both detectors are also equipped with pressure control units. An automatic gain control systems (AGC) provides constant sensitivity. The IR sources are pulsed at high frequency to lengthen their lifetime, while keeping reasonable response time for the correct follow-up of rapidly varying signals.

The detectors deliver digitised voltage answers, which are proportional to the absorbances. These signals are sent to the controlling computer. The latter is programmed to integrate the incoming signals. The integration scheme is based on both the minimum analysis time and the thresholds levels. These values can be chosen using the software interface. The result of the integration is linearly related to the total C (resp. S) contents in the sample. Calibration curves and sample weights are combined to derive the total contents from the calculated integrated signals when measuring an unknown sample. Typically, the time needed to proceed to the full combustion of one sample and to treat the data does not exceed 80 to 90 s.

3 **Practical measurements**

The user's manual provided by the manufacturer of the equipment gives detailed explanations about the practical procedures ^[11]. In this section, we will restrict our comments to complementary information, focusing essentially on the practical tips related to the measurement of one sample. As explained in the user's manual, an experimental campaign should be considered as a new project to be defined using the software. A project includes:

- Set-up data to be defined carefully, as explained in the user's manual;
- Suitable calibration data, for C, for S or for both elements, depending on the targeted measurements. Note that when measuring unknown samples, both C and S can be determined through one combustion experiment when calibration data exist for both S and C. However, elaborating calibration data cannot be done simultaneously for C and S using the same samples. Each calibration point will address only one element, the corresponding result becoming a member of the corresponding calibration data set;
- Measurements.

3.1 Checklist and inspection

3.1.1 Checklist

All products' characteristics are given in the annex. The following material should be at hand prior starting a measurement campaign:

- Safety gloves and goggles;
- A sufficient number of boats that were adequately degassed as previously explained;
- Quartz wool;
- Magnesium perchlorate;
- Sodium hydroxide on a carrier;
- A cylinder of oxygen. One full gas cylinder will be exhausted within approximately 20 hours of continuous measurements. Therefore, it is advisable to foresee spare cylinders, especially if many samples have to be measured;
- Tin pellets;
- Silicon grease: this is necessary if the furnace tube has to be replaced (see user's manual);
- Joins (same remark as above);
- At least one spare dust filter (see user's manual [\[11\]](#)).

3.1.2 Inspection

The following parts should be inspected before starting the measurements:

- Status of the furnace tube: this has to be done when the furnace is cold. The tube should be replaced on the basis of visual inspection. When a large number (> 50) of samples have been measured, dust can possibly have formed excessive deposits on the inner wall of the tube. When this is the case, thermal cycles may also lead to breakage;
- Dust filter: this should also be done when the furnace is cold. Normally, this filter can be cleaned. If not, it has to be replaced;
- Quartz wool filter: replace this filter if any colour has developed due to the previous measurements;
- Drying cartridges: as explained above, they should be replaced if two thirds of the chemical product appear to be exhausted;
- Gas flow rate: turn on the computer, the detectors and the oven, and let oxygen flow through the system. We recall that the outlet pressure of the two stages regulator should be adjusted between min. 1.5 bar and max. 2 bar. Load the software and make sure that the system is not in stand-by. Adjust the right hand flow meter until it reads 70 (on the scale from 0 to 100). The reading on the left flow meter depends on the setting of the mass flow controller. It should be 30 on a scale from 0 to 100, assuming that the mass flow setting is $30 \text{ L}\cdot\text{hr}^{-1}$ (see below). Once these adjustments have been made, the system may be turned off (unless immediate measurements are foreseen). As long as the gas cylinder is not empty and the flow adjustment has not been changed, the flow should return to the adjusted nominal value every time the system is turned on again.

3.2 Experimental procedure

3.2.1 Starting up the system

If not already done, turn on the computer, the furnace and the detectors, open the gas admission and start-up the software. Check the detector LCD panel to verify the status of the system. If these panels indicate that the system is in stand-by, activate the system through the software (see the user's manual [\[11\]](#) for complementary information on how to do this). Adjust the temperature of the furnace to the desired value. For low alloy steels, the set point should be 1350 °C. Let the system run in these conditions during at least two hours. Boats may be degassed as soon as the temperature indicator shows the correct temperature. This happens generally about 15 minutes after the set point has been entered.

While the furnace is heating up, the detectors may show several warning messages, like "System warm up" or "Signal out of range". This appears to be normal. After about 20 minutes, these messages should disappear. The LCD panels should report a value oscillating gently around zero.

The main variables that are adjustable using the manufacturer's software are as follows:

- C high saturation threshold low range: 8.5 V;
- Mass flow: 30 L.hr⁻¹;
- Saturation limit: 9 V;
- Start threshold: 0.01 V;
- Termination threshold: 0.01 V;
- Moving average for measurements: 10 points (5 points for graphs);
- Max. duration of analysis: 600 s;
- Min. duration of analysis: 60 s;
- Values for offset determinations: 50 points;
- Bounce measurements: 5 points.

We invite the reader to consult the user's guide [\[11\]](#) for any check and/or adjustment of the software set-up as well as for a detailed explanation of the meaning of each variable.

3.2.2 Tips for the procedure

Preparing the samples:

- Make sure that the software set-up is correct (see the recommendations given in the user's manual [\[11\]](#));
- Weigh the samples: it is advisable to prepare series of samples to avoid overheads caused by switching between different tasks. Ideally, two operators should collaborate, one preparing the samples, one carrying out the analyses. We recall that the samples should be located in the back end of the boats and that Sn pellets have to be added as accelerator (see figure 1).

Loading and unloading the samples:

- Loading a sample should be done ideally within 10 s after the measuring sequence has been launched through the software. Here again, two operators can ideally collaborate;
- The front end of a boat is equipped with a hole. This hole is not used for loading the samples, because it is difficult to disengage the loading stick when the boat has reached its final position inside the furnace. Instead, the boats are pushed with the stick until the boat has reached its correct end position (i.e. it is blocked by the dust filter). The hole is used for unloading the samples after combustion.

3.2.3 *Typical signals delivered by the detectors*

Typical signals delivered by the detectors are illustrated on figure 6.

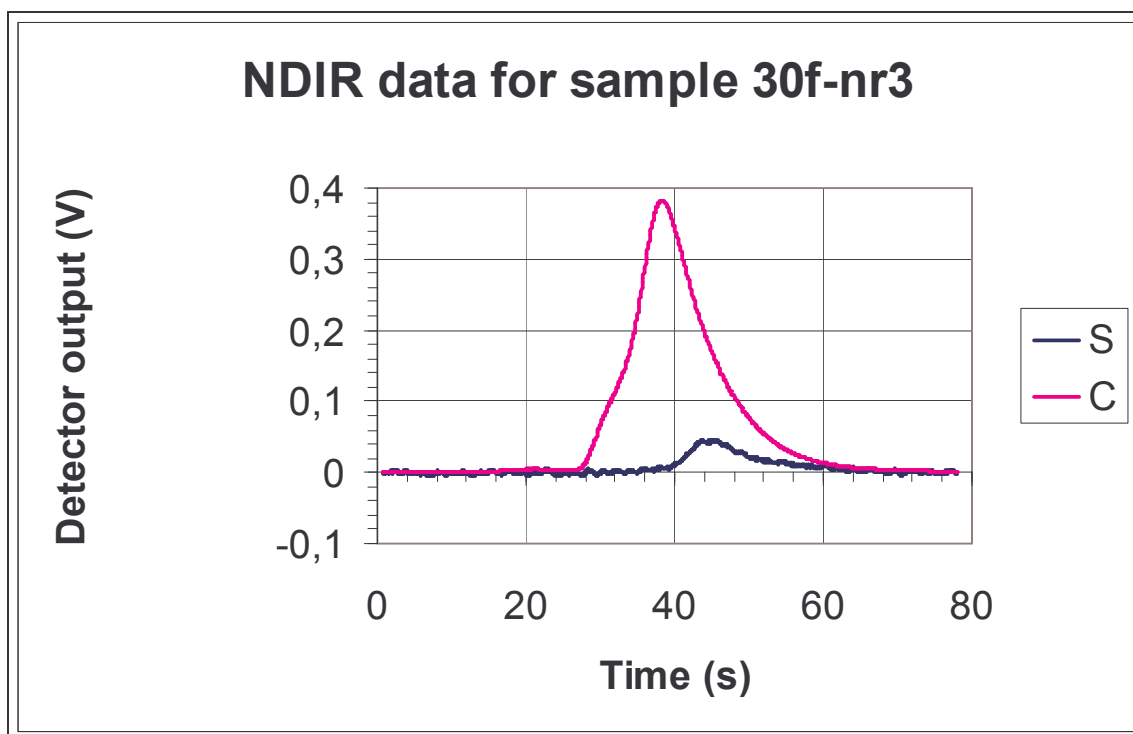


Figure 6: Typical detector signals obtained during the measurement of an unknown sample

One should note that:

- The position of the peaks depends on the time elapsed between the start-up of the measuring session triggered by the computer and the duration of the loading process;
- The S signal is delayed with respect to the C signal as expected (the detectors are mounted in series);
- Multiple peaks may appear. The shape of the curves reflects the time dependent release of the measured gases by the combustion process. If multiple peaks are present, a visual inspection of the boat after unloading is mandatory, in order to check for eventual residues that would not have been fully oxidised.

3.2.4 Shut down operations

To shut down the system, the operator should carry out the following operations sequentially:

1. Make sure that the project has been saved;
2. Switch the system to stand by: the control panels of the detectors should report the stand by status;
3. Turn the detectors off;
4. Exit the software and turn the computer off;
5. If shutting down for at least two days (e.g. for one week end), turn the main switch of the oven to the off position;
6. If shutting down for less than two days, simply adjust the temperature of the oven to 500 °C. This helps extending the lifetime of the heating elements.

4 Example: Validation of the method using ASTM standards

Five ASTM standard steels are available. Their certified C and S contents are given in table 1.

Table 1: Certified C and S contents for available ASTM standard steels

ASTM code	C (wt.%)	Uncertainty on C (wt. %)	S (wt. %)	Uncertainty on S (wt. %)	Remark
361	0.383	0.001	0.0143	0.0003	For validation
362	0.160	0.001	0.0360	0.0003	For calibration
363	0.62	0.01	0.0068	0.0002	For calibration
30f	0.490	0.004	0.0085	0.0003	For validation
291	0.177	0.001	0.020	0.001	For validation

The validation has been carried out in several steps. First, we selected two standard steels for the make-up of calibration data. ASTM 362 and 363 were chosen because their contents in both C and S are located at the boundaries of the concentration ranges offered by the full set of certified steels (0.16 to 0.62 wt. % for C and 0.0068 to 0.036 wt. % for S). Next, we used the calibration data to analyse the three other certified steels (361, 30f and 291). Finally, we performed several replicate measurements using ASTM 361 in order to better assess the dispersion affecting the results.

4.1 Calibrations

4.1.1 General comments

As stated above, the analyser delivers integrated values of the detector signals. For calibration purposes, one relates these variables to the known total amounts of C and S in accurately weighed standard samples. Provided the measurement conditions remain unchanged⁸, one may expect a linear relationship between the total weighed amounts of C and S and the corresponding integrated signals. Indeed, the latter are then directly related to the amounts of CO₂ (resp. SO₂) that passed through the detectors, since the detector outputs are proportional to the concentrations of these gases in the detection chambers at any time.

From now on, a statistical terminology is being used, considering that calibration curves are represented by models that relate dependent variables (= the total amounts of C and S respectively) to the independent variables (= the corresponding integrated detector signals)⁹. A “parameter” is defined as any numerical figure that is no variable, but is being algebraically combined with the independent variables in the models to deliver an estimation of the dependent variables. These parameters are statistically estimated through a fitting procedure. Typically, for a linear model, the slope and the intercept are the parameters. The terminology adopted here is widely recognised in the literature whenever a statistical approach is recommended^[8, 9].

Three calibrations have been carried out, each addressing both C and S. The purposes were to assess how long calibration data remain valid (i.e. tracking possible drifts in function of time) and to identify the ranges of concentrations wherein the calibration parameters remain valid. Calibrations 1 and 2 cover the concentration ranges of the ASTM steels used for validation. The third calibration addresses low contents of C as required for the measurement of some unknown samples that we analysed for an external client¹⁰. We recall that it is not possible to obtain calibration data for both C and S from one series of samples. Although the measurement of both C and S can be carried out on unknown samples provided adequate calibration data are available, the measurement of one calibration point can only be done for one element per sample. This is the reason why we report a data set for S calibration under low C: this curve is the one that was used together with the low C calibration curve for C.

4.1.2 Statistical analysis of the calibration data

A total of 41 calibration points were taken. Table 2 shows the repartition of these measurements between all calibration curves. Using Statistica for Windows^[10], we fitted a linear model to each data set. Table 3 gives the resulting estimated parameters together with the radius of their respective confidence intervals (C.I., calculated for a two-sided significance level of 0.95)¹¹. In this table, non significant figures for each numerical value are given using smaller fonts.

⁸ Pressures and temperatures in the detection chambers, but other experimental factors might influence the results as well, e.g. the progressive deposit of dust on the optical filter or on the IR source may eventually lead to drifts.

⁹ This way of defining the variables may be surprising since during calibration, one determines first the amounts of C and S by weighing, while the integrated responses are known only after the samples have been measured. However, we recall that in normal operation (i.e. when measuring an unknown sample), we must derive the C and S amounts from the integrated signals, using the calibration curves.

¹⁰ The corresponding results are reported in a separate document.

¹¹ Confidence intervals (C.I.) allow to quickly analysing the results. No further t-test is needed to assess the significance of the parameters or to compare them since the radius of the C.I.'s already include the t-Student statistics.

Table 2: Initial degrees of freedom for each calibration curve

Calibration	Element	Number of points
Calibration 1	C	8
Calibration 2	C	7
Calibration with low C	C	5
Calibration 1	S	7
Calibration 2	S	6
Calibration with low C	S	8

Table 3: Estimated parameters obtained by least square regression ^[10]

Calibration	Element	Slope	Radius of C.I. (slope)	Intercept	Radius of C.I. (intercept)
Calibration 1	C	179.8	5.19	-45.7	28.42
Calibration 2	C	188.0	11.07	-56.0	65.83
Low C	C	159.8	8.51	-6.59	5.43
Calibration 1	S	19.9	4.00	1.37	9.44
Calibration 2	S	20.9	3.16	2.16	7.41
Low C	S	21.5	0.93	1.50	2.06

By examining the results given in table 3, we can derive the following:

- The slopes for all S calibrations are statistically equal to each other;
- The intercepts for S calibrations are all statistically equal to 0;
- The slopes for calibrations 1 and 2 in the case of C are statistically equal to each other. The slope obtained for C under “low C” is statistically different from the preceding value;
- For C, only calibration 2 yields an intercept that is statistically equal to 0. The other two calibrations exhibit intercepts that are close to zero, but anyway significantly negative. This demonstrates the need of degassing the boats during a sufficiently long time. The lower the targeted C range, the longer the degassing operation must be. For calibration 1, we degassed the boats during 60 s. For all other calibrations, we used 10 minutes, but this appears not to be enough when addressing lower carbon contents. When residual C remains adsorbed on the boats, it will generate a positive integral for a zero load, which corresponds indeed to a negative intercept on our calibrations since we define the integrated detector signals as independent variables.

The linear models fitted all data satisfactorily. Table 4 reports the proportion of variance explained.

Table 4: Proportion of variance explained by the linear model for each calibration

Calibration	Element	Proportion of variance explained (%)
Calibration 1	C	99.94
Calibration 2	C	99.83
Low C	C	99.95
Calibration 1	S	98.02
Calibration 2	S	99.26
Low C	S	99.87

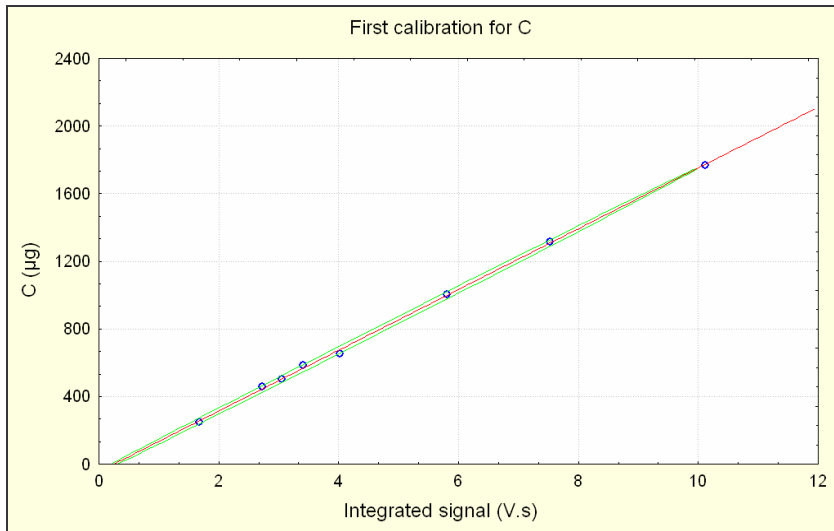
Figures 7 – 12 allow checking the fitting results visually, showing relations between two out of the following variables:

- The independent variable: this is the integrated detector signal. This variable is expressed in V.s;
- The dependent variable: this is the amount of C (resp. S) in the sample, always expressed in μg . When deriving this variable from the sample weight and the certified contents, we obtain the observed variable (referred to as C (or S) (μg), or simply as "Observed values" on the graphs). When calculating this variable from the independent variable, using the fitting curve, we obtain the "Predicted values";
- The residues: they are obtained by subtracting the predicted values from the corresponding observed values. They are referred to as "Residual values" and are expressed in μg (of C or S).

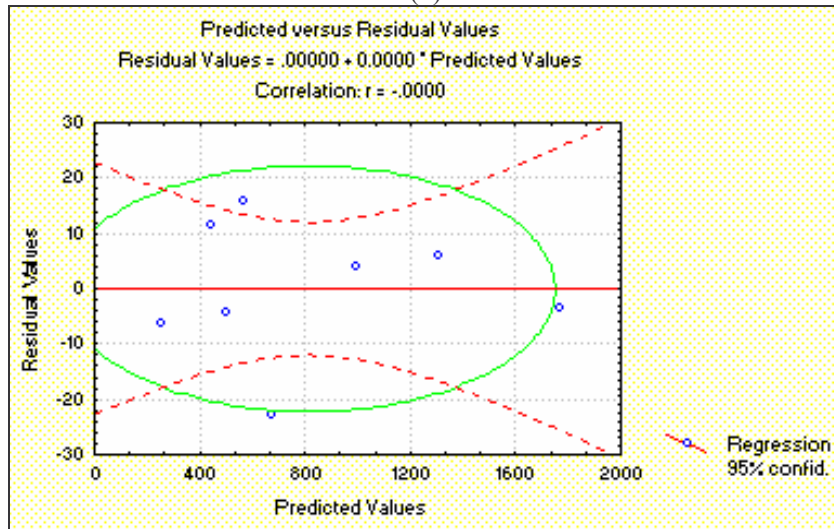
Each figure contains three graphs:

- Graph a is a classical plot of the dependent variable *versus* the independent variable. Dots correspond to the experimental values of the dependent variable (weighed amounts). The straight line depicts the linear model. This graph shows also the confidence ellipse (level 0.95);
- Graph b is a plot of the residuals *versus* the predicted dependent variable. This graph is very useful to check for any remaining correlation that would not be included into the model. Indeed, one may expect that if no particular correlation was overlooked, the residuals should be randomly distributed around zero on this graph. One rough method to check for this is to carry out a linear regression on these data, the expected outcome being a horizontal line located at zero as mean residual value. The graph shows also two additional regions:
 - The 95 % confidence region for the predicted value: this region is located between the two curved interrupted lines. These loci depict the limits (at 95 % confidence) of the confidence intervals of the corresponding dependent variable (in this case, the residuals) all along the regression. They illustrate the increase of uncertainties as the distance between the actual independent variable with respect to its mean value increases. This stresses also the risks of errors associated to extrapolations;
 - The confidence ellipse (level 95 %) wherein all data points should ideally be included. Any point significantly outside this region should be regarded as an outlier¹²;
- Graph c is a plot of the observed *versus* the predicted dependent variable. A linear model fitted to these data should exhibit a slope equal to 1 with a zero intercept and a strong correlation coefficient. This graph shows also the loci corresponding to the confidence interval (95 %) of the predicted values all along the regression.

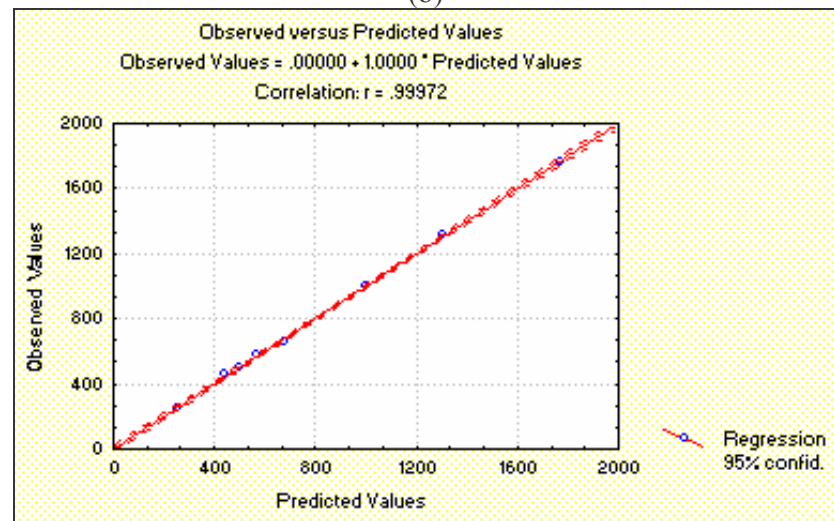
¹² This approach is generally more severe than the classical one relying on threshold bands for the detection of outliers.



(a)

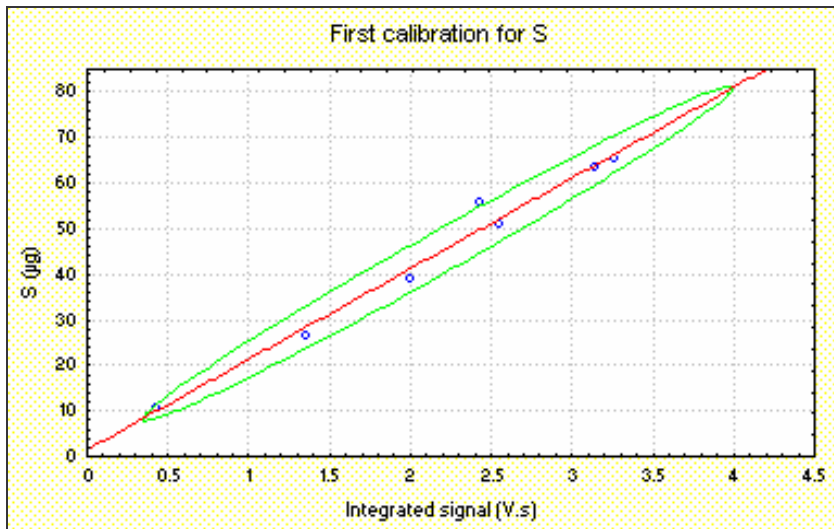


(b)

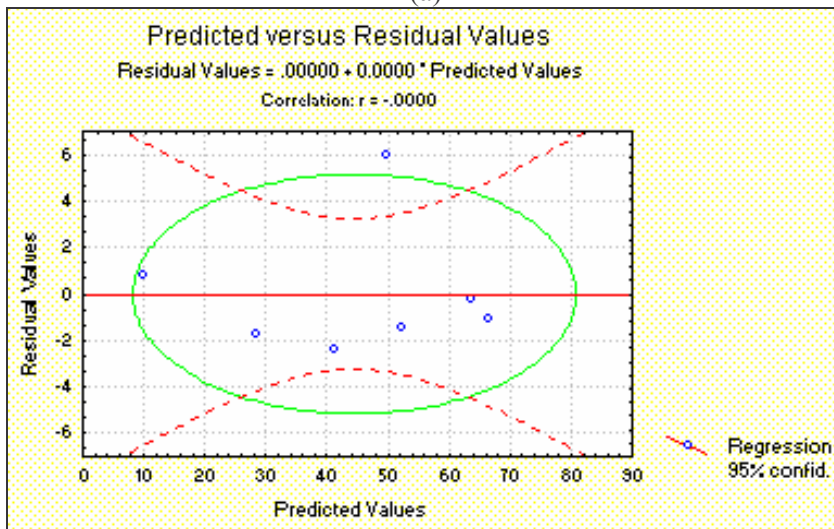


(c)

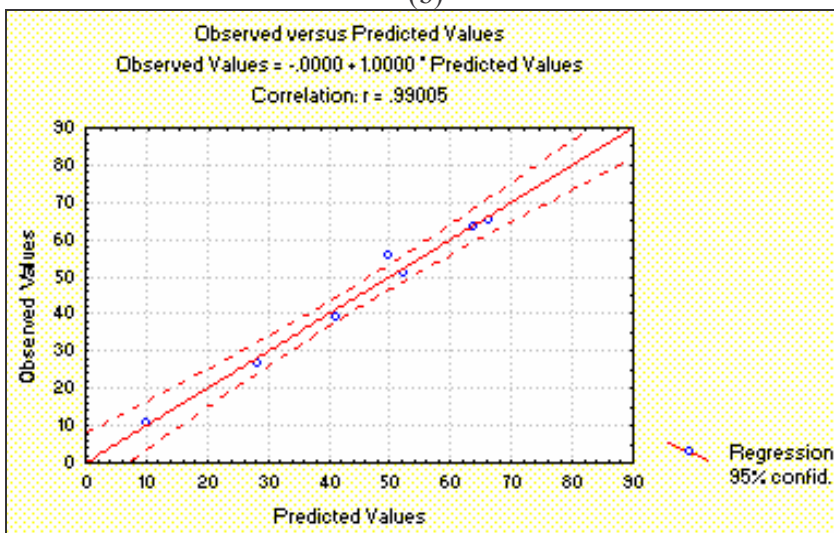
Figure 7: Calibration 1 for C



(a)

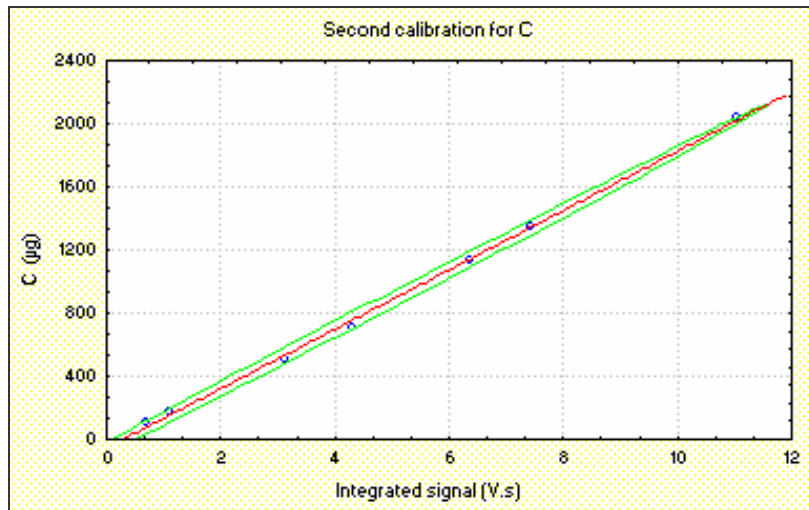


(b)

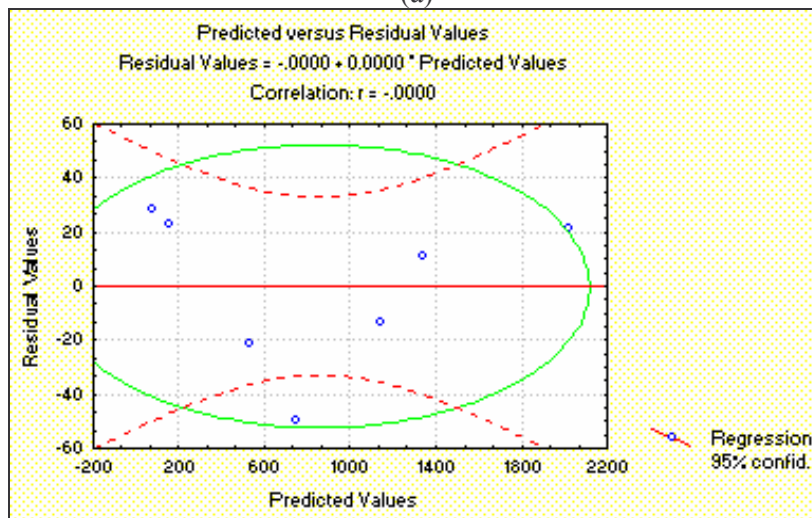


(c)

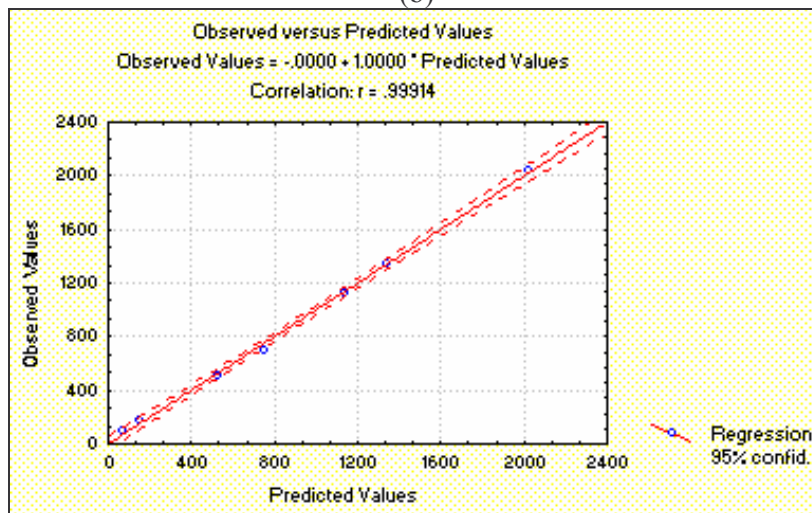
Figure 8: Calibration 1 for S



(a)

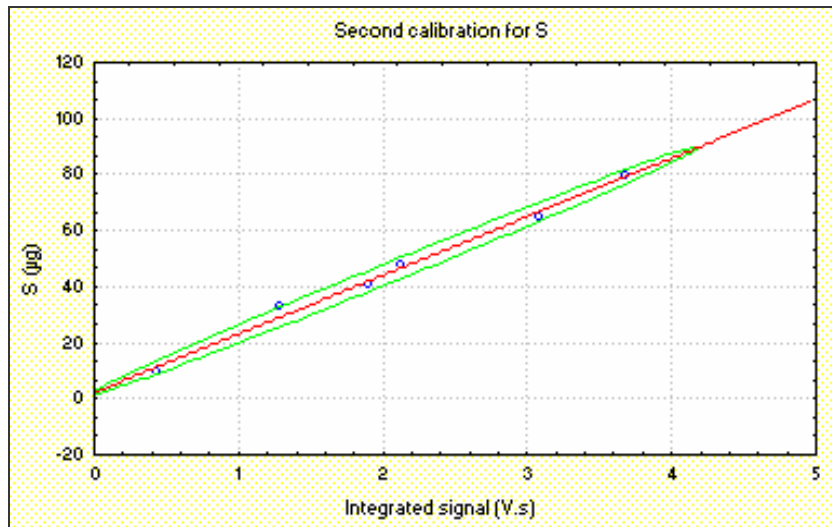


(b)

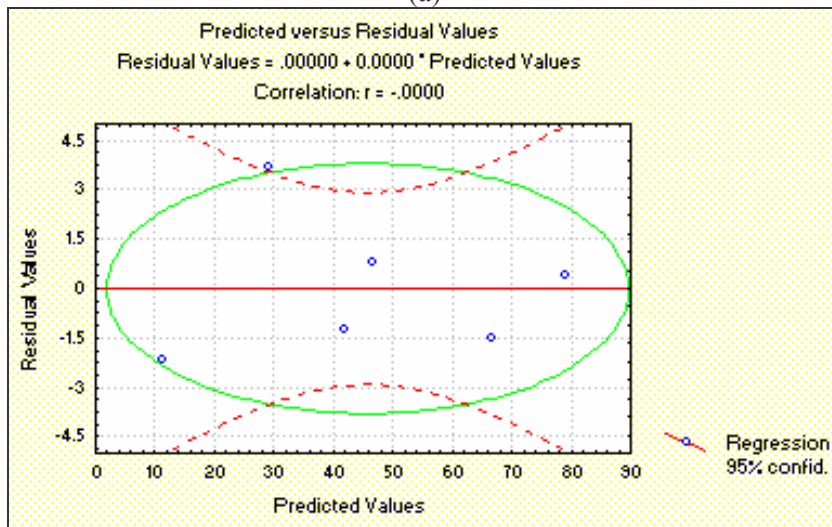


(c)

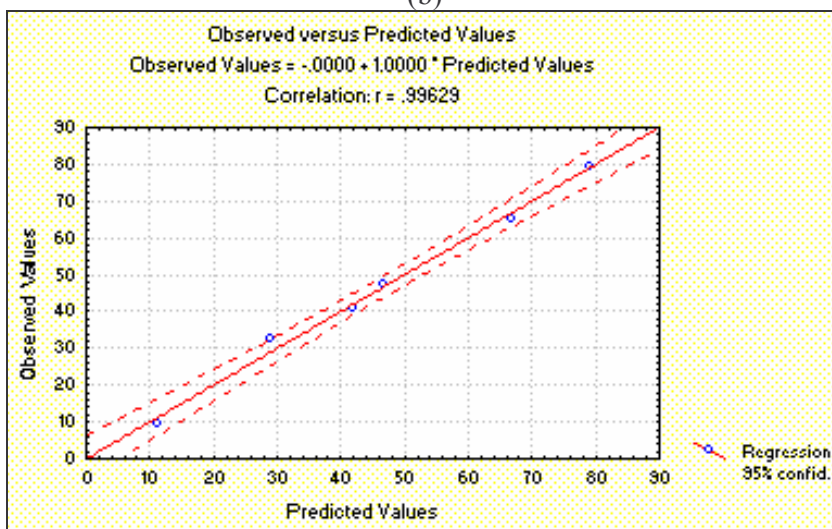
Figure 9: Calibration 2 for C



(a)

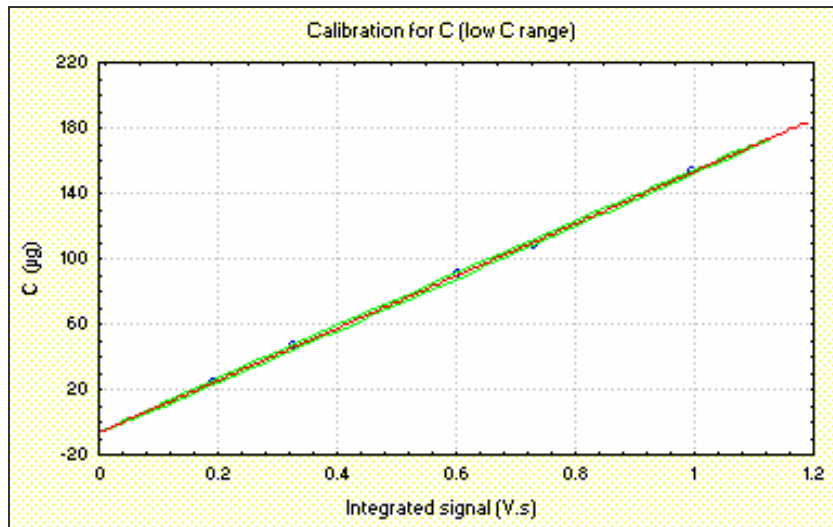


(b)

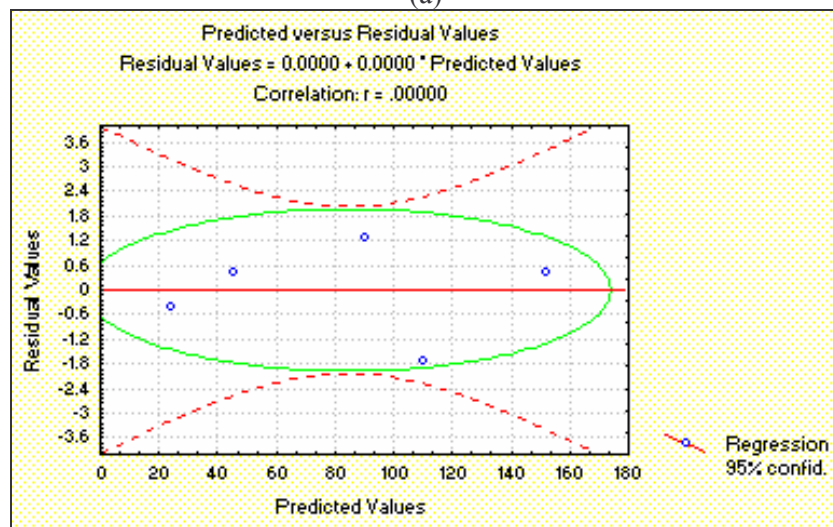


(c)

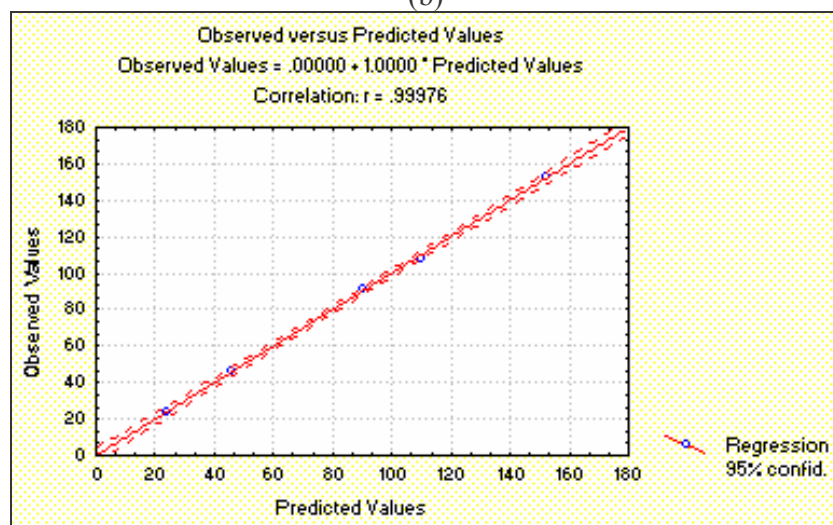
Figure 10: Calibration 2 for S



(a)

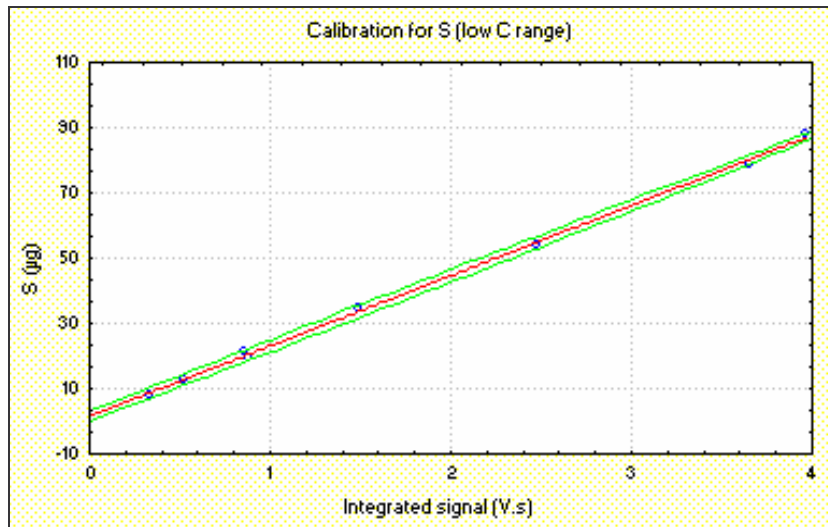


(b)

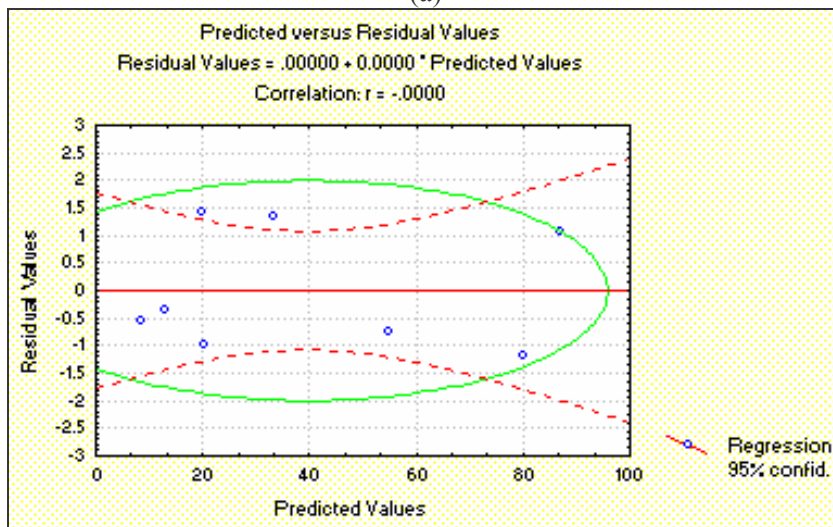


(c)

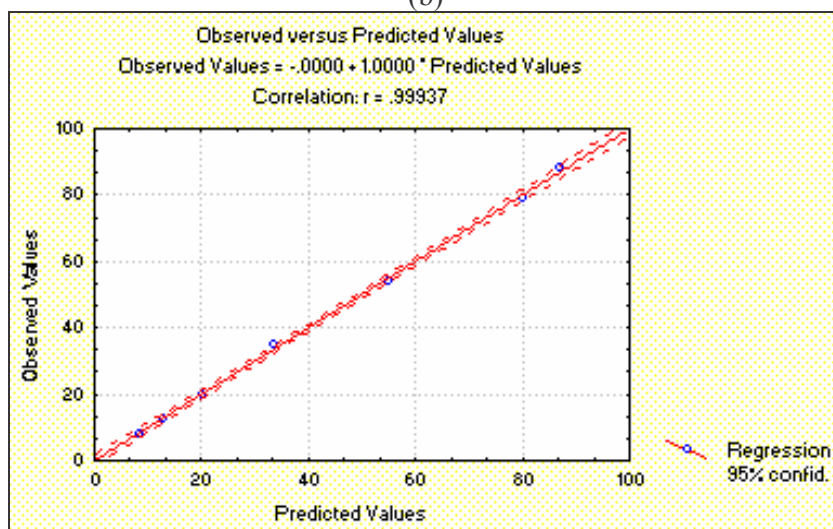
Figure 11: Calibration for C (low carbon)



(a)



(b)



(c)

Figure 12: Calibration for S (low carbon)

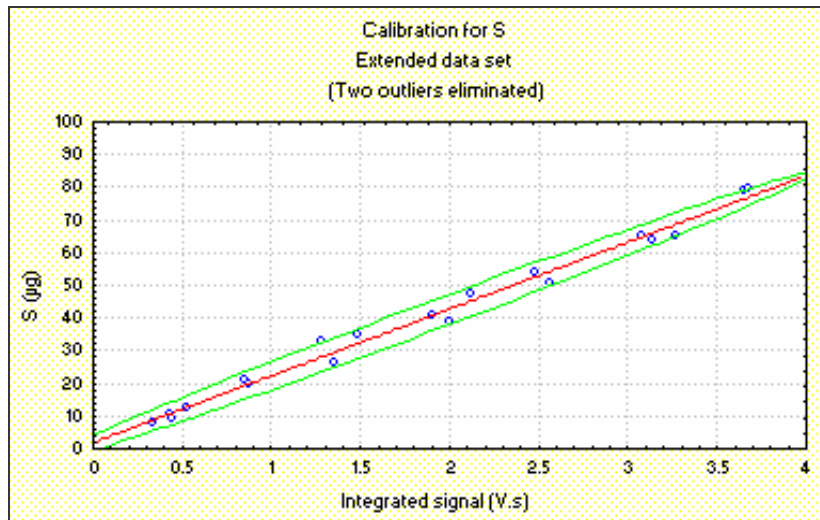
The analysis of the fittings leads to the following conclusions:

- For all calibrations, the linear model is statistically validated: there exists no residual correlation between the residues and the predicted variables, while the fits of the observed *versus* predicted variables are all excellent;
- Due to the severity of our criterion related to the detection of outliers, we consider that points that are outside of but adjacent to the confidence ellipses for the residues (graphs b) are no outliers. This leads to the conclusion that only one outlier can be identified within the dataset for S under calibration 1 (Figure 8);
- For S:
 - Normally, there is no need to fit a linear model that includes an intercept. However, keeping an independent term into the model allows checking for possible artefacts. Therefore, we will maintain the general formulation of the model;
 - Having seen that all calibrations yield statistically equivalent curves, we gathered all data (except the identified outlier) and carried out a single fitting on the extended dataset. Doing so allowed identifying one further outlier (the point with the highest S content from the third calibration. This point was already lying at the limit of the acceptance region on figure 12b). The extended calibration will be used for all subsequent measurements (a/o validation measurements);
- For C:
 - From a statistical point of view, we could also gather the data of calibrations 1 and 2 and perform a fitting on the extended data set. However, recalling that the C measurements are sensitive to the degassing procedure and that measurements making use of any calibration were also made with a degassing procedure similar to the one associated to the said calibration, we will refrain from gathering the data;
 - Still in relation with the sensitivity to degassing, but even more important, we will use the low C calibration as such for low C determinations.

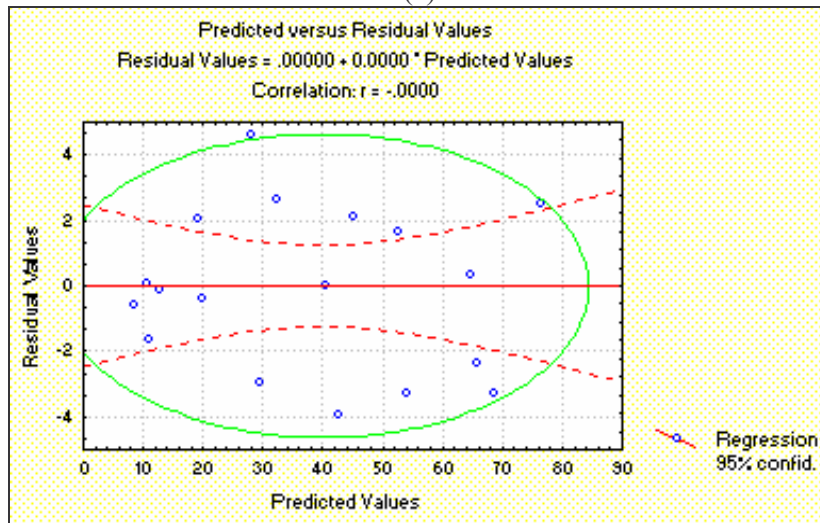
After having gathered all S data (without the outliers) and having performed the linear fitting on the extended data set, we obtain the results given in table 5, and illustrated on figure 13.

Table 5: Calibration for S, carried out on the extended dataset

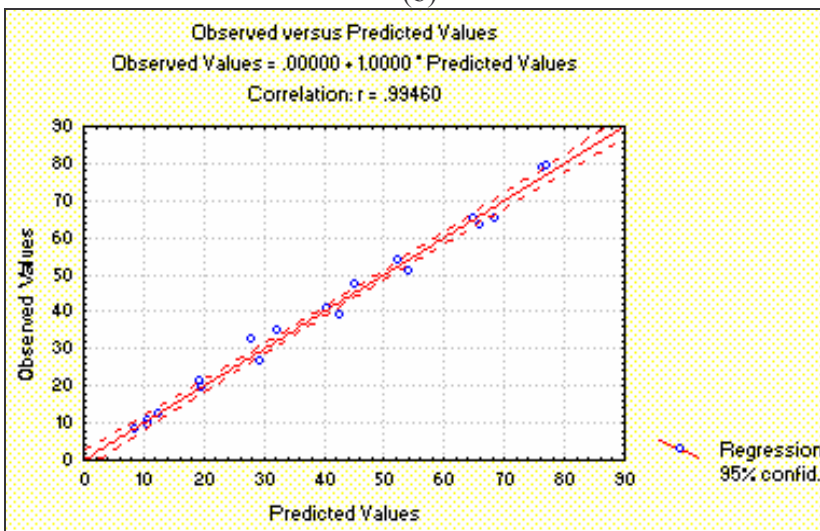
Statistical data	Value
Initial degrees of freedom	19
Proportion of variance explained	98.92 %
Slope	20.4
Radius of I.C. for the slope (95 %)	1.3
Intercept	1.9
Radius of I.C. for the intercept	2.8
Intercept statistically equal to 0?	Yes
Slope statistically equal to previous values?	Yes



(a)



(b)



(c)

Figure 13: Calibration for S (extended dataset without outliers)

4.2 Validation

As foreseen (see table 1 and the associated discussion), three ASTM low alloy standard steels were submitted to analysis for validation. The results obtained for C are reported in table 6, while table 7 give the results for S.

Table 6: Measurement of C in three certified ASTM standard steels

Steel	Certified content (wt. %)	Mean measured content (wt. %)	I.C. Radius (95 %)	Number of points	Statistically equal to certified value?
30f	0.490 ± 0.004	0.48	0.011	6	Yes
291	0.177 ± 0.001	0.174	0.0059	7	Yes
361	0.383 ± 0.001	0.380	0.0069	5	Yes

Table 7: Measurement of S in three certified ASTM standard steels

Steel	Certified content (wt. %)	Mean measured content (wt. %)	I.C. Radius (95 %)	Number of points	Statistically equal to certified value?
30f	0.0085 ± 0.0003	0.0079	0.00070	6	Yes
291	0.020 ± 0.001	0.017	0.0010	7	No
361	0.0143 ± 0.0003	0.014	0.0014	5	Yes

All measured data (mean values) are statistically identical to the certified values, except in the case of steel 291 for S, for which the measured value is 13 % below the certified mean value. We have no explanation for this. Even when considering the error on the certified value, the observed result remains statistically lower than the certified concentration of S. An attempt to check for an eventual influence of the use of an extended calibration failed: using the calibrations associated to each individual measurement yields the same conclusion. In fact, calibration 2 seems to deliver low values while calibration 1 delivers high values. These calibrations were taken at different days. A particular point is that the ambient temperature was particularly high, and changed quite a lot during the day for calibration 2. We suspect that the temperature in the detector chambers may have been influenced as a result of ambient temperature variations. This may be due to the fact that the Peltier elements are cooled by forced convection of air¹³. Water cooling would be preferable. The alternative is to install the system in a lab equipped with air conditioning. Another point is that a possibly enhanced combustion accelerator could be checked, pretty much as is done in the case of nickel alloys ^[12].

Temperature effects may also be responsible for the observed dispersions, which are somewhat greater than the values reported by the manufacturer (better than 2 % for contents < 100 ppm and better than 1.5 % for contents > 100 ppm). For the sake of comparison, we calculated the ratio of our I.C. radii on the corresponding mean values. Results are given in table 8.

¹³ One counter argument might be that neither the detector displays nor the software reported abnormalities in relation with the detector temperatures.

Table 8: Comparison of the expected dispersion (manufacturer spec.) with observed errors

Steel	Element	Manufacturer spec.	Ratio of I.C. radius on mean
30f	C	< 1.5 %	2.3 %
291	C	< 1.5 %	3.4 %
361	C	< 1.5 %	1.81 %
30f	S	< 2 %	8.8 %
291	S	< 2 %	5.7 %
361	S	< 2 %	9.7 %

Generally, for analytical measurements in the ppm ranges, dispersions around 5 to 10 % are acceptable. Therefore, one may consider that the results are good, although we have the feeling that they could be better if they were carried out in thermostatic conditions. Another point is that for S, we are pretty close to the reported detection limit, while we used not more than about 400 mg for each sample. Using more material would help, but then, considering the need to carry out replicates whenever possible, the total amount of material needed for the determinations may impair the local character of the required sampling.

4.3 Further assessment of the dispersion through replicates

Eight additional measurements were carried out with ASTM 361. All measurements for this steel were considered as one single dataset. Table 9 shows the summarized results.

Table 9: Further study of the dispersion by carrying out replicates

Element	Certified content (wt. %)	Mean measured content (wt. %)	I.C. Radius (95 %)	Number of points	Statistically equal to certified value?
C	0.383 ± 0.001	0.394	0.010	13	Yes ⁽¹⁾
S	0.0143 ± 0.0003	0.0141	0.00069	13	Yes

(1) Only if we combine the error both on the certificate and the measurement

These results indicate that:

- The relative dispersion remains above the manufacturer specifications, although the number of measurements increased markedly: for C, the radius of the I.C. represents still 2.8 % of the mean. For S, we have 4.9 %. Here, we do not present a full analysis of the variance, but it is worth mentioning that a close look at the detailed results reveals that a non negligible part of the observed dispersion is due to the different calibrations;
- All calculated means are statistically equal to the certified value, but for C, we had to consider the error reported on the certificate to conclude positively. This is a common way of doing, but not equivalent to the more severe one sample t-tests according to which the centre of each interval should be inside the other interval;
- Nonetheless, considering that an error around 10 – 12 % is acceptable for low level measurements, we consider that the method is validated.

5 Conclusions and recommendations

A new method allowing the determination of total S and C in solid samples has been made operational. The method has been successfully validated. However, we observed that although the precision of the results is fully acceptable (better than 5 % for C and better than 10 % for S), the accuracy may suffer in some circumstances. We recommend the following enhancements for future measurements:

- If possible, use more material (up to 1000 mg) when measuring low contents. This may increase the risk of facing incomplete combustion, but the quality of the results should be better. Throughout our study, we used limited amounts of materials, essentially because we wanted to maintain the local character of future sampling operations, but this may be one of the reasons why some results (slightly) lacked accuracy. On the other hand, the availability of enough material remains a limiting factor for doing so;
- For C measurements and since we did not have a separate furnace, we degassed the boats during maximum 10 minutes. We recommend increasing this time up to at least 20 minutes. A separate furnace for the pre-treatment of the boats would greatly help in keeping the overall analysis time for series within reasonable limits;
- If possible, install the system in a laboratory equipped with air conditioning. We suspect that the part of the variance due to calibrations carried out in different ambient conditions (particularly under high ambient temperature) may result from temperature effects on the detectors;
- For calibrations, 5 points taken within the targeted concentration ranges appear to be a minimum;
- The software is equipped for carrying out linear fittings on calibration data, but we recommend to export all the data for closer examination using Excel;
- For future calibrations, give the preference to making use of more than 2 certified steels. This is because the errors on the certified values are included in the calibration results. The more different steels are used, the more likely these errors will be randomly distributed, thereby decreasing the risk of biasing the results;
- If sufficient material is available, carry out at least 4 replicates for each measured sample.

Next to these recommendations, we recommend to further assess the influence of the combustion accelerator, considering also alternate products. Future work may also cover additional activities. Indeed, the configuration of the device is versatile, especially considering that the detectors are physically separated from the furnace and its associated control units. Therefore, the following perspectives are of interest:

- Additional detectors may be mounted for the NDIR detection of other gases (e.g. CO, NOx), with or without coupling to the oven;
- It would also be easy and cheap to conceive a gas loop in which a gas sample could be injected and further quantified by passing through the existing detectors. Particularly, a TIC unit could be easily conceived;
- An interesting enhancement to address even lower contents of the targeted elements consists in chemically and reversibly trapping them on adequate cartridge. The trapped gases can then be released in one shot and be analysed by passing through the detectors. Such enhancement has been described in the literature in the case of ultra-low levels of S ^[12].

6 Acknowledgements

We are indebted to W. Claes, M. Eykmans, J. L. Puzzolante, L. Sannen, S. Van den Berghe and G. Verpoucke for their assistance in allowing these results to be delivered timely. We aim also to thank N. Van der Borgt for having carefully reviewed the layout of the document, and S. Bruers (company Anatec) for fruitful exchange of information.

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8 Annex: Detailed characteristics of the chemical products

8.1 Combustion accelerator

We used tin pellets manufactured by Riedel de Haën and distributed by Sigma-Aldrich. The product reference is "Sn granulated ref. 14507". The CAS number is 7440-31-05. The purity is given in table A1. One pellet corresponds to approximately 120 mg of Sn.

Table A1: Tin certificate

Element	Specified value
Br	< 0.02 wt. %
Cu	<0.01 wt. %
Fe	< 0.02 wt. %
Pb	< 0.05 wt. %
Sb	< 0.05 wt. %

8.2 Ascarite[®]

Ascarite[®] is a registered trademark owned by Arthur H. Thomas & Co for designating sodium hydroxide-coated silica. We recommend a particle size of 8-20 mesh, as distributed by Sigma-Aldrich, under the reference number 223913. The CAS number is 081133 – 20 – 2. There is no particular analysis certificate for this product.

8.3 Anhydrone[®]

Anhydrone[®] is a registered trademark owned by Mallinckrodt Baker, Inc. for designating anhydrous magnesium perchlorate. The product is manufactured by Alfa Aesar (Johnson Matthey) and distributed by VWR international under the reference ALFA 11636.36. It is an analytical grade reagent (ACS). The CAS number is 10034 – 81 – 8. No detailed certificate was provided by the manufacturer. The lot number of the product we used is I28P15.

8.4 Oxygen

The Premium quality from Air Products is recommended. The certification as given by the manufacturer is reported in table A2, together with the reference numbers as reported on the gas cylinder that has been used for the validation work.

Table A2: Oxygen certificate

Item	Number or certified content
PR number	PR28275
RT number	RT25129
MSDS number	300000000110
Lot number	46.17/06/2005-8945
H ₂ O	< 5 ppm
CO + CO ₂	< 1 ppm
THC (as CH ₄)	< 1 ppm
H ₂	< 1 ppm
N ₂	< 40 ppm