

**QUANTIFYING SOURCES OF
VARIATION IN PROCESS
ANALYTICAL MEASUREMENTS**

**Identification, estimation and reduction of sources
of variation in the production, sampling and
analysis of steel**

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Faculteit der Natuurwetenschappen, Wiskunde en Informatica

*Variety's the very spice of life,
That gives it all its flavour*

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Voorwoord

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Tenslotte bedank ik mijn vader voor het aanhoren van mijn verhalen over mijn proefschrift tussen zijn eigen verhalen door. En Ingrid, ♪....^a, ik zou niet weten wat,

A handwritten signature in black ink that reads "Renger". The signature is written in a cursive style with a long horizontal stroke underneath the name.

^aVoorwoord in proefschrift I.J. Bosman, 1996

Chapter 1

General introduction

In production process environments, many sources of variation have an influence on the quality of the final product. To comply with product specifications, the production process has to be monitored and controlled. For process control, reliable analytical, preferably on-line, chemical measurements are needed. A problem arises when the total variation apparent in the measurements approaches, or even exceeds the allowed variation as specified in the product specifications. Analysis results are used for both process control and qualification of products. In case of qualification, a product can be accepted, downgraded or rejected based upon analysis results obtained from samples taken from the product. Because of the variation in the analysis results, errors in these decisions are inevitable. Two types of errors can be recognized:

1. Acceptance of a product while it does not meet the product specifications.
2. Rejection of a product while it meets the product specifications.

In the first case a product that does not meet the requirements is delivered to the customer. The second case results in downgrading or even total rejection of a product that is well suited for the application it is produced for. Both errors cause economic damage and should be prevented. To prevent both false rejection and false acceptance of the product, the variation in the analysis results should be small compared to the allowed product variation. If this prerequisite is not met, variation reduction is needed to comply with the demands from clients.

Another situation can occur as well. When clients request for products with improved product specifications, the process needs to be optimized in such a

way that variations in the product are reduced. To reduce the process variation and thereby improve the product quality, the process needs to be controlled more strictly. This is possible only when the variation in the measurements for process control are reduced. Hence, before optimizing the production process, both sampling and analysis have to be improved to be able to measure the consequences of adjustments made to the production process.

At the Dutch steel company *Hoogovens^a Staal BV^b* research on the topic of variation reduction in the production, sampling and analysis of steel was initiated to ensure that concentrations of the element in the final products comply with demands from clients, now and in the future. Others¹⁻⁸ have recognized as well that improvements in the process analytical measurements are needed and that variation reduction is an important issue in the control of the steel making process. Although current demands give no rise to concern, effort has to be put in variation reduction in the analysis results because demands will become more and more stringent in the future.

The production of steel products such as soda cans and car parts is a complex process. Chapter 2 describes this process in some detail to put the research presented in this thesis into perspective. The research concentrates on that part of the production process where liquid iron has been transformed into steel and is ready to be cast into moulds to form slabs of steel.

One method of improving the analyses is the development of more accurate and precise methods of analysis. Many researchers have searched for methods to improve process control in steel production. Several investigations involved the use of a laser as both a sampling and an excitation source. Others focussed their research on in-situ analyses. In Chapter 3, an overview is presented of studies that may give more insight in possibilities of improving process control in steel production.

Currently, spark optical emission spectroscopy (spark OES) is still the most favourite analysis method for analysing steel samples. The method is fast and both accuracy and precision meet the required conditions. With spark OES, solid steel samples are analysed and analysis results for the elements C, Mn, P, S, Si, Al, Cu, Sn, Cr, Ni, Mo, Nb, V, B, Ti and Ca are reported to the process engineer. A detailed description of the spark OES and the used samples is presented in Chapter 4.

^aThe name *Hoogovens* translates to blast-furnaces in English.

^b*Hoogovens Staal BV* merged with *British Steel plc* in 1999 forming a new company called *Corus Group plc*. The research described in this thesis was performed before the two companies merged and therefore, only the Dutch steel company is mentioned.

The analysis results of the spark OES are used to monitor and control the chemical composition of the steel bath. As stated before, the customer demands are expected to become more and more stringent in the future and therefore, improvement of the analyses is needed. Replacing the spark OES with laser based analysis methods is one solution but these methods still need to prove their applicability. Another method is improving the currently used methods of sampling and analysis. Such improvements can be performed by means of trial and error but this is not preferable because the model according to which the variation is build-up will be unknown. A more strategic approach in which possible sources of variation are taken into account will give a better insight in the structure of the total variation apparent in the final analysis result. Chapter 5 presents such a strategic method consisting of six steps, each to be performed consecutively. The strategy has been applied to the sampling and analysis procedure as used at the *Hoogovens Staal BV Laboratory for Process Control*.

Two chapters are devoted to the subject of identification and quantification of variation in the production, sampling and analysis of steel. Chapter 6 describes the setup of the experiments and reports the results for one type of steel^c. To test whether results for one type of steel holds for other types of steel as well, Chapter 7 presents the results obtained for three different types of steel.

In Chapter 4, a description is given of the calibration method used for the spark optical emission spectrometers (spark OES) at the Hoogovens laboratories for process control. This method has been developed and changed time after time over the years based on new insights and the introduction of better instruments. The calculation is a rather complex combination of different procedures. Although this method has been developed and improved over the years, alternative methods may be used to improve the accuracy and precision of the analytical results. However, before implementation, such methods need to be verified to certify the continuation of the steel making process. Implementation of an alternative method might result in further deviations thereby influencing the process control. Experiments presented in Chapter 8 have been performed to test whether changes to the current calibration method can reduce the variations in the analysis results. The experiments concerned simulations in which alternative methods to calculate the concentrations from intensities were tested. Results for the elements carbon (C), manganese (Mn) and phosphorus (P) are shown in this last chapter.

^cSteel can be produced in many different compositions. Steel with a certain composition, for instance composition 1, is called type 1 steel in this thesis.

Chapter 2

Production of steel; from iron ore to soda cans

Production of steel is a complex process in which iron ore is reduced to metallic iron. Further refinery of the formed iron to steel is performed by carefully removing and adding certain elements such that finally the product meets certain quality standards. The description of the production of steel given in this chapter concerns the steel production process currently in use at the Hoogovens steel company. In the future, probably other methods such as thin slab casting of steel will become more common because of the decreased time between order and delivery. This introduction to the production of steel should help the reader to put the research presented in this thesis into perspective. Therefore, a general description of the production process is given with some more detail of those parts of the production process that were included in the research^a.

2.1 Raw materials

For the production of steel mainly two raw materials are of importance: iron ore and coke. Besides these two, other materials such as scrap, pure (or near to pure) metals and gas like oxygen and argon are used during the production process. Iron ore and coke, however, are the two starting materials which are fed into the blast-furnaces.

^aThe information presented in this chapter has been gathered from a technical report⁹ and personal communications.¹⁰

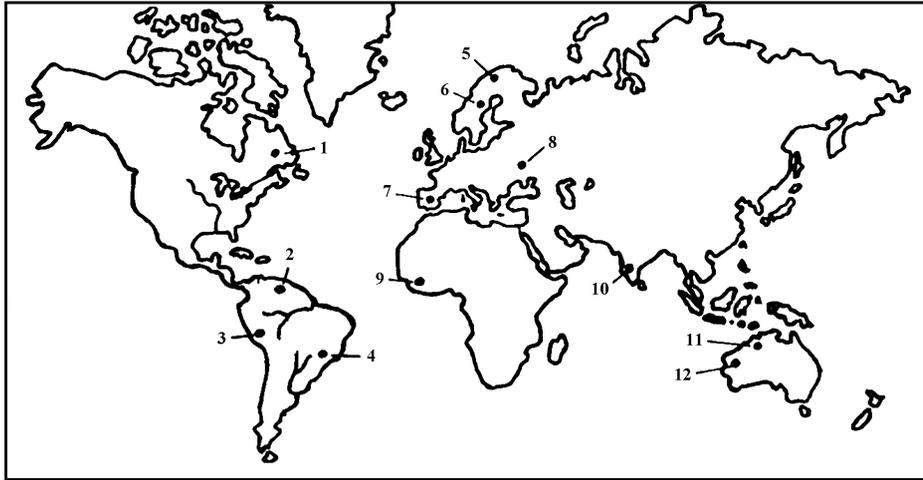


Figure 2.1: Places where iron ore is found over the world. 1) Carol Lake and Mount Wright, Canada; 2) Orinoco, Venezuela; 3) Marcona, Peru; 4) Itabira, Ferteco and Samarco, Brazil; 5) Kiruna, Sweden; 6) Malmberget, Sweden; 7) Granada, Spain; 8) Krivoi Rog, Russia; 9) Bong Range, Liberia; 10) Goa, India; 11) Mount Newman, Australia; 12) Hamersley and Robe River, Australia.

2.1.1 Iron ore

The solid crust of the earth consists for approximately 5% of Iron (Fe). Concentrated regions of iron oxide are found as magmatic or sedimentary deposit. Magmatic iron ores originate from molten magma that penetrated the solid crust of the earth. The ferrous compounds crystallized at an early stage and precipitated to layers of iron oxide which can become huge such as Swedish magmatic iron ore reserves in Kiruna and Malmberget (5 and 6 in Figure 2.1). These reserves consist mainly of Fe_3O_4 and therefore are called magnetite ores. Magnetite ores consist for 72.4% of Fe.

Another source of iron ore is sedimentary iron ore. Iron minerals became concentrated when, due to erosion (wind, water, frost), parts of the earth crust were transported to, for instance, the bottom of the sea. Due to selection (based on particle size and other physical properties) natural concentration took place. The so-called sedimentary iron ore is found as haematite (Fe_2O_3) which consists for 70% of Fe. Haematite is found at for instance Carol Lake, Mount Wright and Itabira (1 and 4 in Figure 2.1).

A third kind of iron ore is of lateritic origin. This kind of ore is a residual of

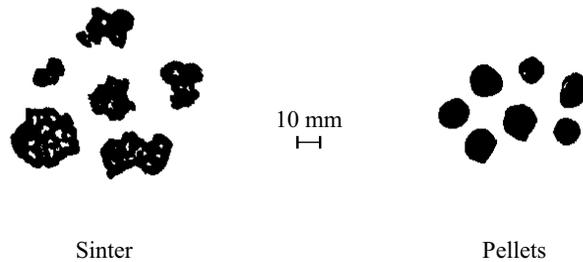


Figure 2.2: Drawings of two forms in which coke is used for steel making: sinter (5-25 mm) and pellets (10-15 mm).

material which resided after all other components of the rock was washed away by water. Again, natural concentration occurred leaving the water containing oxide limonite ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) behind which contains approximately 50-60% of Fe. Places where oxide limonites are found are Orinoco, Goa and Robe River (2, 10 and 12 in Figure 2.1).

Iron ore dug from the mines has to be prepared in such a way that an optimal process control is possible in the blast-furnace. Many factors have a certain influence on the efficiency of the blast-furnace process. One of those factors is the quality of the iron ore which has to comply with two important properties:

- The reducing gasses which flow through the blast-furnace must not be obstructed (open structure of the ore).
- The reducing gasses must be able to reach the iron ore in order to let reduction of oxidic iron take place quickly (high surface to volume ratio of the ore).

A good permeability of the blast-furnace can be obtained by choosing the right particle size of the charge (between 5 and 50 mm). Besides that, the particles need to be strong enough during reduction in order to prevent crumbling of the particles which would reduce the permeability. Two forms of prepared iron ore are used in the blast-furnace namely sinter and pellets (Figure 2.2).

Production of sinter

Sinter production is started by mixing iron ore, coke (fuel) and additives together to produce a homogeneous mixture. Water and quicklime are added in order to produce micropellets. In the sinter furnaces, the small particles are baked together to form larger particles of sinter. The temperature in the

furnace (1300 °C) is high enough to ignite the fuel (coke) which is mixed with the iron ore. The temperature increases to 1400 °C which is just high enough to let the iron ore particles melt together. The large slabs of sinter are broken and cooled down. The cooled down sinter is sieved and particles in between 5 and 25 mm are used for the blast-furnaces.

Production of pellets

Pellets or balls of iron ore are formed from very fine particles of iron ore and additions. As a first step in producing pellets, iron ore and additions are ground thoroughly to form particles smaller than 0.045 mm. After grinding, the powdered material is mixed with water to form so-called green pellets. These green pellets are still wet and soft and have to be baked into hard pellets. After baking at a temperature of 1320 °C, the pellets are sieved and the fraction smaller than 3 mm is used for the production of sinter. The fraction in between 3 and 25 mm is used in the blast-furnaces.

2.1.2 Coke

For the production of coke, coals are used. These coals originate from the remains of plants that lost their gaseous constituents such as hydrogen, carbon dioxide and methane under influence of temperature and pressure. The more gaseous constituents are lost, the higher the carbon concentration becomes. An increase in carbon content results in a change of appearance ranging from brown vegetable mould through black graphite and transparent diamond. The coals used for steel production contain in between 18 and 35% gaseous components. The coke which is produced from the coals have three main functions in the blast-furnace process:

- Fuel in order to keep and bring the furnace up to the right temperature.
- Reduction of iron oxide to atomic iron.
- Means to maintain the permeability of the blast-furnace charge for gases.

As a first step in forming coke for the blast-furnace, the coals are broken into pieces. After breaking, 70% of all particles must be smaller than 2 mm. The particles of coal are prepared by heating in coke ovens until approximately 1000 °C. During this process, the coals are isolated from air. The gaseous compounds are separated from the solid carbon and the small particles of coal melt together thereby forming the coke which is needed. The coke is “well

done” at this stage of the process. At that moment the coke has been heated during a period of in between 16 and 20 hours. After this time, the coke is removed from the coke machine and to prevent the coke from burning it is quenched with water. The cooling is performed with a predestined amount of water to ensure that the water content is in between 4 and 5%. The coke is sieved and three fractions are distinguished:

- 0-20 mm: Used for iron ore preparation.
- 20-35 mm: Fine coke for usage in blast-furnace.
- > 35 mm: Rough coke for usage in blast-furnace.

Besides the coke produced in the coke ovens, also powdered coals are used in the blast-furnaces. These so-called injection coals are produced by grinding the coals in ball mills.

2.2 Blast-furnaces

In Figure 2.3 a schematic drawing of a blast-furnace is presented. The mouth of the furnace is situated at the top and is shut off from the air by means of a gas lock which consists of 2 valves. The base material of steel (sinter, pellets and coke) and additional material is elevated to the mouth and cast into the top of the blast-furnace above the small valve (Figure 2.3^a). When the small valve is opened, the material enters the space in between the small and the large valve (Figure 2.3^b). The small valve is closed again and the space in between the upper and the lower valve is filled further by repeating the above sequence. After a few sequences, the small valve is closed and the large valve is opened. The usage of the two valves prevents contact between air and contents of the blast-furnace. As soon as the large valve is opened, the raw material falls into the furnace via armour plating (Figure 2.3^c) that can direct the material to predestined places in the furnace. Other types of blast-furnaces exist but the description of other set-ups is beyond the scope of this chapter.

Iron ore is a mixture of mainly iron oxides and gangue^b. In the blast-furnace, iron oxide is reduced to metallic iron and it is thereby separated from the gangue. The gangue appears as slag floating on the surface of the liquid metal. The processes of reduction and separation can only take place when heat and a reducing agent are provided and here is where the coke comes back into the

^bGangue is the commercially worthless matter in metal or mineral deposit.¹¹

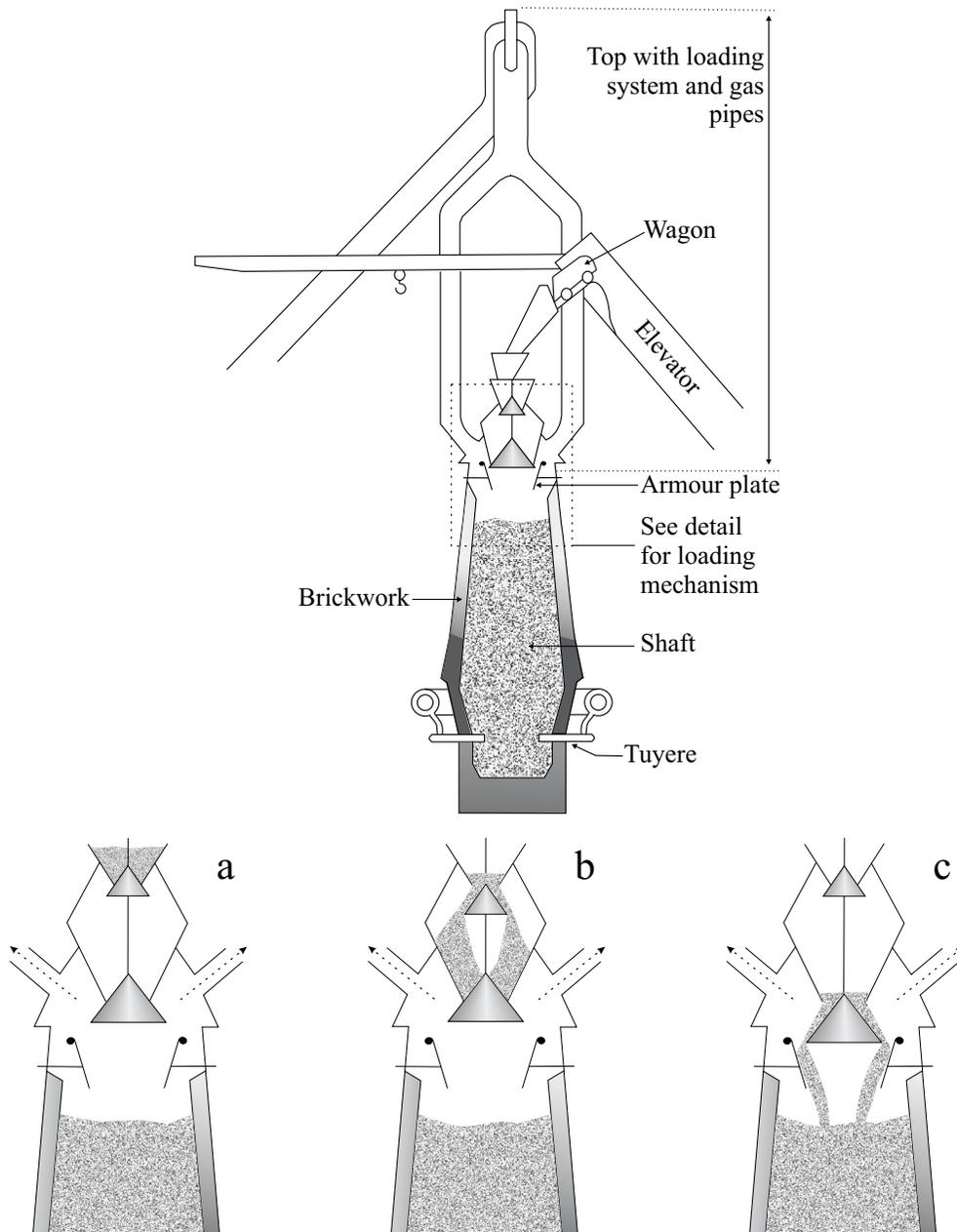


Figure 2.3: Schematic presentation of a blast-furnace and the use of valves for filling the blast-furnace; a) both valves closed; b) small valve opened, large valve closed; c) small valve closed, large valve opened, the material falls into the blast-furnace shaft.

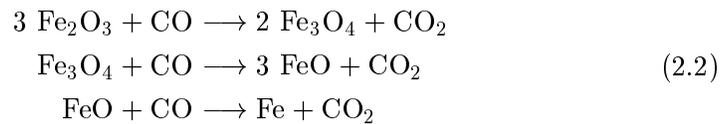
picture. Coke works both as a reducing agent and as a source of heat. Also, coke has a high melting point and therefore serves as a kind of matrix which gives porosity to the contents of the blast-furnace. Porosity is needed for both flow of liquid metal and flow of gas. Without this porosity, the furnace would clog.

Filling of the blast-furnace is performed almost continuously. While new solid material is added to the top, preheated air with a temperature between 950 and 1300 °C (even higher when powdered coals are injected) is blown in at the bottom. Coke, close to the points of entrance of the preheated air burns intensively and at those points, temperatures between 2000 and 2400 °C can be reached.

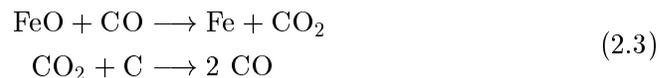
The coke in the blast-furnaces will burn and the formed carbon dioxide will reduce immediately to carbon monoxide due to the intense heat (equation 2.1).



The carbon monoxide will react with the iron oxide. An example of such a reaction is presented in equation 2.2 in case of the iron oxide Fe_2O_3 .



This type of reduction is also known as indirect reduction and takes place in the upper part of the blast-furnace where the temperatures are in between 570 and 1000 °C. Lower in the blast-furnace where temperatures above 1000 °C prevail, the CO_2 formed according to equation 2.2 immediately reduces back to carbon monoxide according to equation 2.3 due to the high temperature and the abundance of carbon (coke).



Combining both reactions in equation 2.3 and deleting equal components on both sites of the equation, equation 2.4 is obtained which is known as direct reduction. Indirect reduction is preferred because that type of reduction is less energy consuming.



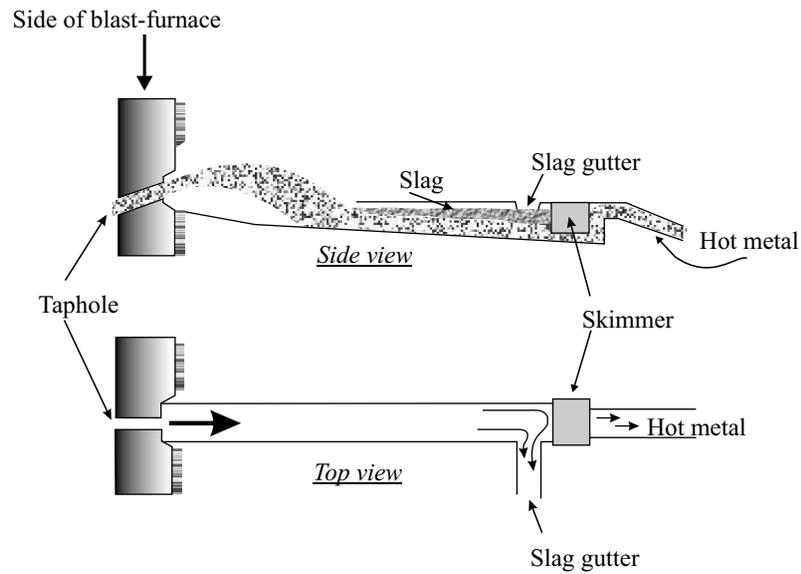


Figure 2.4: Schematic presentation of the separation between hot metal and slag at the outlet of the blast-furnace.

2.2.1 Tapping

The liquid metal formed in the blast-furnace is called hot metal (sometimes referred to as pig iron) and still needs to be converted to steel. Hot metal and slag flow out of the blast-furnace and are separated from each other by means of a skimmer (Figure 2.4). The hot metal (which still contains some slag) is cast into torpedos (Figure 2.5) which transport it to the steel factory by railway.

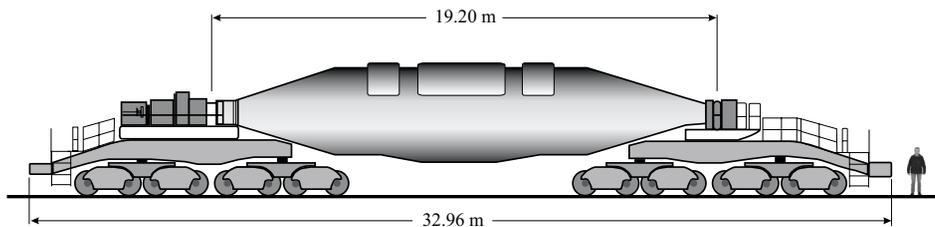


Figure 2.5: A so-called torpedos, used for transport of hot metal by railway.

Table 2.1: Examples of the composition of a number of steels.

Type	Properties	Added elements
Alloyed, refined steel	High strength and toughness	Ni, Cr, V, Mo, Wo
Durable steel	Higher durability	Mn, sometimes Cr or Mo
Stainless steel	Resistant to rust and acid	Extra Cr, Ni, Mo, Ti
Heat resistant steel	Resistant to high temperatures. Suitable for exhaust pipes of motors	Cr or Cr and Ni, possibly Ti
Alloyed tool steel	Loses toughness above 600 °C	Wo, Cr, V, Co

2.3 Steel Production

Many different procedures have been invented for the conversion of hot metal into steel (Frischen, Puddle process, Bessemer process, Siemens-Martin process, Thomas process, Oxygen steel processes and electrical processes such as arc-furnace, induction-furnace and resistance-furnace). All techniques have in common that the carbon is reduced to an acceptable level by means of combustion. The production of pure oxygen can be performed in an economically sound way and therefore, at Hoogovens, oxygen is blown on the liquid metal bath to reduce the carbon content in the metal bath.

2.3.1 What is steel?

Steel is malleable iron. The reason why the hot metal produced in the blast furnace is not referred to as steel is that the carbon content is too high and therefore, the hot metal is not malleable. During the reduction process in the blast-furnace, carbon has been dissolved in the liquid iron and appears as iron carbide (Fe_3C) or as graphite in the iron. The amount of carbon in hot metal ranges from 4 to 4.5% and causes the solid material to be hard and brittle. Milling or welding of this material is not possible. Reduction of the carbon content below a concentration of 1.9% results in obtaining a material that is referred to as steel. Summarizing, in the blast-furnace carbon is added to remove oxygen bonded to iron and in the next phase, oxygen is added to the liquid metal bath to remove dissolved carbon.

Many different types of steel exist of which a number are summarized in Table 2.1. Even small differences in concentration can make a large difference in properties of the steel product.

Table 2.2: Typical desired concentrations in hot metal for the oxygen steel process.

Element	Concentration in hot metal	Concentration in steel
C	4.50%	0.06 %
Mn	0.70%	0.35 %
Si	0.57%	0 %
P	0.11%	0.014 %
S	0.020%	0.010 %

2.3.2 Oxygen steel process

Hot metal is the main base material for the oxygen steel process. To guarantee continuity of the process, certain elements have to be present in a certain concentration as shown in Table 2.2 for most types of steel.

Phosphorus and sulphur need to be removed from the hot metal. Adding simultaneously oxygen and lime causes most of the phosphorus to end up in the slag layer that floats on top of the hot metal. For the desulphurization, lime is needed as well. Before further processing the material, the slag layer is removed to prevent the sulphur from re-entering the hot metal at a later stage of the process.

Besides hot metal, also scrap is an important base material. The concentrations in scrap material are already at or near the target concentrations if the material originates from the own factories. Scrap material obtained from other sources are added as well but may contain significantly different concentrations than those apparent in own scrap. Due to this diversity, input of scrap has to be controlled such that target concentrations of certain elements, which are difficult to remove, are not exceeded. Refinement of hot metal is based on the oxidation or combustion of undesirable elements. Some elements more readily bind to oxygen and are therefore more easy to remove than others. In the process of oxidation the sequence of combustion is as follows: silicon, manganese, carbon, iron. Carbon oxide escapes as a gaseous compound while silicon oxide, manganese oxide and iron oxide are absorbed by the slag layer. Oxidation of the various elements frees a huge amount of energy in the form of heat which is used for melting scrap material. Addition of solid scrap is needed to prevent the convertor from being damaged by extensive heat development.

A pear shaped convertor is used for the oxygen steel process. Oxygen (99.6 %) is blown on the surface of the steel bath in order to oxidize the undesirable elements. The convertor is loaded with liquid hot metal (75%), solid scrap (25%) and additional material (for example lime to form a slag

layer). After loading the convertor, oxygen is blown on the surface of the liquid metal. The blowing of oxygen on the surface takes place with such a force that the slag layer floating on top of the liquid metal is blown aside. Temperatures in the range of 2500 - 3000 °C are reached at the spot where direct contact between metal surface and oxygen occurs. In order to obtain a good mixing effect, gas (argon) that enters the convertor through holes in the bottom, is blown through the liquid metal. This helps to homogenize the contents of the convertor in both temperature and composition.

When the batch of steel has reached the target composition and temperature, the batch is cast into a ladle while additional materials such as ferrous manganese and aluminium are added. The amount and type of additions are dependent upon the demand of the customer. When the steel is cast into the ladle, part of the slag is cast into the ladle as well. The steel in the ladle is transported to the stirring station or to the vacuum ladle degasser.

At the stirring station, the inert gas argon is blown through the liquid steel to obtain homogeneity in both content and temperature. Ladle additions are made as well depending upon the type of steel to be prepared. The time needed to obtain the target temperature and the amount of additions needed to obtain the target concentrations are estimated from measurements and models. Before sending the batch of steel to the casting machines, a final sample is taken and measured through spark optical emission spectrometry (see Chapter 4).

After the conversion of hot metal into steel in the convertor, the obtained material contains a lot of dissolved oxygen. One method of removing the oxygen from the steel bath is by addition of aluminium and/or silicon to the steel. A disadvantage of this method is that inclusions such as Al_2O_3 and SiO_2 will evolve. As inclusions are not allowed in some types of steel, the vacuum ladle degasser has been developed with which dissolved gas in the steel bath can be removed without adding aluminium or silicon to the steel bath. Still, aluminium is added to the steel bath to remove oxygen but the aluminium oxides are allowed to migrate to the slag layer by extending the waiting time between degassing and further processing of the liquid steel. The vacuum ladle degasser is used when:

- Only an extremely low level of inclusions is allowed.
- A very low carbon concentration has to be obtained.
- A very low hydrogen concentration has to be obtained.

In the vacuum ladle degasser (Figure 2.6) the pressure is reduced from 1000 mbar to 0.7 mbar. Due to this low pressure, dissolved gas in the steel bath will

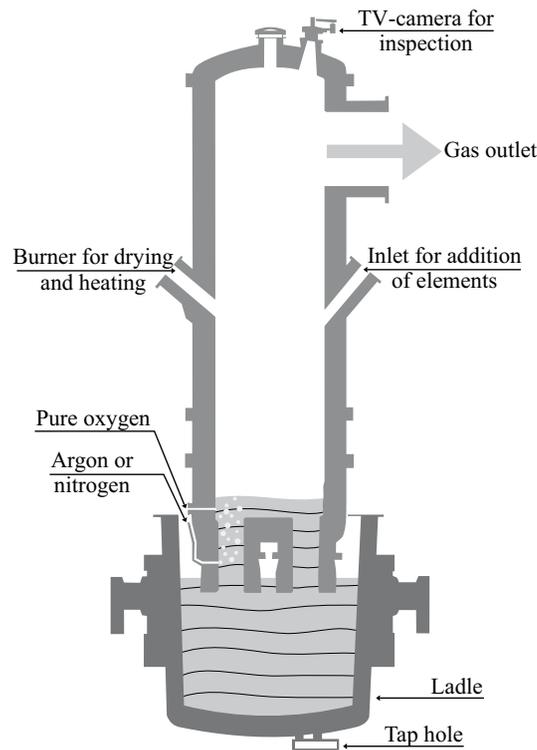


Figure 2.6: Schematic representation of the vacuum ladle degasser.

diffuse more readily from the dissolved to the gaseous state. To obtain a low pressure, a so-called vacuum vessel is immersed into the steel bath. Next, the pressure is reduced by pumping gas out of the vacuum vessel which consists of two snorkels. Through one of these snorkels, argon or nitrogen gas is entered. The combination of blowing and suction, causes the steel bath to be pumped around. When the target concentrations are reached, atmospheric pressure is retained and the batch of steel is transported to the casting machine.

2.3.3 Continuous Casting process

A schematic representation of the continuous casting machine is shown in Figure 2.7. A ready made batch of steel coming from the stirring station or the vacuum ladle degasser is cast into the so-called tundish (a) through the submerged entry nozzle or SEN (b). The steel flows through the two outlets

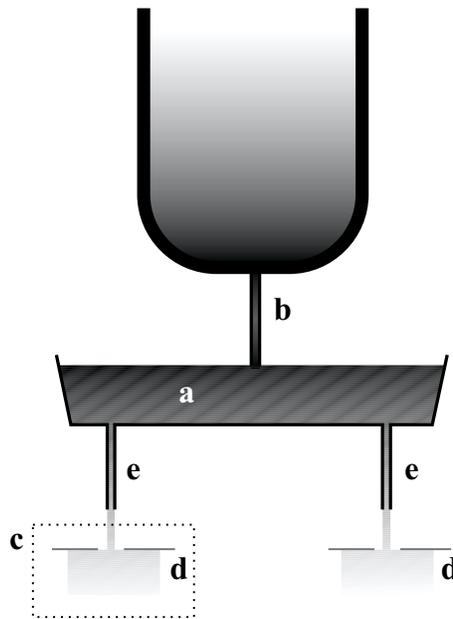


Figure 2.7: Schematic presentation (front view) of the casting machine. a) tundish; b) submerged entry nozzle; c) mould; d) slabs; e) outlets of the tundish.

(e) into the mould (c) where the steel is shaped into slabs (d) or blooms^c.

In order to obtain slabs of a certain length, cutting torches are used to cut the slabs into pieces of a certain length. Figure 2.8 shows a more detailed presentation of the continuous casting machine.

The tundish serves both as a buffer and a distribution tank. A buffer is needed to be able to cast a number of ladles of steel after each other without interrupting the casting process. From the tundish, the steel flows into the moulds in which the steel is cooled down and shaped as rectangular slabs while moving continuously (Figure 2.9).

During the casting process, the steel surface in the tundish is covered with a powder which has three purposes:

- To prevent the steel bath from cooling.
- To prevent oxidation of aluminium.
- To absorb non-metallic compounds such as aluminium oxide.

^cThe steel can be cast into blooms or slabs. The research was focussed on the production of slabs and therefore, only the casting of slabs of steel will be discussed.

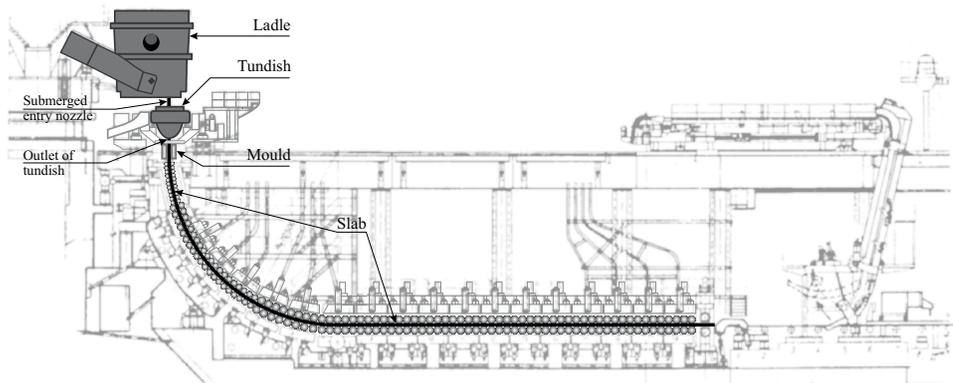


Figure 2.8: Schematic presentation (side view) of the casting machine.

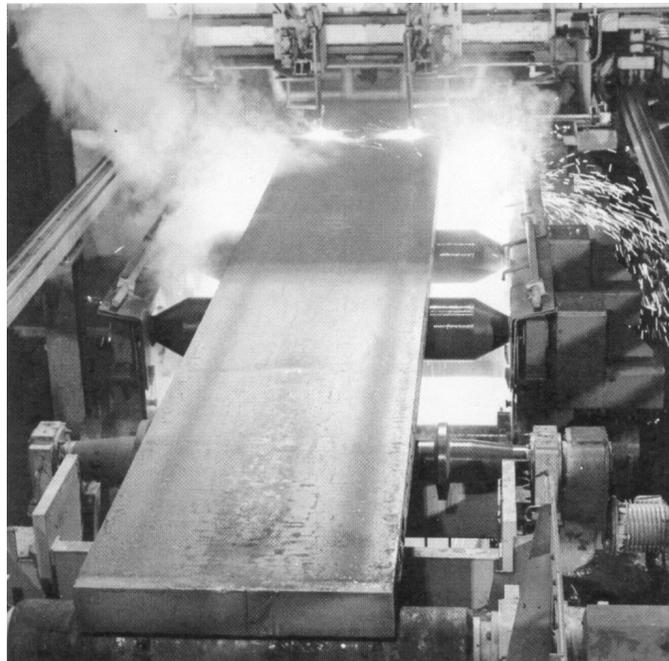


Figure 2.9: A slab of steel ejected from the casting machine is cut while moving out of the mould.

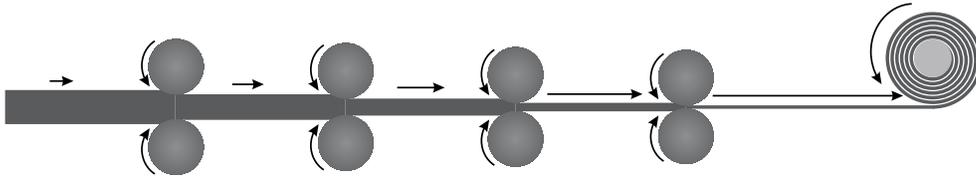


Figure 2.10: Schematic representation of the hot mill.

To grease the mould, casting powder is added to the mould. The molten powder is a good heat conductor and provides for a good heat conduction between the solidified surface and the mould. In the mould, a solid layer of steel of about 15 mm is formed. Further solidification takes place in the remainder of the casting machine under influence of cooling by water or a mixture of water and air. The formed slabs are cut into pieces of desired length by means of oxygen-methane burners which move along with the slab while cutting the slabs.

2.4 Rolling Mills

2.4.1 Hot milling

Slabs of steel with a maximum thickness of 228 mm can be reduced to a minimum thickness of 1.5 mm by means of hot milling. Before this process, the steel is heated to a temperature in the range of 1150-1270 °C. Heating of the material has two purposes: improvement of the structure on a microscopic scale and facilitation of the milling process. Milling is performed by means of pressure practised on the steel slabs by means of a series of cylinders as shown schematically in Figure 2.10.

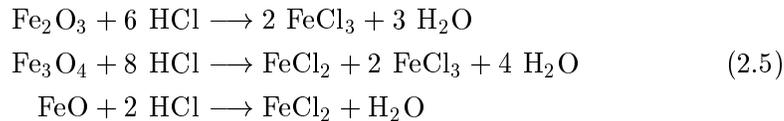
The slab becomes thinner and thereby also longer. At the end of the milling process, the steel is rolled onto reels. The rolls of steel can be transported to customers outside the steel company or processed further to improve durability or to transform the steel into products like thin plates for soda cans.

2.4.2 Cold milling

Further reduction of the hot milled product with a thickness of 2-5 mm to a product with a thickness of 0.15-3 mm is possible by means of cold milling. Cold milling of steel is performed because:

- it results in a product with a higher surface quality than the half product, hot milled steel;
- the thickness of the final result can be controlled better than is the case with hot milling;
- a thinner product is needed and this is possible with the cold milling process.

During hot milling, an oxidized surface is formed on the steel surface due to oxidation by oxygen from the surrounding air. This oxide hide is capable of doing much damage to the milling cylinders of the cold milling machine and therefore the oxide hide has to be removed before cold milling. Removal takes place by means of pickling of the oxide surface through acid. During the pickling the iron oxide on the surface of the steel is reduced according to the chemical reactions presented in equation 2.5.



Three different chemical reactions are shown because the oxide layer consists of haematite (Fe_2O_3), magnetite (Fe_3O_4) and wüstite (FeO). After removal of the oxide layer, the steel plate is rinsed with water and dried by air. Next the surface is covered with an emulsion of 25% oil in water to reduce the friction between mills and steel plate.

The thickness is reduced by the cold milling machine which is presented schematically in Figure 2.11. The extra support rolling mills are needed to prevent the working mill from bending due to the high pressure. Due to the strong transformation during milling, the structure of the cold milled material has changed dramatically which results in a very tough but breakable material.

In order to obtain a strong material that is less vulnerable to breaking, an annealing treatment is performed after cold milling the thin plate. An improved structure on microscopic scale is obtained by means of controlled heating of the cold milled plate material.

A final milling process (post milling) after the annealing treatment is performed to improve the crystalline structure of the steel plate.

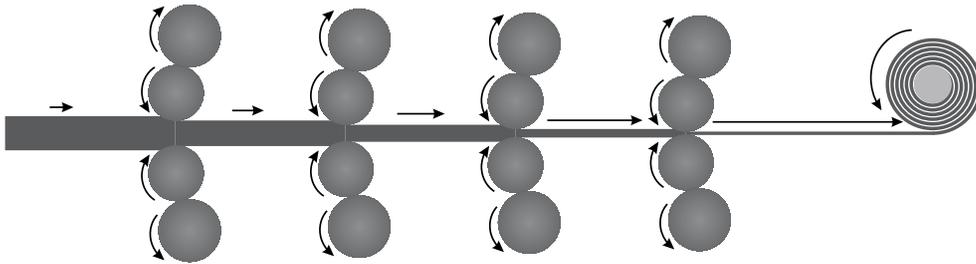


Figure 2.11: Schematic representation of the cold mill.

2.5 Further handling

To give added value to the product, the cold milled plate material can be further processed by means of galvanization, tinning or painting. Applications for these kind of thin covered plate material can be found in automobile industries, ceilings, walls, prefab buildings, central heating boilers, venetian blinds, etc.

Tinplate is used for the production of, for example, soda cans. The process of tinning is performed by means of electrolysis. Finally, from the iron ore described in the beginning of this chapter, the material is produced that forms the basis for soda cans. It should have become clear that process control and scheduling play important roles in the total process of steel making. The process steps are strongly tied together and therefore improvement of one process phase involves many of the other process phases. A high standard in process control and therefore also a high standard in analytical measurements is needed in order to meet the targets given by the customers.

Chapter 3

The need for better process control in steel production

3.1 Introduction

An increasing demand for better quality and therefore an increasing demand for better quality control exists within the steel industry.^{3,4,12-17} Quality of products and efficiency of the production process depend on fast and accurate control.¹⁶ Due to an ever increasing demand for high quality steel, the field of process analytical chemistry in steel industry has been characterized by a series of technological advances over the last decade. As a result, standards in process analytical measurements are high for steel and other metal industries.¹³ Customer demands have had great impact on improvements obtained in the last decade. These improvements are a result of interaction between different disciplines.³

In the past, wet chemical analysis methods were the only tool for process analytical measurements at steel plants. These methods needed extensive sample preliminary treatment¹⁴ and were therefore not suitable for fast process control. Nowadays, methods such as XRF^a and OES^b enable fast process analytical measurements. For quality control, still methods such as AAS^c and ICP-AES^d are in common use but those methods are too time consuming to be used for control of the steel making process.

^aX-Ray Fluorescence¹⁸

^bOptical Emission Spectroscopy^{18,19}

^cAtomic Absorption Spectroscopy¹⁸

^dInductively Coupled Plasma - Atomic Emission Spectroscopy¹⁸

Saeki⁴ states that the commonly used method of spark OES is still the best method available to analysts for process control in the steel production. Especially due to the increase in production of high performance steels and scrap recycling, an improvement in the precision, accuracy and response time of OES is vital.

In contrast to Saeki,⁴ who sees many challenges for engineers working in the field of analytical chemistry, Berglund² is concerned whether chemists will be needed in the future in process metallurgy. Future developments will reveal whether this concern is valid. Of course, nowadays sampling and analysis of steel can be performed within a short period of time. Instruments can be handled by employees which have no or little chemistry background and results can easily be interpreted. However, due to the increasing demand of high quality steel, improvements are needed in the analysis and these improvements can only be implemented by skilled analytical chemists.

The analysis of steel is a very broad field. In this chapter interest lies in reporting alternative methods that have potential to improve the accuracy, precision and speed of process analytical measurements. Dulski¹³ states: “*Analytical technology has a key function in the international competition: to ensure quality at unprecedented levels and to monitor production processes at unprecedented speeds*”. In order to fulfil this demand, various new methods have been developed to increase the quality of process analytical measurements. The following sections show alternative methods and recent developments in the analysis of steel. These methods involve off-line, at-line, on-line and in-situ methods. For a detailed description of the currently used method (spark OES) the reader is referred to Chapter 4.

3.2 Alternative analysis methods

An overview of the development of analytical methods for steel analysis in the past is given by Koch.²⁰ New methods have been developed to keep pace with the processes which demand fast analysis results in order to steer the process towards the target. In spark OES, the development of HEPS (High Energy Pre Sparking) and HRRS (High Repetition Rate Source) decreased the total analysis time dramatically from approximately 180 seconds to 20 seconds for a measurement in duplicate.

In 1992, Saeki⁴ gave an overview of developments in the analytical control of steel production with OES in Japan during three decades (1960-1990). The author concludes that OES still is the best available analysis method to control the steel production process and states that an improvement in the precision

and accuracy of OES is vital in order to cope with the increase in production of high performance steels and scrap recycling.

To improve the total analysis time, an improvement in efficiency of the analysis time is needed and therefore, the response times need to be improved. According to Hocquaux et al.¹⁶ this can be achieved by using other means of emission such as laser ablation, a method that will be discussed in Section 3.2.1.

Besides optimisation of instrumental aspects such as time resolved analysis, also new data treatment algorithms must be used to optimise the analysis methods. Not only the bulk chemistry but also the cleanness of steel will become more and more important. Hocquaux et al.¹⁶ predict that development in steel analysis will occur in three directions:

1. On-line and on-site measurements will be developed.
2. Integration into the process will be of importance.
3. OES will be used for inclusion detection and surface analysis.

A number of new analysis methods have been developed in the last few decades to improve process control. Many of these methods involve the use of lasers as a substitute to a spark source which is commonly used as an excitation source for the analysis of solid steel samples. The next sections will give an overview of methods other than spark OES which have been developed or are still under development for process analysis of the steel making process.

3.2.1 Laser Ablation (LA)

Laser radiation can be used to bring solid, liquid or gaseous material into a plasma (for an explanation about plasma, see Inter-mezzo: plasma). The laser gained potential for direct metal analysis in solid samples without sample preparation due to an increase and improvement in lasers and detectors.²¹ The laser serves both as a tool to sample part of the sample taken from the product and, for some analysis methods such as laser ablation optical emission spectroscopy (LA-OES), as an excitation source.

Two prime reactions can take place when a laser beam is focussed on the surface of a solid: vaporization and ablation. When the laser pulse is in the range of microseconds or longer and the radiation is lower than 10^6 W/cm², vaporization of the sample is the dominant process. A pulse length in the range of nanoseconds and an radiation energy of more than 10^9 W/cm² will result mainly in ablation^e of the sample surface. Vaporization of material has

^eWith ablation, a portion of the material instantaneously explodes into vapour.

the disadvantage that preferential vaporization of elements with high vapour pressure will occur and therefore laser ablation is more advantageous for quantitative analysis of steel samples.

Intermezzo: plasma

In physics, a plasma is an electrically conducting medium in which there are roughly equal numbers of positively and negatively charged particles, produced when the atoms in a gas become ionised. It is sometimes referred to as the fourth state of matter, distinct from the solid, liquid and gaseous states.

When energy (e.g. heat) is continuously applied to a solid, it first melts, then it vaporizes, and finally electrons are removed from some of the neutral gas atoms and molecules to yield a mixture of positively charged ions and negatively charged electrons, while overall neutral charge density is maintained. When a significant portion of the gas has been ionised, its properties will be altered so substantially that little resemblance to solids, liquids, and gases remains. A plasma is unique in the way in which it interacts with itself, with electric and magnetic fields, and with its environment. A plasma can be thought of as a collection of ions, electrons, neutral atoms, molecules and photons, in which some atoms are being ionised simultaneously with other electrons recombining with ions to form neutral particles, while photons are continuously being produced and absorbed.

Laser ablation (LA) is an application of the ability of lasers to concentrate energy in time. It occurs when a high radiance short pulse-width laser beam is focussed onto a material surface. In which amount absorption of the laser radiation takes place, is highly dependent upon the characteristics of the material and the wavelength of the laser. Vaporization of material will take place at the surface if sufficient energy is absorbed. The vaporized material can serve as a seed for the formation of a plasma.²² Further heating of the formed plasma may occur if the formed plasma absorbs the incoming laser radiation. When the plasma is heated to a certain level, further removal of sample from the sample surface occurs not any more due to the laser radiation but due to the heat evolved by the plasma. This is especially the case when IR (Nd:YAG) lasers are used for laser ablation. Laser radiation with wavelengths in the IR region is absorbed by the formed plasma because the plasma works as a shield absorbing the laser radiation. The plasma is transparent for laser radiation with wavelengths in the UV region (XeCl and ArF excimer lasers). For UV lasers a more explosive reaction with the sample is seen.²³ Some scanning electron microscope images show that craters formed by UV-laser shots have a nice, circular shape while the craters formed by IR-laser shots are more rough.²⁴ Even though the IR-laser is more focussed, the size of the crater formed by IR laser shots is larger than the crater formed by UV laser shots.

Geertsen et al.²⁴ investigated a number of parameters that are important for the operation of lasers in laser ablation. It appears that the efficiency of laser solid sampling depends upon:

- the melting temperature of the sample;
- laser wavelength;
- atmosphere used for plasma ignition (air, argon, nitrogen);
- laser energy.

Laser ablation is used as the basis for many new techniques for the simultaneous analysis of multiple elements in steel samples (and other solid materials such as steel slag, minerals containing stones and biologic materials). The fundamentals of this laser technique are not yet fully understood and the properties of the vapour are highly dependent upon the circumstances under which laser ablation takes place. The method is not commonly used because the laser-material interaction is not fundamentally defined so prediction and control of the ablation is still difficult. Some of the difficulties still to be solved are mentioned by Russo:²⁵

- Fluctuations in the laser's temporal and spatial profiles and nonlinear power density dependence contribute to the uncertainty in the amount of ablated material.
- The physical and chemical matrix influence the processes appearing at the sample surface and therefore the amount of ablated material.
- The particle size distribution influences the transport efficiency to the excitation source.

To understand the properties of laser ablation and increase the reproducibility of the method, all interactions need to be identified and investigated in detail. One of the properties of a laser induced plasma is that it exists at a certain distance from the ablated material. Lee et al.²¹ showed that the laser-generated plasma obtained for copper and lead samples extended respectively 2 mm and 5 mm from the sample. The choice of the optimal position for spectroscopic analysis (highest line to background ratio) is highly dependent upon the metal under investigation. Also the temperatures for the two kinds of plasma differed (13.200 - 17.200 K for copper and 11.700 - 15.300 K for lead). The main factors that influence the ablation can be summarized:

- Laser pulse:
 - Pulse width
 - Spatial and temporal fluctuations
 - Power fluctuations
- Properties of the sample:
 - Mechanical
 - Physical
 - Chemical

Compared to other analysis methods, laser ablation has several advantages of which the following are the most important:

- Solid, liquid and gaseous material can be excited.
- Conducting and non-conducting samples can be excited.
- Only small sampling regions are possible (micro meter scale²⁶) and therefore spatial analysis is a possibility.²⁷
- Small mass of sample is required (sub micro-gram scale).²⁷
- Little to no sample preparation is needed.^{26,27}
- Sample vaporization and excitation is possible in a single step.
- Real-time analysis can be performed.
- In-situ analysis in harsh and dangerous environments can be performed (by using optical fibers to transport the radiation to and from the sample).

Some disadvantages that will be discussed in more detail in the following sections are:

- The accuracy of laser ablation based analysis methods depends upon the heterogeneity of the sample.²⁷ Experiments on a microscopic scale are very useful for surface analysis but for the analysis of bulk material such as a few tons of liquid steel the overall concentrations in the complete batch are of more interest. To obtain such results, homogeneous samples which are highly relevant to the contents of the ladle of steel are needed.

The problem of heterogeneity of samples can be solved by scanning a part of the sample surface and reporting the average of the analysis results. By averaging the analysis results, the problem of heterogeneity can be reduced. However, if the sample is not highly representative for the ladle contents, a systematic error remains. A disadvantage of scanning part of the sample surface is that the response time increases.

- Small amounts of surface contaminants can complicate analysis.
- Reproducibility may be degraded by changes in surface composition and character (e.g. roughness).

Laser ablation can be coupled directly to an optical emission spectrometer but coupling to other (secondary) analytical techniques can help to increase the sensitivity, accuracy and precision of the analyses. The following sections give an overview of analytical techniques that are potential successors of the classical spark OES technique which is up till now the most frequently used technique for the analysis of solid steel samples.

3.2.2 Laser Induced Breakdown Spectroscopy (LIBS)

Laser ablation breakdown spectrometry (LIBS), also known as micro-probe spectro-chemical analysis, laser ablation optical emission spectroscopy or laser ablation spectro-chemical analysis²⁸ is a spectro-chemical analysis method that uses the radiation emitted by the laser formed plasma to quantify the chemical composition of samples. In LIBS, a laser pulse is focused on the substrate to create a plasma spot and to ablate material from its surface. The ablated material is excited in the hot plasma, and its spectral emission is recorded and analysed to identify and quantify its elemental composition.²⁹ The main advantage of this method, which applies to other laser ablation based methods as well, is that only minimal sample preparation is needed.³⁰

According to Wisburn et al.²⁹ the method is still not commonly in use because many experimental factors must be controlled in order to achieve a reasonable reproducibility. For example, the exact location of the breakdown point (place with highest emission intensity) relative to the sample and to the collecting optics is very critical but not easy to control when samples of various shapes have to be analysed. If, however, the shape of samples is standardized (as is the case in the steel industry) the position of the emission collecting optics can be optimised.

The two-dimensional *spatial distribution* of a time-integrated emission from laser-induced plasmas in air at atmospheric pressure has been investigated by Aragón et al.³¹ It seems that there is a large influence of laser energy on

the spatial distribution. The distribution also depends highly on the material under investigation. In the centre of the plasma the signal is disturbed by Stark effects (line broadening) and an intense continuum. Off-centre there is less disturbance but the intensities are also much lower. The intensities for ion-lines are only visible near the centre where the temperatures are high enough.

Besides the spatial distribution of the plasma, also the *temporal distribution* is of importance. Grant et al.^{32,33} investigated whether quantitative elemental analysis of iron ore is possible by laser-induced breakdown spectroscopy. In this study a fiber optic cable was used to transport the radiation from the plasma to the detector. The elements Ca, Si, Mg, Al and Ti were studied. It turned out that time resolved spectroscopy, in which only a part of the analytical signal is used, had a significant influence on the line to background (L/B) signal. The laser induced plasmas have a lifetime of several microseconds and in the first 250 ns the plasma emits a continuum in the wavelength range of interest. Later, a line spectrum can be detected. A cooler plasma gives more narrow lines which are therefore better resolved. Line broadening can be attributed to the doppler effect and pressure driven broadening.¹⁸ By using only a part of the analytical signal (Time Resolved) the L/B signal is increased resulting in a better accuracy.

Leis et al.³⁴ investigated the influence of the *sample matrix* on the temperature of the plasma. Both the number density of atoms and the temperature of the plasma influence the intensity of the emitted lines. Temperature and the amount of ablated material are reciprocally related. Thus more ablated material means a lower plasma temperature. The strong dependence upon the sample composition implies that calibration of the method has to be carried out with samples whose composition are as close as possible to that of the samples to be analysed. This could cause problems because many calibration samples are not similar to production samples.

The *lens focal plane position* (LFPP) is an important factor as well. The focal point should be some distance below the sample surface. According to Aragón et al.³⁵ the LFPP should be 30 mm below the sample surface. When the laser is focused below the sample surface, a larger but less intense ablation spot is obtained. Although the laser is focused below the surface of the sample, a rather small (μm) laser spot is obtained so the analysis results are representative for only a small part of the sample. When the sample is heterogeneous, this can result in obtaining analysis results which are not representative to the complete sample and therefore are not suited for process control. Because of this, the samples need to have a certain degree of homogeneity or a number of LIBS measurements need to be performed on different parts of the sample

surface to obtain reliable results.

Samples can be ablated in air, but argon serves as a better *atmosphere* than air for laser induced breakdown spectrometry, at least when carbon is one of the constituents to be determined.^{35,36} Also nitrogen can be used to reduce the background signal from carbon in air.³⁷ González used laser ablation in a N₂ filled chamber in order to improve the results of sulphur analysis. Thiem et al.³⁸ used LIBS in an ultra-high vacuum atmosphere for the quantitative simultaneous elemental analysis of alloys. A reduction of the background radiation is claimed but unfortunately a reason for this is not given.

Laser induced breakdown spectroscopy can be performed at a distance. Creemers³⁹ investigated the feasibility of using this method to analyse metals at distances between 0.5 and 2.4 m from the focusing lens and light-collection optics. The influence of variation in the lens to sample distance and the variation in the position of the fiber optic cable were studied. The distance between the sample and the lens that focuses the laser on the sample appears to be important. Focusing is important in order to supply sufficiently energy to the sample surface for ablating material. The position of the fiber optic cable determines the amount of emitted light being detected by the OES which is connected to the other end of the fiber optic cable.

Application of LIBS in other processes

LIBS is usable in other applications than in the field of process analysis of steel.⁴⁰ Determination of contaminants found on electronic micro-circuits fabricated on alumina substrates through laser ablation OES was the purpose of an experiment reported by Ottesen et al.⁴⁰ In this application, the small focus is an advantage while in steel process control this probably is a big disadvantage due to the micro-scale heterogeneity of samples taken from the liquid steel bath.

A second application of LIBS in another field than process control of steel is discussed by Ernst et al.⁴¹ LIBS has been performed in order to control radiation embrittlement occurring due to impurities of copper in steel. The use of optic fibers to deliver laser radiation to the target material was not possible and therefore, mirrors and lenses were used. For the collection of the emitted radiation by the plasma, optic fibers worked successfully. In this paper the Cu/Fe intensity ratio was used to correct for fluctuations in the emission and detection of fluorescence light. The authors warn that care has to be taken that the laser power and focusing parameters are kept constant within the same range for which the calibration curve was determined.

Geertsen et al.⁴² used laser ablation OES for microanalysis of steel, aluminium and alloys. It seems that the ablated amount of material depends upon the laser being used. UV lasers perform best because for these lasers the amount of ablated material has a linear relationship with the melting point of the material. It is stated that the method can be used for on-line and in-situ analysis.²⁶ Instability of the laser gives a need for averaging of multiple shots.

Slag, which is an amorphous and non-conducting material that is produced during steel making, is mostly analysed by XRF but Eggiman et al.⁴³ claim that analysis by means of LIBS is possible as well.

3.2.3 Laser Ablation Inductively Coupled Plasma OES (LA-ICP-OES)

In stead of detecting the emission occurring from the laser formed plasma, a secondary analytical technique can be used to increase the sensitivity of the analytical measurements. In this case, laser ablation is used as a sampling device. The ablated material is introduced into a secondary excitation instrument such as ICP for excitation of the sampled material. In laser ablation inductively coupled plasma optical emission spectroscopy (LA-ICP-OES) the laser ablated material is swept into an ICP torch by means of argon flowing over the sample and through the plasma into a tubing that leads to the ICP torch. The particles that are released from the sample by means of laser ablation are decomposed to atoms and ions in the ICP torch and the emitted radiation is detected by an optical emission spectrometer.

LA-ICP-OES can be used for both conducting and non-conducting materials and simultaneous analysis of elements is possible. A problem with the method is the small amount of material ablated by means of laser ablation which raises the limit of detection. However, according to Gagean et al.²⁶ the limits of detection are equal or better than those for spark OES. Other advantages of LA-ICP-OES compared to spark OES are: i) better reproducibility; ii) easier calibration; iii) wider range of elements to be determined.⁴⁴

In a study performed by Carr et al.²⁷ it was shown that heterogeneity of the sample is an important source of variation in LA-ICP-OES. Several other parameters can have an effect on the accuracy of the measurements such as:

- ICP emission signal duration.
- Number of laser shots used for determination.
- Time paused between laser shots.
- Laser focus.

In order to obtain reliable results, ICP signals have to be averaged over a certain period of time. Would this period of time be too short, then systematic errors are more probable to occur. The number of laser shots are important for the same kind of reason: averaging the signals from a number of measurements reduce the influence of sample heterogeneity and fluctuations during the measurements. The time paused between laser shots should be long enough to allow the sampling spot to cool down. If the paused time is too short, vaporization would prevail over ablation and this results in preferential vaporization.

The preferential vaporization during laser ablation inductively coupled plasma atomic emission spectroscopy was studied by Mao et al.⁴⁵ For this study, the Zn to Cu ratio in brass^f was measured. Laser ablation is influenced by a couple of laser beam properties such as: i) pulse width; ii) wavelength; iii) power density. Because of the preferential ablation, calibration samples should be comparable to the sample material to obtain reliable results. Pre-ablation before ICP-measurements gives an enhanced precision. It is stated that thermal vaporization that occurs due to plasma shielding is not suitable for analytical purposes. Plasma shielding influences the measured Zn/Cu ratio in three ways: i) optical density (absorption); ii) temperature (scattering); iii) interaction between plasma and solid sample (sputtering). A problem which is noted earlier is the preferential absorption of material in the transport tubing from sample to ICP. Certain elements are absorbed relatively more on the tubing than other elements. Also large particles can give some typical problems in the ICP torch.

To transport the ablated material (metal samples) from the ablation chamber to the ICP torch Ishizuka et al.⁴⁶ used PVC-tubing. The length of the tubing has a large influence on the analysis results when small amounts of material are ablated. Part of the transported material is retained in the tubing and the influence is larger when already a small amount of material is swept into the tubing.

In another study⁴⁴ concerning LA-ICP-OES, analytical results for C, Mn, P, S, Cr, Si, V, Cu and Mo in steel samples are reported. Of these elements, silicon gives rather bad results which, according to the author, is due to heterogeneity of this element or due to mass loss during transport from plasma to ICP.

^fBrass is a yellow alloy of copper and zinc.

3.2.4 Laser Ablation Inductively Coupled Plasma MS (LA-ICP-MS)

Arrowsmith⁴⁷ combines laser ablation using a Nd:YAG laser with inductively coupled plasma (ICP) connected to a mass spectrometer (MS) in order to overcome a number of problems associated with the more traditional methods for injection of sample material into a mass spectrometer. Obviously, using LA-ICP-MS, dissolution of the solid sample is not needed. Instead, the ablated material is injected directly into the ICP and MS. LA-ICP-MS is also a very fast method due to the ease (or almost lack) of sample preparation. A third advantage involves again the fact that no sample preparation in the form of dissolving is needed. In solutions, typical molecules may introduce interference. The lack of solvents excludes the possibility of having these kinds of interference.

For laser ablation, the laser is focussed on a small area of the sample which is a disadvantage when the sample is heterogeneous and the analysis result is to be used for process control. Huang et al.⁴⁸ turn this disadvantage into an advantage when trying to inspect small areas (microns) of samples with LA-ICP-MS.

Many instruments using a laser are still rather expensive but according to Baker et al.²³ the instrumental costs can be reduced by using a compact laser. A problem which probably hinders a fast optimisation of the LA based techniques is that laser ablation interactions are not yet fully understood.^{23,49} More research is needed to model the interaction between laser and sample before systematic optimisation of laser ablation related techniques is feasible.

Because of the interactions occurring with LA, the amount of material being ablated and introduced into ICP-MS is unknown. Normalization using an internal standard of the MS results is needed to correct for fluctuations in the amount of ablated material. Besides this, matrix matched standards are needed to include the effects of matrix specific interactions into calibration models. Baker et al.⁴⁹ investigated the feasibility of light scattering for normalization of signals in LA-ICP-MS measurements. The scattering signal is produced from the transported ablation aerosol. A laser source is used to send light through the ablated material. The scattered light is detected perpendicular to the laser. Materials investigated in this study include: brass, glass, soil and ceramic.

The choice of lasers to be used for LA-ICP-MS is a compromise. As stated in Section 3.2.1, the interactions occurring during ablation depend upon the type of laser being used. Radiation of UV lasers is not absorbed by the laser

induced plasma so all energy provided by the laser is used for laser ablation. Geertsen et al.²⁴ promote the use of UV lasers combined with ICP-MS because with this type of laser, ablation has better reproducibility, less matrix effects, better quantification, better spatial resolution and better sensitivity. The only problem with the UV laser is that the amount of ablated material per laser shot is larger than with the IR laser. This can cause problems for LA-ICP-MS as this method can only process a limited amount of ablated material per time unit. A material splitter might help in solving this problem.

3.2.5 Spark Source Mass Spectrometry (SSMS)

Besides the laser, also a spark source can be used to remove material from a sample surface. Spark source mass spectrometry (SSMS) has high sensitivity and is suitable for determination of all elements from lithium mass 7, to uranium mass 238. A necessary requirement for the sample is that it must be conducting. Compared to laser ablation based techniques, that can be used for both conducting and non-conducting materials, this requirement is an important disadvantage when analysing other materials than steel. Furthermore, a spark can be attracted to certain spots in the sample such as aluminium oxide inclusions leading to a systematic error in the analysis results.

Nicholas⁵⁰ examined the suitability of SSMS for the analysis of carbon, nitrogen and oxygen in steel samples. It seems that laser ablation mass spectrometry is superior to SSMS in terms of detection limits for the mentioned elements. It is unclear however, whether this method is suitable for process control in the steel making process.

3.3 On-line analysis

In the previous sections, alternative methods of analysing steel samples have been discussed. An important disadvantage of current methods is the amount of time needed to take, transport and prepare samples. In order to improve process control, fast, precise and accurate analyses are needed. Accuracy and precision can possibly be improved by using other analysis methods such as laser ablation combined with secondary methods such as ICP with MS as detection method. The time within which analysis results become available can hardly be reduced because samples still have to be transported and prepared. Therefore, on-line methods of analysis for which sample taking can be ignored, can provide for an improvement in response time. On-line analysis can provide further service to the process engineer at a number of stages and in many cases a decrease in time of sampling and delivery of results can result in a decrease

of costs and an increase of productivity.⁵¹ On-line analysis of steel during the molten phase concentrates on three principles:

- Detection of emitted or absorbed radiation.
- Analysis of evolved gases.
- Electro-chemical potential measurements.

Many researchers in the steel industry have been looking for an analysis method to analyse the chemical contents of a steel ladle on-line. The most important advantage of analysing on-line is that the process can be controlled more accurately. Off-line methods have the disadvantage that the analysis results become available only after some time t_{total} which is a summation of the time needed for sampling, sample transport, sample preparation, analysis and reporting of the analysis results. Optimal control can be expressed as a function of the above parameters and other properties of the system (the system being the production process, sampling and analysis).⁵²

An overview of attempts to achieve real-time, in-situ or on-line analysis of molten steel is given by Jowitt et al.¹⁵ It is stated that liquid steel analysis is seen as the ultimate form of control for steel-makers. Unfortunately, the mentioned methods cannot cope yet with the standard methods in terms of accuracy and precision. However, according to the theory of Van der Grinten,⁵² less accurate but fast analyses can add value to the controllability of processes. So, even though the figures of merit (accuracy and precision) are not satisfactory, the mentioned methods can add some value to process control in the steel making process.

At British Steel, methods for analysing steel in-situ have been studied. Jowitt⁵³ described the investigations of two principles aimed at providing in-situ liquid steel analysis results. Both systems involve the impact of laser light on the liquid metal surface. One method detects the emitted light from the excited atoms at the steel surface. The other method uses ablated material that is transported to and analysed by an inductively coupled plasma spectrometer. The first system suffers from large background scattering upon which the signal of interest is superimposed. Another problem is the huge amount of light which is lost during the transport from the emitting source to the spectrometer. The second system showed poor accuracy for a number of elements (Mn and Cu) for which no explicit reason is given.

Noll et al.⁵⁴ described a method based upon laser ablation as well. With this described method, raw material can be analysed by means of optical emission spectrometry without actually taking samples. This method should provide

for a faster method of analysis of for example scrap metal. However, the results are not satisfying at the moment to replace spark OES.

A high speed sensor/probe for the in-situ analysis of steel is reported by Nelko.⁵⁵ The method works as follows: a penetration tube is introduced into a molten metal bath. When a representative molten steel surface is met at a preset distance from the sensor/probe, an intense laser pulse is triggered. Pattern recognition algorithms are used to obtain the elemental composition of the molten steel. A great advantage of the method is the short analysis time (< minute). It is claimed that a laser-produced plasma sensor/probe makes rapid in-process steel analysis possible by permitting steel-makers to analyse the chemical composition of molten steel straight from the furnace. It is referred to as "*tasting steel from the bowl*". A laser produced plasma is used for the determination of the chemical composition. The statistical properties (accuracy, precision) of the method are not (yet) comparable to those of spark OES.

A study in which laser induced breakdown spectroscopy was used for remote elemental analysis is presented by Cremers et al.⁵⁶ A single fiber-optic cable is used to deliver the laser light to the sample and also to capture the light emitted by the plasma which is produced by laser ablation. The study involves the analysis of Ba and Cr in soil. Cremers et al.⁵⁶ report a large loss of intensity due to the use of fiber-optical cables and other optical parts. An increase in intensity can probably be obtained by using 2 different fiber-optic cables. Different cables suitable for applied laser radiation and radiation, emitted by the plasma can be chosen. The same setup has also been studied for the determination of steels.³⁹ In this study it is claimed that real-time analysis of molten metal streams is also a possibility but this is doubtful as scattering of the laser light, the slag layer and other disturbing factors will give very poor results when the method is used for liquid metal streams.

Besides the before mentioned methods in which lasers are used to induce emission by the constituents of the steel bath, direct detection of radiation emitted by hot steel can be performed as well. Real-time analysis in the converter can be performed by means of spectrometric measurements at the hot-spot in the converter during oxygen blowing. Due to the high temperatures, excitation and emission takes place at the hot-spot. According to Chiba,⁵⁷ the concentration of manganese can be measured with a reasonable accuracy in the range of 0.26 - 1.09 %.

Exhaust gases from the converter can be sampled and analysed by means of AAS. Ishibashi⁵⁸ reports such a method in which dust was sampled in order to determine the concentration of manganese in the converter. The particle

size of the dust appeared to be important for the correlation between the manganese concentration in the sample and the converter.

Another method (electro-chemical potential) involves mainly the analysis of oxygen by means of solid state sensors that directly measure the activity in the molten steel although new methods have been developed to measure silicon, aluminium, nitrogen, calcium and sulphur.¹³

3.4 On-site or at-line analysis

Another subject that received attention in process control is on-site analysis which means that samples taken from the process are analysed close to the process. Because the analyses have to be performed by employees which have no analytical background, the analysis procedure has to be automated as much as possible. Lambie⁵⁹ describes a system which is implemented and which results in a reduction of two minutes in response time (time between sample taken and analysis result given). Still, analytical knowledge is needed for maintenance but the system works satisfactory in 90% of the time.

Watson⁶⁰ reports the use of portable optical emission spectrometers based upon CCD (Charge Coupled Device) optics. The portable spectrometer can be used in order to verify the grade of metals. A number of requirements of on-site instruments for the identification of metals are given amongst which the simplicity of use, operation on a wide range of sample surface conditions and a wide range of concentrations, and stability are the most important. The described method was feasible due to the development of fiber optics. It is claimed that this method will be used in the future for in-situ analysis when the CCD is combined with laser ablation.

3.5 Inclusion and surface analysis

Most of the analytical techniques described in the former sections are used to perform analyses on the surface of samples taken from the process. The surface of the sample is then thought to be representative for the complete batch where the sample has been taken from. In applications like steel coating however, interest lies in analysing just the surface. Steel has the image of being a high strength bulk material. With value-added products such as tinplate, stainless steel, galvanised steel, and organically coated steel, however, it is the constitution and integrity of the surfaces that determines fitness for purpose.⁶¹ With variations in processing parameters, it is possible to control the surface properties of steel sheets over considerable range. These surface properties

influence the further processing steps for metallic and organic coating and the working or end-properties at the customer, such as phosphatability, paint ability and corrosion behaviour. Thus the chemical composition is very important for the surface properties.⁶²

Glow discharge lamps can be used for in-depth analysis of coated steels. Bengtson et al.⁶³ investigated the relation between the sputtering rate (amount of material removed from the surface in a certain time) and the concentration of the elements analysed at a certain depth. The sputtering rate depends highly upon the element concentrations and therefore correction of the signals are needed to get a concentration profile of the surface. Analysis with the glow discharge lamp might also be interesting for research on homogeneity of cast steel.

Pulsed discharge analysis OES (PDA-OES) can be used for the elemental determination and characterization of oxide inclusions in steel.⁶⁴ In normal spark emission, the intensity of a number of sparks is integrated but with pulsed discharge analysis each discharge or a selected part of a discharge can be recorded. The method appears to give results within seconds but the reliability of the method is highly correlated to the representativity of the samples because only a very small part of the sample is analysed.

Cleanliness (absence of inclusions) of steel becomes more and more important. Meilland et al.⁶⁵ show that PDA-OES can be used for the qualification of inclusions. For this kind of analysis spark is used as an excitation source. This causes problems when non-conductive inclusions exist because due to lack of attraction of the spark, more surrounding material is evaporated. The opposite problem occurs when dealing with inclusions which attract the spark more than the matrix. So, the examination of size, composition and distribution of the inclusions still is problematic. PDA-OES is suitable for investigating large areas on the metal surface in detail when a scanning mode is used.

Detection of inclusions can also be used to fingerprint or classify steel products. Pichilingi⁶⁶ uses Glow Discharge Mass Spectrometry (GDMS) to get a fingerprint of steel by means of depth profiling.

Depth profiling can also be performed by means of Glow Discharge OES (GD-OES).^{67, 68} Improvements in calibration of GD-OES are presented by Bengtson et al.⁶⁸ The calibration method compensates for variations in the emission yield (Intensity per sputtered atom). The correction involves the estimation of a correction factor which is to be determined per element. GD-OES is used for the analysis of various coated steel products: i) electroplated steel sheets; ii) hot-dipped galvanised steels; iii) phosphatized steels. For this type of analysis, the GRIMM type GD lamp is the most commonly used source for depth profiling applications.

3.6 Automation

Automation in the laboratory is often seen as a tool which helps in reducing variation, manpower and time of analysis. Palmer⁶⁹ reported that automation of analysis did not result in a reduction in manpower and the response times even increased. Reduction of manpower could not be reduced because maintenance of the equipment became the responsibility of the laboratory. Response times increased because the automated system was somewhat slower than a comparable manual system. In contrast, automation projects at *Hoogovens Laboratories for Process Control* showed an decrease in required manpower and better response times.⁷⁰

At Baoshan Iron & Steel Corp in China,⁷¹ process analytical measurements have been automated as well. The automation has not been performed in order to reduce labour costs. Reduction in labour costs is not sufficient to justify investment, bearing in mind the competitiveness of labour costs in China. The main motivation at Baoshan is associated with production quality and the improvement of production control reliability to satisfy increasingly stringent product specifications and to improve laboratory response times.

A system for the automated analysis of stainless steel samples by means of XRF and OES is described by Engkvist.⁷² The automation is motivated by an increase in production. For the analyses, two lollipop samples are used per analysis. The XRF results (Si_{XRF}) are checked with OES-results (Si_{OES}) as shown in equation 3.1. If the quotient is significantly different from one, new analyses are needed.

$$\frac{Si_{XRF}}{Si_{OES}} \quad (3.1)$$

A dangerous remark is made: *“train converter personnel for analysis because they are better aware than lab staff what analysis results should be”*. This can generate biased results because when unexpected results are obtained, the sample is rejected and a new sample is obtained from the process.

Also grade verification is often performed by non experts in the analytical field because it is often needed at places where analytical laboratories are not nearby. In order to increase the speed of identification, a portable instrument has been developed by Avesta Sheffield AB.⁷³ This half automatic instrument includes a grinding machine and an OES. The instrument is easy to use and with some modifications it can be used as well for scrap identification. Some remarks can be made however about the handling of *wrong* analysis results. When an analysis result does not match the chosen grade, a second and even a third analysis is performed. The chances of obtaining the required analysis

results increase with the number of analysis being performed. The analysis results however need not be necessarily correct.

3.7 Conclusions

Much effort is put on improving process analytical measurements in the steel industry. Analytical techniques based upon laser ablation are being investigated by a large number of researchers and promising results are reported in some cases. Laser ablation based techniques will possibly replace spark excitation based techniques in the future. Unfortunately, none of the researchers give any detail about the sources of variation to be reduced. Therefore, it is unknown whether more accurate and precise analytical techniques will improve the measurements. If for example the samples are not representative for the complete batch of steel, extremely accurate and precise analytical methods are not the solution.

Besides more precision and accuracy, researchers are also interested in improving the response time by in-situ analysis. In-situ and on-line analysis in liquid steel are still in their infancy. Newly developed techniques lack accuracy, precision and stability. On-site analysis of steel samples has more future than in-situ analysis of the liquid steel bath. The hostile circumstances under which in-situ measurements have to be performed might necessitate the instrument to be adjusted often. During adjustment, measurements cannot be performed and process control is delayed.

The on-line methods mentioned in Section 3.3 still cannot be used at a commercially viable way because of several reasons such as lack of stability and lack of robustness. If, however, an on-line analysis method can be developed with reasonable precision and accuracy for a range of elements, on-line process control has a future in control of the steel production process.

Chapter 4

Sampling and analysis of steel

4.1 Introduction

In the previous chapter a number of alternative methods for the analysis of steel for process control are considered. While these methods promise to be of assistance to the process engineers in the future, spark optical emission spectrometry (spark OES) which is the method currently used for process analysis in steel making has proven to be a reliable and fast method for the analysis of solid steel samples. With spark OES, the concentrations of C, Mn, P, S, Si, Al, Cu, Sn, Cr, Ni, Mo, Nb, V, B, Ti and Ca in steel are measured within a short period of time (response times are typically in the range of a 20 to 30 seconds). For this type of analysis, so called double thick samples (Figure 4.1) are taken from the steel bath. Besides spark OES, also fusion and combustion methods are used on these samples to determine respectively concentrations of nitrogen and low concentrations of carbon. This chapter however will handle only the practical and theoretical aspects of the analysis of solid samples with spark OES as that is the analysis method considered in this research. Also, the types of sample probes will be discussed.

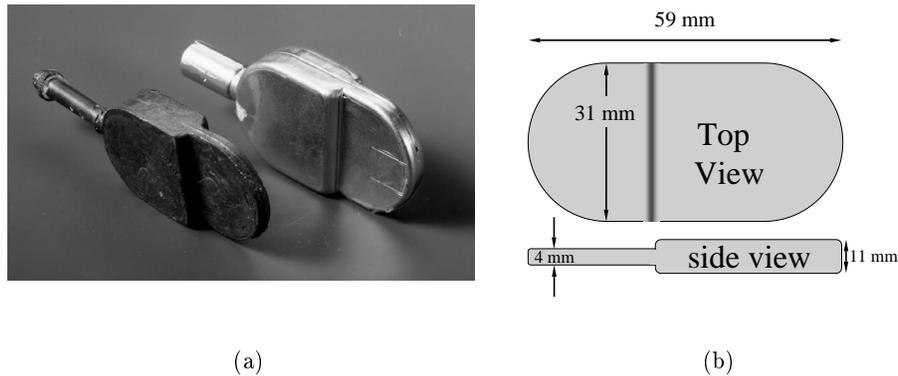


Figure 4.1: Double thick samples; a) photograph of sample with and without sample holder; b) schematic representation of a double thick sample.

4.2 Sampling

Sampling of double thick samples^a can be performed at different stages of the process but only the process phases *stirring station*, *vacuum ladle degasser*, *tundish* and *mould* are discussed.

From both stirring station and vacuum ladle degasser, double thick samples are taken by means of a sample probe as presented in Figure 4.2(a). At the vacuum ladle degasser, the sample probe is placed automatically into the steel bath. Due to the high temperature, the metal cap melts away and steel flows into the sample chamber where solidification takes place immediately. The sample probe is removed from the steel bath, the sample is taken out of the sample chamber and cooled in water.

From the tundish, samples are taken by means of a sample probe alike the one used for the stirring station and the vacuum ladle degasser as shown in Figure 4.2(a). Handling of the sample probe can be performed automatically in the vacuum ladle degasser, but in the tundish this action is performed manually. The paper tube is fit on a bend metal bar because the temperature and fumes above the tundish are too hostile to take samples from above. The inlet of the sample chamber is closed by a metal cap which melts away only after the sample probe has entered the liquid steel bath. This prevents the

^aOther names such as lollypop samples, tongue samples and thick-and-thin samples appear in the literature but the name double thick samples will be adhered to throughout this thesis.

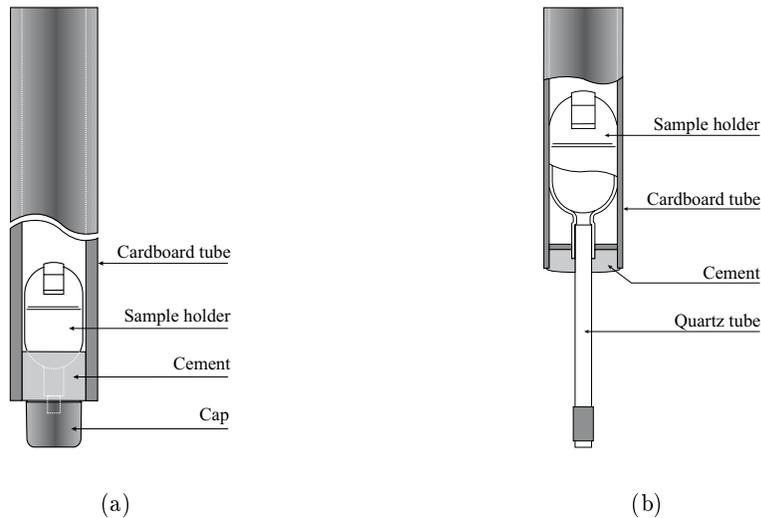


Figure 4.2: Schematic presentation of the sample chambers in sample probes;
 a) sample probe for stirring station, vacuum ladle degasser and tundish;
 b) sample probe for the mould.

powder covering the steel surface from entering the sample chamber. After sampling, the solidified sample is removed from the sample chamber and cooled down in water.

The third sample probe considered in this chapter is the one used for taking samples from the mould (Figure 4.2(b)). In this process phase, dipping the relative large sample probe into the liquid steel would disturb the process resulting in irregularities in the cast product. An alternative sampling method is used for the mould where the liquid steel is sucked up into the sample chamber through a quartz tube. An inert gas (argon) is blown through the sample probe and only when the quartz tube is positioned at the required position, the argon flow is stopped. The liquid steel flows into the sample chamber through suction, and becomes solid within a short period of time. The sample is removed from the sample chamber and cooled down in water.

Although the same type of sample is taken from the steel bath for the four process phases stirring station, vacuum ladle degasser, tundish and mould, the obtained samples are different from each other in terms of microscopic structure and heterogeneity. These differences are caused by the differences in circumstances under which the samples are taken from the different process phases. The cooled sample is analysed on-site by means of spark OES or send

to the laboratory through pneumatic dispatch and analysed there by means of spark OES (and other methods if needed).

4.3 Sample preparation

The surface of the double thick samples obtained from the steel making process is heterogeneous and not representative for the product in the steel bath due to for example oxidation. Also the core of the sample is not completely representative for the constitution of the steel bath because of inclusions and migration of elements. A surface which is representative for the contents of the batch is obtained by means of grinding a thin layer (approximately 0.6 mm) from the surface of the steel sample. Another method which could be used is milling but only grinding is considered in this research because it is the most common used method for preparing double thick samples which are to be analysed by means of spark OES.

4.4 Analysis

Spark OES has many advantages among which the following few are important:

- It is a fast method.
- The principles are readily understood, although they are complex.⁷⁴
- A broad range of elements can be analysed simultaneously.
- A simple sample preparation suffices.
- Analysis can be performed on the solid sample.

A schematic representation of the spark OES is given in Figure 4.3. During analysis, the sample (b) resides in the spark stand (i) which is kept under an argon atmosphere. Argon is used for four reasons:

- Usage of an inert gas, such as argon, avoids interaction with the sample or with the electrode.
- Argon transmits UV light relatively well.
- The spark-over voltage is rather low which diminishes the necessary power.
- Argon is available in large quantities.

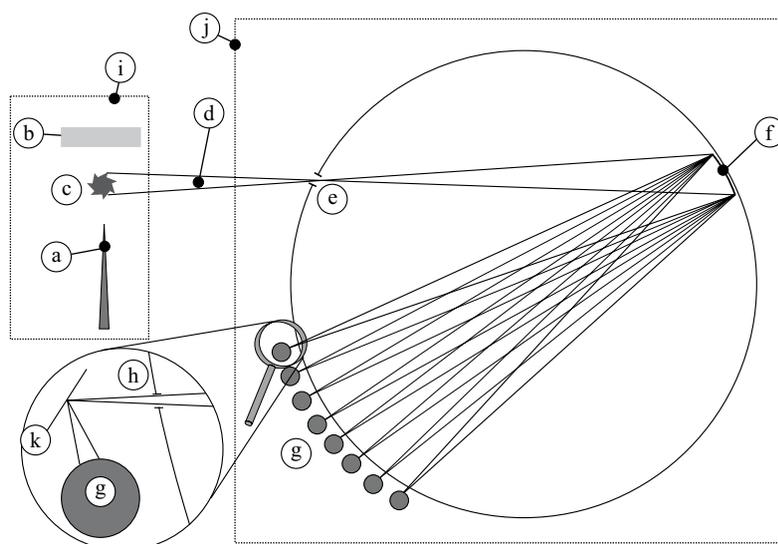


Figure 4.3: Schematic representation of a spark optical emission spectrometer; a) tungsten counter electrode; b) double thick sample; c) plasma formed by the spark; d) emitted radiation; e) entrance slit; f) disperse grating; g) photo multiplier tube; h) outlet slit; i) spark stand; j) vacuum chamber; k) mirror

Between the tungsten counter electrode (a in Figure 4.3) and the sample (b in Figure 4.3), a potential difference is applied. The space in between the sample and the counter electrode is called the analytical gap. In the electronics of the spectrometer a so-called auxiliary gap exists which is used to control the spark at the analytical gap. So, a controlled spark is discharged on the sample. Due to the high amount of energy applied to the sample within a short period of time, a small part of the sample evaporates and forms a plasma (c in Figure 4.3, see also Intermezzo: plasma in Chapter 3).

Electrons in the atoms and ions (ions are produced due to the high temperature in the plasma) which appear in the plasma are excited due to the high temperature (20.000-40.000 K^{18,75}). During relaxation, radiation is emitted. Part of the radiation (d in Figure 4.3) enters the optical part of the spark OES through a lens and an entrance slit (e in Figure 4.3). The optical parts of the spectrometer are situated in a vacuum (j in Figure 4.3) to prevent scattering and absorption by, for example, nitrogen in air.

The captured radiation is focussed on a grating (f in Figure 4.3) which disperses the radiation of different wavelengths over a number of outlet slits (h in

Figure 4.3). Each wavelength^b focussed on an outlet slit is captured by mirrors (k in Figure 4.3) and focussed on a photo multiplier tube (g in Figure 4.3). The radiation from only one spark is not enough to obtain reliable results. Therefore, a number of sparks are used for each measurement on a steel sample. For the naming of analyses see the Intermezzo: naming of analysis.

Intermezzo: naming of analysis

In this thesis a number of names are used for different events dealing with measurements performed on double thick samples. A spark is one occurrence of applying a spark on a sample. A number of sparks applied, enough to get one reading for each element is called a measurement. To get reliable (accurate and reproducible) results, a number of measurements are needed (typically 2 or 3 for spark OES). The combined results of these measurements are called an analysis:

spark	→	measurement	→	analysis
(1)		(m sparks)		(n measurements)

The result of a measurement is an integrated number of photons detected by the photo multiplier tubes (PMT's) for each element. These measurements (intensities) still need to be transformed to concentrations. The total trajectory from intensity to concentration concerns a number of steps which are needed to obtain reliable results. One of these steps is the adjustment which is needed to correct for instrumental drift and for shifts in the measured intensity that occur in the analytical signal due to cleaning of the spark stand.

4.5 Adjustment

During sparking of the steel samples, small particles of steel are deposited on the instrument parts in the spark stand. The lens, for instance, is covered with a small layer of dust which reduces the total amount of radiation entering the optical part of the spectrometer. Besides the lens, also the counter electrode is polluted by sample material and this results in a less condensed plasma.

A third cause of instrumental drift is the polymerisation of oil in the vacuum part of the spectrometer. Oil enters the optical part due to the vacuum pump needed to obtain and retain a vacuum in the instrument. The radiation that enters the vacuum is in the UV-range and radiation within this range of wavelengths is able to cause polymerization of the oil. The polymer precipitates

^b Actually, a small band of wavelengths is captured per outlet slit as the dispersion by the grating is continuous rather than discrete.

on the optical parts of the spectrometer and thereby absorbs and scatters the incoming radiation partly.

To reduce these effects which have a negative influence on the performance of the instrument, the spark stand is cleaned every eight hours. The dust is blown away by air and the counter electrode is wiped mildly. The vacuum part of the spectrometer is not cleaned on a daily basis because a possible shift of mirrors or other optical parts would cause much more harm than is corrected for by cleaning the optical parts.

The cleaning actions result in a change of the instrumental behaviour which can best be described as a random shock. Correction for this random shock is needed to obtain reliable analytical results from the instrument. The correction method used for the spark OES is a two-point correction method called adjustment.

For the correction, a number (4 or 5) of adjustment samples are measured. For each element measured, a low and a high intensity is obtained. From earlier measurements, it is known which intensities should be measured when the instrument is stable. These intensities are called the nominal values. A relation is estimated between the nominal values (I_n) and the measured intensities (I_o) as shown in equation 4.1.

$$I_{n,e} = \alpha_e \cdot I_{o,e} + \beta_e \quad (4.1)$$

The parameters α_e and β_e which transform the measured intensity of element e ($I_{o,e}$) to the nominal intensity of element e ($I_{n,e}$) are calculated by means of equations 4.2 and 4.3 respectively.

$$\alpha_e = \frac{I_{n,e,h} - I_{n,e,l}}{I_{o,e,h} - I_{o,e,l}} \quad (4.2) \quad \beta_e = \frac{I_{n,e,l} \cdot I_{o,e,h} - I_{n,e,h} \cdot I_{o,e,l}}{I_{o,e,h} - I_{o,e,l}} \quad (4.3)$$

The intensities $I_{n,e,h}$ and $I_{n,e,l}$ are the high nominal value and the low nominal value respectively for element e . The other two intensities, $I_{o,e,h}$ and $I_{o,e,l}$ are the measured high intensity and the measured low intensity respectively for element e .

The intensities (I_o) for an unknown sample are corrected by means of equation 4.1. The ideal values for α and β are 1 and 0, respectively. In this case, $I_n = I_o$ and therefore, the measured intensities are not influenced by drift or random shocks. However, in reality the state of the spectrometer after cleaning the spark stand is such that the intensities measured for the adjustment samples differ from the nominal values. Therefore, estimation of the adjustment parameters α and β is performed each time the spark stand is cleaned.

Table 4.1: Maximum and minimum values for adjustment parameters α and β . Ratio is for elements that are measured relative to iron.

	Minimum	Ideal	Maximum
α	0.5	1	1.5
β (ratio)	-0.25	0	0.25
β (absolute)	-25	0	25

The adjustment parameters α and β are limited to certain values. The spark OES needs to be serviced if one of both values α or β are outside the limiting values presented in Table 4.1. Adjustment values outside these ranges indicate that the instrument suffers too much from instrumental drift. The values for β differ for ratio and absolute measured elements. In absolute values larger fluctuations are allowed to be able to correct for larger fluctuations in the measured intensities.

A second condition for the adjustment measurements is that the intensities measured at adjustment period t differ no more than 10% from the intensities measured at adjustment period $t - 1$. This check is made to prevent errors caused by accidentally swapping samples.

4.6 Verification

The adjustment parameters α and β are subject to errors due to the fact that analytical measurements are the basis for calculation of these values. The correction performed on the I_o values of subsequent measurements by means of the adjustment values has to meet certain quality standards to ensure that the measured intensities are corrected rather than worsened. Therefore, after each adjustment, a pair of verification samples is analysed and the analysis results are verified with the known values (concentrations). A certain deviation from the true values is allowed (analytical measurements always contain errors and also the known values for the verification samples are subject to errors by chance). However, when the obtained concentrations are out of range, the adjustment procedure is repeated after which verification takes place again. If the obtained concentrations are still not within the specification limits, the instrument is not ready for process analytical measurements and needs a check up.

4.7 Calibration

Calibration curves are needed to transform the measured intensities to concentrations. For this purpose, a calibration curve is estimated for each element every three months. During these three months, a large amount of calibration samples^c is measured resulting in a number of intensities for each element. These intensities are related to the (certificate) concentrations by means of calibration curves for which the parameters are estimated by means of least squares. So, for each element a model as presented in equation 4.4 is obtained ($I_{n,e}$ is substituted by $I_{n,e,ratio}$ for ratio measured elements).

$$c_e'' = b_{e,0} + b_{e,1} \cdot I_{n,e} + b_{e,2} \cdot (I_{n,e})^2 + b_{e,3} \cdot (I_{n,e})^3 \quad (4.4)$$

In this equation c_e'' is the concentration of element e , $b_{e,0} \dots b_{e,3}$ are the regression coefficients and $I_{n,e}$ is the measured intensity of element e . Depending upon the complexity of the relation between the intensity and the concentration, a first order model ($b_{e,2} = 0$ and $b_{e,3} = 0$), a second order model ($b_{e,3} = 0$) or a third order model is needed to describe the relation between intensity and concentration.

The concentration (c_e'') of element e , obtained with equation 4.4 still needs to be corrected because disturbances such as interelement effect and spectral interference¹⁹ disturb the measured intensity of some elements. The correction factors, needed to take the interelement effect and spectral interference into account, are estimated only once when a spectrometer is brought into use for the first time.

4.7.1 Interelement effects

The disturbances called *interelement effects* have a systematic multiplicative influence on the measured intensity of the disturbed elements. This means that there exists a relation between the concentration of disturbed element e and the concentration of disturbing element d . These effects may have a physical or a chemical cause. A number of these causes are mentioned here. For a more extensive list of causes of interelement effects, the interested reader is referred to Slickers.¹⁹

The edges of inclusions attract the electrical spark more than the surrounding part of the sample.⁷⁶ As a result, the measured concentrations of the elements in the inclusion are overestimated. The occurrence of certain inclusions depend

^cMost of the calibration samples are internationally recognized ECRM (European Certified Reference Material) samples.

upon the concentration of an other elements. So, the amount of inclusions of say element a depends upon the concentration of element b . The measurement for element a then needs to be corrected by the measurement obtained for element b .

The rate of evaporation of the sample can change when certain elements occur in the sample. A lower melting point due to the lower evaporation enthalpy causes the measured intensities to be too high because less energy is needed for the vaporization. When an appropriate reference line is used, the increase of the intensities due the lower vaporization enthalpy is corrected by dividing the intensity of element a by the intensity of the reference line.

The probability of excitation of an element a can be influenced by an element b . This change in probability is then caused by a change in plasma temperature due to other elements with varying ionisation energy. In the presence of elements with low ionisation energy compared with the base element, the temperature of the plasma drops, so that the intensity of elements with high excitation energy becomes weaker and of those with low excitation energy becomes stronger. On the other hand, in the presence of elements with high ionisation energy compared with the base element, the plasma temperature increases and the spectral lines with high excitation energy become stronger and those with low excitation energy become weaker.

These and other so-called interelement effects can be corrected by means of a multiplicative correction as shown in equation 4.5.

$$c'_e = c''_e \cdot \left[1 + \sum_d (K_{e,d} \cdot c''_d) + \sum_d (L_{e,d} \cdot (c''_d)^2) \right] \quad (4.5)$$

In this expression, c'_e is the concentration of element e corrected for the interelement effects caused by element d , c''_e is the uncorrected concentration of element e , c''_d is the concentration of disturbing element d and the correction factors are denoted by the parameters $K_{e,d}$ and $L_{e,d}$.

4.7.2 Spectral interference

A second kind of disturbance is caused by line overlap, band overlap, background interference or diffused light. In the design of the spectrometer, analytical lines are chosen such that as little as possible overlap occurs. However, inadequate resolution (line overlap), radiation from poly atomic particles such as CN and AlO (band overlap), samples with a different matrix than normally used (background interference) or reflections in the optics of the spectrometer (diffused light) all may have a negative influence on the accuracy of the measurements.

The influence of spectral interference can partly be corrected for by applying a linear correction according to equation 4.6.

$$c'_e = c''_e + \sum_d (M_{e,d} \cdot c''_d) + \sum_d (N_{e,d} \cdot (c''_d)^2) \quad (4.6)$$

In this expression, c'_e is the concentration of element e corrected for the spectral interference, c''_e is the uncorrected concentration of element e , c''_d is the concentration of element d causing the disturbance and the correction factors are denoted by the parameters $M_{e,d}$ and $N_{e,d}$.

The procedures described in the sections 4.5 through 4.7 are summarized in the flow chart presented in Figure 4.4. This flow chart shows the steps followed for the spark OES under normal operating conditions during an adjustment period of 8 hours.

4.8 From intensity to concentration

The calculation of the concentrations from the measured intensities is a rather complex procedure compared to most OES measurements where only a calibration curve is needed to transform the measured intensity to a concentration. For standard methods, an internal standard is used very often but the procedure is seldom more complicated. Unfortunately, this is not the case for measurements performed on the spark OES. In the first step, the intensity measured for most of the elements (Table A.1 in Appendix A) is divided by the intensity measured for iron. The variation of these elements is highly correlated to the variation of iron. By dividing the intensities of these elements by the intensity measured for iron, instrumental drift is corrected to a certain amount. In equation 4.7, the absolute intensity for element e ($I_{o,e}$) is divided by the absolute intensity for iron ($I_{o,Fe}$) resulting in the relative intensity $I_{o,e,ratio}$ for element e .

$$I_{o,e,ratio} = \frac{I_{o,e}}{I_{o,Fe}} \quad (4.7)$$

The next step in the trajectory from intensity to concentration is the adjustment. The absolute ($I_{o,e}$) or the relative intensity ($I_{o,e,ratio}$) is transformed to a nominal intensity ($I_{n,e}$ and $I_{n,e,ratio}$) as shown in equation 4.8. Every eight hours, the adjustment parameters α and β are recalculated with equations 4.2 and 4.3 respectively.

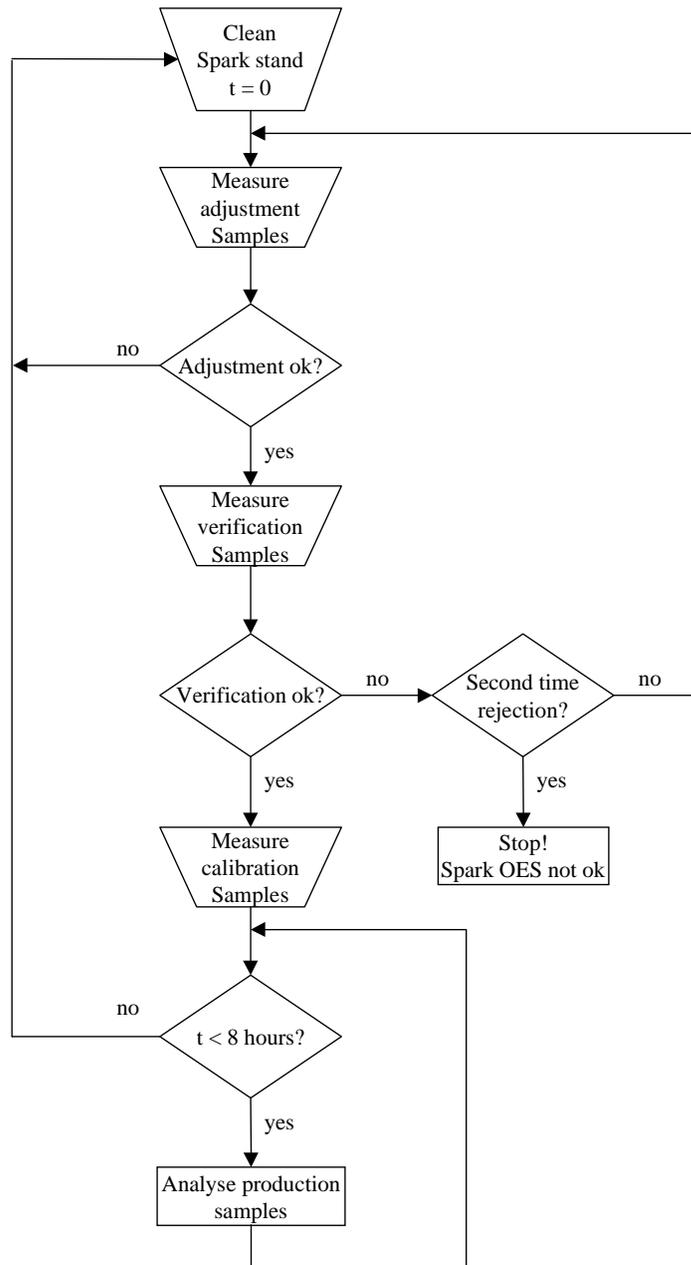


Figure 4.4: Flow chart for the spark OES under normal operating conditions during an adjustment period of 8 hours.

$$I_{n,e} = \alpha_e \cdot I_{o,e} + \beta_e \quad I_{n,e,ratio} = \alpha_e \cdot \frac{I_{o,e}}{I_{o,Fe}} + \beta_e \quad (4.8)$$

From the absolute nominal ($I_{n,e}$) and the ratio nominal ($I_{n,e,ratio}$) intensities, concentrations are calculated by means of equation 4.4 resulting in the uncorrected concentrations c_e'' for each element e . For elements that are disturbed by interelement or spectral interference, equation 4.5 or 4.6 are used respectively to obtain the corrected concentration c_e' . For other elements c_e' equals c_e'' .

So far, the concentrations of most elements have been calculated relative to the iron concentration as a result of dividing the intensities of the alloying elements by the intensity of iron. As a result, the sum of all concentrations is not equal to 100%^d. For the concentrations of elements for which the intensity is not divided by the intensity of iron, c_e (the reported concentration of element e) is equal to c_e' . The concentrations of elements for which the intensity is divided by the intensity of iron, the relation between the alloying element and iron (equation 4.9) has to be taken into account.

$$c_e = c_e' \cdot \frac{c_{Fe}}{c'_{Fe}} \quad (4.9)$$

where c_e is the reported concentration of element e , c_e' is the *iron diluted concentration* of element e , c'_{Fe} is the iron diluted concentration of iron and c_{Fe} is the *true*^e concentration of iron.

Assuming that the total concentration of all measured elements is equal to 100%, the relation in equation 4.10 applies.

$$c_{Fe} + \sum_{ratio} c_e + \sum_{absolute} c_e = 100 \quad (4.10)$$

Two summations are applied: the summation of all elements for which the intensities are related to the intensity of iron (\sum_{ratio}) and the summation of all elements for which the absolute intensity is used ($\sum_{absolute}$).

Substitution of equation 4.9 and the relation $c_e = c_e'$ for absolute measured elements into equation 4.10 results in equation 4.11 after rearrangement.

^dThe assumption is that the summed concentrations of all measured elements is equal to 100%.

^eTechnically, it is wrong to speak about the true concentration because also the iron concentration corrected for the iron dilution is still a measurement. However, the name *true measured concentration of iron* would probably be even more confusing.

$$c_{Fe} = \frac{100 - \sum_{absolute} c'_e}{c'_{Fe} + \sum_{ratio} c'_e} \cdot c'_{Fe} \quad (4.11)$$

The concentration of iron relative to iron (c'_{Fe}) is equal to 100%. When applying this knowledge to equation 4.11, the true iron concentration can be calculated with equation 4.12.

$$c_{Fe} = \frac{100 - \sum_{absolute} c'_e}{100 + \sum_{ratio} c'_e} \cdot 100 \quad (4.12)$$

Applying the same relation ($c'_{Fe} = 100$) to equation 4.9 results in equation 4.13 which gives the concentration of element e when the intensity of this element is measured relative to the intensity of iron.

$$c_e = c'_e \cdot \frac{c_{Fe}}{100} \quad (4.13)$$

For each measurement, a concentration is obtained for all elements for which intensities are obtained. Variations such as heterogeneities in the sample, fluctuations in the spark and errors by chance cause the measured concentrations to be unequal to the concentrations in the sample. To be sure that the measured concentrations are reproducible, a number of measurements is performed for each analysis. If the measured concentrations from two measurements are reproducible (according to predefined specification limits), the mean concentrations from the two measurements are reported. If reproducibility is not obtained, a third measurement is performed. Then the reproducibilities of measurements 1 and 3, 2 and 3 and the three measurements 1, 2 and 3 are tested subsequently^f. If a reproducible pair (or triple) of measurements is found, the mean of these measurements is reported to the process engineer. The procedure of selecting reproducible results is presented in a flow chart (Figure 4.5).

^fFor some spectrometers, the maximum amount of measurements taken into account for a mean concentration is two.

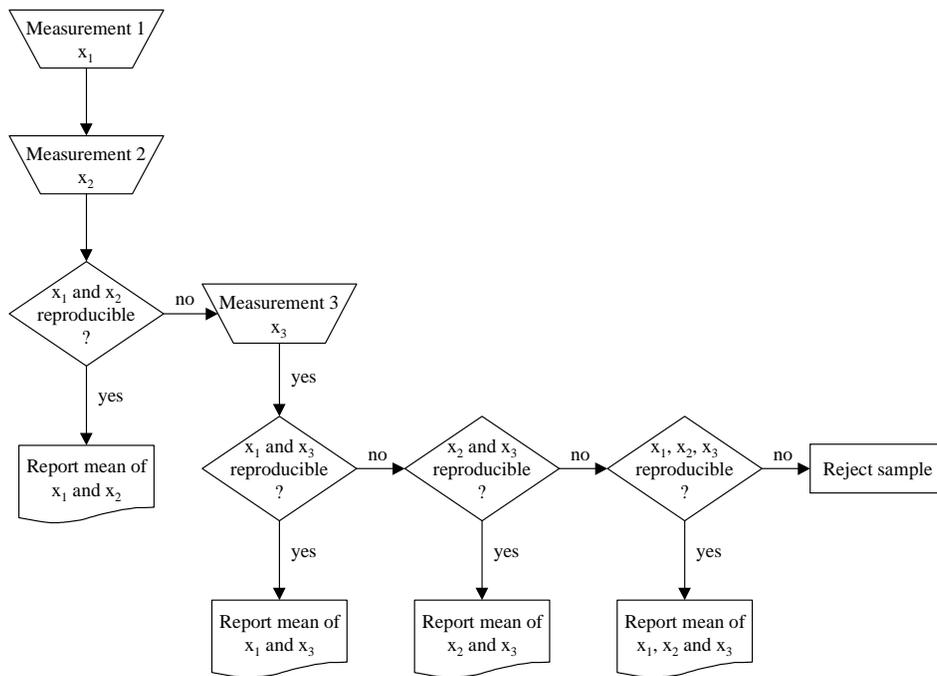


Figure 4.5: Flow chart for the analysis of a production sample.

Chapter 5

Strategy to quantify sources of variation in process analytical measurements

5.1 Introduction

One of the conditions for monitoring and controlling processes in an accurate way is to ensure that the total variation apparent in chemical analysis results is small compared to the allowed product variation. Processes are controlled based on analysis results. If the analysis results lack accuracy, process steering based on chemical analyses will become inaccurate as well. While customer demands towards products like cast steel become more and more stringent, the total variation apparent in the final analysis results should be reduced to an accepted level. Reduction of variation in process analytical measurements is often performed by means of trial and error. In this way, reduction of variation is possible but the model according to which the variation is build-up is still unknown. A more strategic approach in which all possible sources of variation are taken into account gives a better insight in the structure of the total variation apparent in the final analysis result.⁸

The strategy shown in this chapter comprises the following 6 main steps which will be discussed in more detail in this chapter:

1. Identify and select factors that contribute to the total variation of the response factors.
2. Select a model that includes the factors chosen in step 1.
3. Design an experiment which is efficient for estimating the effects of the factors included in the model.
4. Perform the experiments according to the experimental design.
5. Estimate the effects of the factors included in the model on the total variation of the response factors.
6. Interpret and discuss the results of the estimations.

The strategy helps in finding those factors which contribute mostly to the total variation. Applications of this strategy in the reduction of variation in the production, sampling and analysis of steel are shown in chapters 6 and 7. Further explanation of the individual steps is given in the sections 5.2 through 5.7.

5.2 Factor identification and selection

Step 1 For the identification and selection of factors, brainstorming sessions should be organized. Factors which give rise to variation in the response factors have to be chosen. In most cases, not all identified factors will be included in the experiment. The choice of factors to be included in the experiment depends on interest in certain factors, feasibility of including factors in an experiment and the expected magnitude of the sources of variation.

Preliminary studies in which a small number of experiments are performed according to a simple experimental design can be helpful in determining which factors are important in the build-up of the total variation. At this stage, also historical datasets can be useful in getting a rough estimate of the magnitudes of the sources of variation. These rough estimates can then be helpful in the selection of factors.

5.3 Model selection

Step 2 The factors chosen in step 1 are included into one or more models. In this step a choice has to be made for each factor whether it is included as a fixed or a random effect. A choice out of three types of models can be made:

- Fixed-effects model (also known as model I).
- Random-effects model (also known as model II).
- Mixed-effects model.

The third (mixed) model includes both random and fixed effects. The model presented in Equation 5.1 is a mixed effects model presented in words for ease of explanation. When measurements are performed in a process, the response is a summation of the overall mean, fixed effects such as the place of sampling, random effects such as the operator taking the sample and the residual which contains all variation not explained by the effects included in the model. Although the mean is a fixed effect and the residual is a random effect, the name of the model (I, II, mixed) depends only upon the other factors included in the model.

$$\begin{array}{rccccccc} \text{concentration} & = & \text{mean} & + & \text{fixed effects} & + & \\ & & & & \text{random effects} & + & \text{residual} \end{array} \quad (5.1)$$

$$y_{ij} = \mu + \alpha_i + \varepsilon_{ij} \quad (5.2)$$

Equation 5.2 shows a simple linear statistical model with one effect α which can be used as both a model I as well as a model II. In this equation, y_{ij} is the j th observation of treatment i of effect α , μ is the overall mean, α_i is the treatment effect, and ε_{ij} is the residual or random error component. This model is called the one-way or single-factor analysis of variance (ANOVA) model because only one factor is included in the model. Each α_i (where $i = 1 : n$) represents an effect of a certain treatment i .

The factor α could, for example, represent time of sampling and y then could be the carbon concentration. If during an experiment, samples are taken at specific points in time i , tests can be performed whether samples taken at one point in time have significantly different concentrations than samples taken at another point in time. The point in time would then be considered as being a

fixed effect: it is chosen explicitly by the experimenter and the outcome only gives information about the investigated levels i of the factor α . This type of experiment facilitates making decisions about which level(s) i of the factor α are to be used. Level i is repeated a number of times, represented by j in ε_{ij} (where $j = 1 : a$), in order to obtain a good estimate for the residual (j are repeated measurements at level i of factor α). This is a fixed-effect model.

In another situation, the factor α could be the process engineer controlling the process. Each level i then would be a different process engineer but these levels would be a random sample from a larger population of process engineers rather than a explicitly chosen group of process engineers. This type of experiment is performed to investigate to what account the factor α contributes to the total variation in y . Here again, level i of factor α is repeated a number of times (j). In this case the process is operated a number of times by process engineer i during the experiment. This is a random effect model.

Besides the situations described above in which only one fixed effect or one random effect is included in the model, any combination of both types of factors can be used resulting in a model with multiple random and/or fixed effects.

Interaction

Certain factors can interact with each other, which means that the effect of one factor is not independent of the presence of a particular level of another factor. If factor α has a combined effect with factor β , interaction exists. In the model, this interaction is included as γ_{ij} (equation 5.3). So every level i of α and j of β is combined in the factor γ .

$$y_{ijk} = \mu + \alpha_i + \beta_j + \gamma_{ij} + \varepsilon_{ijk} \quad (5.3)$$

Including the interaction factor results in obtaining information about the combined effect of factors α and β . For example, for the growth of a plant there exists a combined effect for the amount of water and the amount of light given to a plant.

Nesting

Nested (or hierarchical) analysis of variance occurs when the levels of one factor are not crossed independently with all levels of another factor. A crossed experiment is one where all possible combinations of levels of the factors exist. Thus, the cells of data are formed by each level of one factor being in combination with each level of every other factor.

Table 5.1: Example of two factors crossed independently from each other.

Analyst	Spectrometer	
	1	2
1		
2		

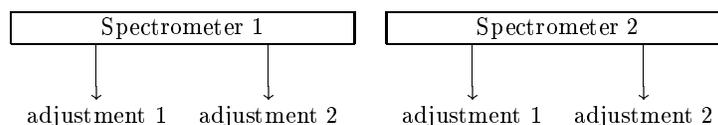
In a situation as presented in Table 5.1 the factors spectrometer and analyst are completely crossed. Analyst 1 operates both spectrometer 1 and 2 just as analyst 2 operates both spectrometers. Hence, analyst 1 (or 2) operating spectrometer 1 is physically the same as the analyst operating spectrometer 2. In Figure 5.1 a nested design is presented. The two factors spectrometer and adjustment^a are crossed but the adjustment of one spectrometer is not comparable to the adjustment period of another spectrometer. In other words: the state of spectrometer 1 during adjustment 1 is completely independent from the state of spectrometer 2 during adjustment 1. Therefore, Figure 5.1 shows more correctly the situation during such an experiment.

5.4 Experimental design

Step 3 After selecting one or more models in step 2 of the strategy, experiments have to be set-up. Much has been written about the design of experiments. Among many others, the books written by Montgomery⁷⁷ and Mead⁷⁸ give a good overview of the available techniques.

Experiments in which several factors are varied but only one factor at a time (one-factor-at-a-time), are very disadvantageous (Figure 5.2(a)). While one factor may not have much influence on the response factor, the combined influence of two or more factors could result in a change in the response factor.

^aAdjustment is the two point recalibration performed after cleaning the spark stand (Explained in more detail in Chapter 2).

**Figure 5.1:** Nested or hierarchical design.

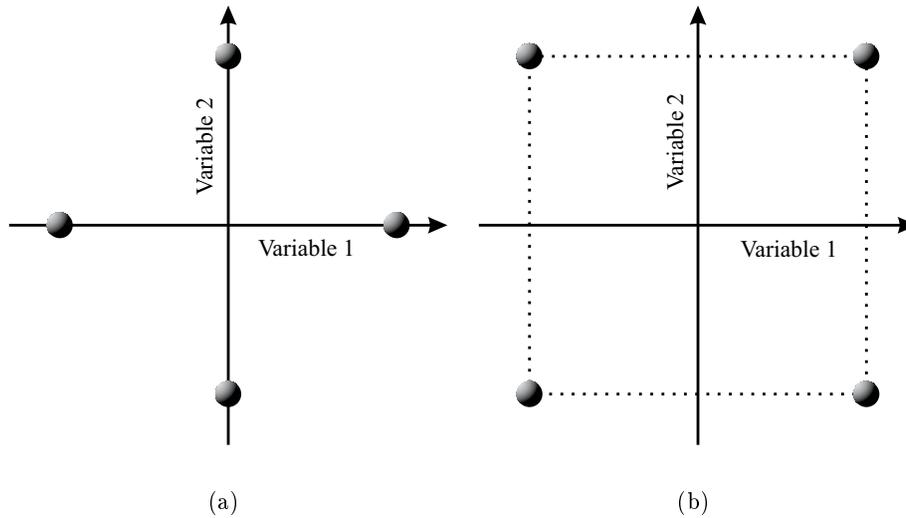


Figure 5.2: Experimental designs with two factors, two levels each; a) one-factor-at-a-time design; b) a factorial design

As an example, changing the amount of water only or the amount of light only given to a plant may have a certain effect but the combined effect (interaction) will probably be much more effective. In other situations, such an effect may not always be as obvious as in this simple example but when experiments are performed according to an experimental design in which more than one factor is varied at the same time, chances are high that interactions will be found if they exist. When an experiment is performed according to a factorial design (Figure 5.2(b)), interactions can be estimated.

A factorial design does not necessarily results in better results. Experimental designs such as fractional factorial designs have been developed which allow for the estimation of all factors of interest without doing all the experiments. A fractional factorial design is presented in Figure 5.3. By using fractional factorial designs, a reduction of the amount of experiments can be accomplished. In such a design not all combinations of all levels of the factors need to be investigated. These designs will not be discussed here further and interested readers are referred to excellent books written on this subject.⁷⁷⁻⁷⁹

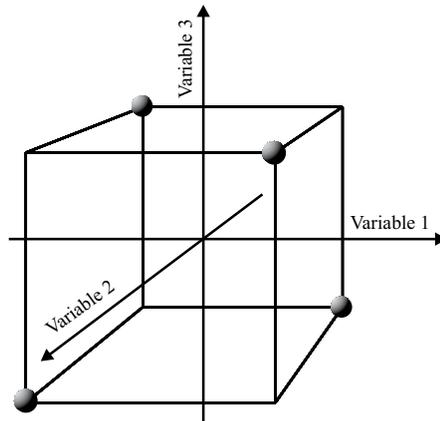


Figure 5.3: A two-level, three-factor fractional factorial design.

5.5 Experiment

Step 4 At this stage the actual experiments are performed according to the experimental design. It should be stressed towards the analyst(s) performing the experiments that occurring abnormalities should be reported. When remarks about abnormalities (i.e. turbidities in a liquid sample which normally should be clear) are written in a journal, unusual results can be explained more easily and removal of outliers can be justified. Also, only those factors included in the experimental design should be varied. Other factors should be kept as constant as possible. Extra variation included in the analysis results will end up in the residual variation when estimating the factors. Significance of the effects included in the model are tested relative to this residual variation and therefore it is of importance to maintain other factors at a constant level. If for example the temperature of the environment can not be kept at a constant level, inclusion of the factor into the model can be considered to estimate the effect of this factor.

5.6 Factor estimation

Step 5 In ANOVA, for the estimation of the effects in the models, many techniques are available. Most of these techniques use least squares or maximum likelihood methods. In this thesis, the main goal is to identify those factors which have the largest influence on the variation apparent in the response fac-

tors. Feedback is needed to the first two steps of the strategy (brainstorm and selection of the model). Possibly another model can be chosen with less factors in order to increase the reliability of the estimates. This is common when in the original model interactions are included and when after estimation of the factors it appears that certain interactions have no significant effect on the total variability of the response factor.

The estimation methods least squares and restricted maximum likelihood are given in general terms only. A more exhaustive explanation of the methods can be found in many textbooks on statistics and applications in statistics.⁸⁰⁻⁸³

5.6.1 Least squares

Consider the following linear statistical model:

$$\mathbf{y} = \boldsymbol{\alpha} + \mathbf{X}\boldsymbol{\beta} + \boldsymbol{\varepsilon} \quad \boldsymbol{\varepsilon} \sim N(0, \sigma^2 I) \quad (5.4)$$

where \mathbf{y} is a vector of responses, \mathbf{X} is the design matrix, $\boldsymbol{\beta}$ is the vector of regression coefficients, $\boldsymbol{\alpha}$ is the intercept vector (or mean in this case) and $\boldsymbol{\varepsilon}$ is the residual error that is assumed to be independent, normally distributed with mean zero and variance $\sigma^2 I$. Estimates of $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$ and $\boldsymbol{\varepsilon}$ that are i) unbiased and ii) have the smallest standard errors of any unbiased estimators that are linear expressions in the y 's can be obtained by minimising the sum of squares presented in equation 5.5.

$$\min \sum (\mathbf{y} - \hat{\boldsymbol{\alpha}} - \hat{\boldsymbol{\beta}}\mathbf{X})^2 \quad (5.5)$$

The resulting estimates for the regression coefficients in the vector $\hat{\boldsymbol{\beta}}$ are tested against the obtained residuals for significancy.

5.6.2 Maximum likelihood

A problem associated with the use of mixed and random models in case of unbalanced data has been the estimation of the variances of the random effects, i.e., the estimation of the variance components. The development of effective computational maximum likelihood solved this problem.⁸⁴ Maximum likelihood is a method for obtaining estimators for a statistical model where a specific distributional assumption is made about the vector of sample observations.⁸⁰ Like the method of least squares, the method of maximum likelihood is a general method for finding good estimates of parameters in models. It reduces essentially to the method of least squares when the observations are

normally distributed but does not depend on normality, requiring only that the probability distribution of the observations is known. It is therefore more general than least squares.⁸¹

Suppose a sample (X_1, X_2, \dots, X_n) is drawn from a population with the probability function $p(X/\theta)$, where θ is the unknown population parameter to be found. If the sample is random, then the X_i are independent, each with probability function $p(X_i/\theta)$. Hence the joint probability function for the whole sample is obtained by multiplying:

$$\text{likelihood} = p(X_1, X_2, \dots, X_n/\theta) = p(X_1/\theta)p(X_2/\theta) \dots (X_n/\theta) \quad (5.6)$$

The question to be asked is: “*which of all the hypothetical values of θ maximizes this probability?*”. The general idea behind maximum likelihood is that it finds the population value θ that matches the sample best. By taking the log of equation 5.6, equation 5.7 is obtained which is more practical. The maximum likelihood estimate is that value of θ that maximises the right hand term in equation 5.7.

$$\log \text{likelihood} = \log p(X_1/\theta) + \log p(X_2/\theta) + \dots \quad (5.7)$$

The maximum likelihood procedure for estimating the variance components does not take into account the degrees of freedom lost in estimating the fixed effects, and hence they become biased. The restricted maximum likelihood (REML) method corrects for this bias.^{83,84}

When a balanced experimental design is used, estimation of the variance components (random effects) may be obtained by the ANOVA method from the sums of squares corresponding to the random effects in the model. However, ANOVA estimates may be negative^b.

Example of REML versus ML

For a random sample $y_1 \dots y_n$ ($y \sim N(\mu, \sigma^2)$), the maximum likelihood estimator of σ^2 is shown in equation 5.8.

$$\sum (y_i - \bar{y})^2 / n \quad (5.8)$$

^bThe data used in the experiments presented in this thesis are balanced, but for practical reasons (choice of software) the random components have been estimated with maximum likelihood methods.

This equation does not take into account the degree of freedom lost for the estimation of μ by the mean \bar{y} from the individual samples y_i . The REML estimator is obtained by replacing the divisor n by $n - 1$ and is unbiased.

In a mixed model the loss of degrees of freedom due to the fixed effects is even of more concern, resulting in a substantial bias for ML estimators. REML estimators generally yield a smaller bias although this often results in a higher mean squared error.⁸⁵

5.7 Interpretation of the results

Step 6 After estimating the contributions of the various effects to the total variation in the response factor, feedback is needed to the first step of the strategy. Interpretation is best left to the experts which came up with the different sources variation. The results should be presented in such a way that a clear conclusion about the most contributing factors is possible. The results should preferably be presented in the form of graphs and (small) tables. In that way, the end-user is not confronted with large amounts of output from statistical software.

Chapter 6

Identification and quantification of sources of variation in the analysis of steel

6.1 Introduction

To trace and quantify the sources of variation apparent in production, sampling and analysis of steel, the strategy explained in Chapter 5 was applied to part of the steel production process. Focus in this research was on the sampling and analysis of steel. Some process factors have been included as well but the estimation of process factors such as differences between batches of the same type of steel was beyond the scope of the research. In a first effort to find the contributing factors of the total variation in the analysis results, one type of steel was investigated.⁸⁶ Research on other types of steel were part of the project as well but the comparison of the results of different types of steel is the subject of the next chapter.⁸⁷

For the quantification of sources of variation in the production, sampling and analysis of steel in part of the steel production process, a large scale experiment was set-up. The implementation of the strategy will be explained consecutively following the six steps introduced in Chapter 5.

6.2 Factor identification and selection

Step 1 As stated in the introduction, only part of the production process was taken into account. The process phases stirring station, tundish and mould were investigated (see Chapter 2 for more details). As a first step in the strategy, factors have to be identified and selected. For this purpose the problem has been divided into three categories: production process, sampling and analysis. For each category, a number of sources of variation can be identified.

6.2.1 Production process

In the production process, several sources of variation can be recognized. Differences between process phases, within process phases and between batches are three sources. Differences between batches are not investigated further but will end up in the model because samples are taken from different batches of steel (*source of variation: between batch differences*). It is interesting to investigate whether differences exist between the three process phases stirring station, tundish and mould both in terms of average concentration and in terms of variance. At present, samples are mainly taken from the stirring station for process control and from the mould for quality control. Another process phase from which possibly samples can be taken is the tundish. Because samples taken from the process have to be highly representative (only 1/25,000,000 part of the total batch is sampled and of this sample only 1/10,000,000 part is used for analysis) for the batch, it is important to know what location and what point in time is optimal for taking samples.

Within one batch, several sources of variation exist. Concentrations of elements change going from one process phase to the other as a cause of process steps such as addition of ferro alloys to the steel bath, blowing of oxygen into the liquid steel bath or blowing of argon through the liquid steel bath. Changes due to process steps like this are more or less known to the process engineers and are therefore not included in the experiment. Included in the experiment, however, are the spatial and temporal differences of concentrations in the process phases (*source of variation: heterogeneity in the process phase*). Besides the heterogeneity, other sources of variation such as *process operator* and *process circumstances* should be mentioned. These sources of variation are difficult to control and therefore are not selected.

6.2.2 Sampling

From the process phases investigated in this research, double thick samples are taken. It is interesting to know whether samples taken at a certain location and at points in time t and $t+\Delta t$ (where Δt is in the range of 10 to 20 seconds) are similar to each other. Differences between these (duplicate) samples can be caused by *heterogeneity of the process phase* on a small scale and/or by difficulties occurring during sampling such as *inclusion of casting powder*.

Repeatability of sampling is indicative for the efficiency of sampling in the steel bath. The repeatability of sampling can be investigated by analysing samples which have been taken from the same place and at approximately the same point in time from the steel bath.

6.2.3 Analysis

Double thick samples can be analysed on one of the available spectrometers. Availability of a spectrometer is one of the criteria to decide which spectrometer will be used for analysis although for some samples there exist a preference for one specific spectrometer.

Not one spectrometer is equal to the other spectrometers albeit that some spectrometers are more equal than others. Differences can exist because of brand, type, wear and software (*source of variation: different spectrometers used for analysis*). Differences between spectrometers will not show up when a sample is analysed on one spectrometer which is normally the case. If however, several samples have to be analysed for process control, a difference between the analysis results can occur when the samples are analysed on different spectrometers although the samples need not necessarily be different. Such an event can result in problems for process control when differences between spectrometers results are larger than the control limits. The control limits might be tightened in the future because of customer demands. Using different spectrometers in this experiment can reveal whether differences between spectrometers cause problems when the control limits are tightened.

Focussing on one spectrometer, differences between analysis results obtained at different points in time can occur due to instrumental drift. As explained in Chapter 4, an adjustment (two point calibration) takes place every eight hours to make sure that deviations due to instrumental drift and cleaning of the spark stand are kept to a minimum. A disadvantage of the adjustment procedure is that for the correction factors to be calculated, measurements have to be performed. These measurements are subject to variation and therefore the correction factors also are a source of variation (*source of variation: adjustment*). As a result, concentrations obtained for one sample measured during

adjustment period I can differ from concentrations obtained for the same sample measured during adjustment period II. This is true, even if drift in the instrumental signal does not occur.

Analysis performed on a double thick sample by means of spark emission spectrometry involves two or more individual measurements which are averaged depending upon their reproducibility (Chapter 4). Individual measurements differ from each other because of *heterogeneity in the sample, differences in circumstances* (the spark is not a completely constant phenomenon) and *inclusions in the sample*. By averaging reproducible analysis results, the variance caused by individual measurements is reduced by a factor n where n is the amount of individual measurements. However, *variation due to heterogeneity, variation due to inclusions* and *variation due to changes in circumstances during spark measurements* still contribute to the total variation in the final analysis results.

6.3 Model selection

Step 2 Of the identified factors, only a selection of factors has been included into models. One of the factors that is available for the production process, sampling and analysis is the operator. It would be difficult, if not impossible, to control this factor for the production process and sampling of the process because both are carried out in shifts and the tasks are performed by the operator at duty at that moment. For the analysis, this problem does not occur and all experiments have been performed by one chemical analyst only to exclude the influence of different chemical analysts. All further variations due to differences between process operators ends up in the residual variation which is a “repository” for all sources of variation not accounted for in the model but apparent in the final analysis results.

Included in the model are: the mean (M), spectrometer (S), batch (B), adjustment (A), duplicate sampling (D), place of sampling (P), time of sampling (T) and the residual variation (R).

For each investigated process phase, a different model has been selected. From the stirring station (equation 6.1) samples have been taken only from one place and at one point in time. Therefore, the only process specific factor in this model is batch (B). Further discussions of the different factors is given after the presentation of the chosen models for the individual process phases.

$$[Concentration] = M + B + S + B.D + S.A + R \quad (\text{Stirring station}) \quad (6.1)$$

Table 6.1: Factors included in the experiment and the codes used in the models for the process phases stirring station, mould and tundish. The columns stirring station, tundish and mould show which factors are included in models for the individual process phases.

Factor	Code	Stirring station	Tundish	Mould	Nested within	Fixed or random
Spectrometer	<i>S</i>	x	x	x	-	Random
Adjustment	<i>A</i>	x	x	x	<i>S</i>	Random
Batch	<i>B</i>	x	x	x	-	Random
Duplicate sampling	<i>D</i>	x	x	x	<i>B</i>	Random
Place of sampling	<i>P</i>		x		-	Fixed
Time of sampling	<i>T</i>		x	x	-	Fixed
Residual	<i>R</i>	x	x	x	-	Random

Equation 6.2 is the model selected for the tundish. It contains both process specific factors time of sampling (*T*) and place of sampling (*P*) which can have an effect on the concentration in the sample.

$$[Concentration] = M + B + S + B.D + S.A + P + T + R \quad (\text{Tundish}) \quad (6.2)$$

The third model (equation 6.3) contains only time of sampling (*T*) as an extra process specific factor.

$$[Concentration] = M + B + S + B.D + S.A + T + R \quad (\text{Mould}) \quad (6.3)$$

Details of the factors in the preceding models are summarized in Table 6.1 and are explained further in sections 6.3.1 through 6.3.7.

6.3.1 Spectrometer (*S*)

When a sample is analysed on different spectrometers, different analysis results are likely to be obtained. The samples used for spark OES can be analysed more than once with only little sample preparation needed in between the analyses. The factor spectrometer is included as a random factor so that an estimation can be made of the variation occurring when a sample is analysed on any of the available spectrometers. The postulation is that the spectrometers used for the experiment are a random drawing from the total population of spectrometers available. The choice of spectrometers was restricted to the instruments currently available at *Hoogovens Staal BV* but in the future other

spectrometers will be used and the conclusion should extend to new spectrometers as well. Hence, the variation (estimated with the model) of an analysis will include the fact that a sample can be chosen to be analysed on one of the available spectrometers.

6.3.2 Adjustment (A)

The factor adjustment (A) represents the differences between measurements performed in different adjustment periods. Adjustment is included as a random factor because the period within which the experiments are performed, are periods randomly chosen from a large population of available periods. Furthermore, adjustment is nested within spectrometers because there is no relation between adjustments of instrument A and adjustments of instrument B.

6.3.3 Batch (B)

The batch variation is included to be able to include samples in the experiment that are taken from different batches of steel. The estimates of this random factor will not be discussed further since the emphasis of the thesis lies in estimating the magnitudes of the sources of variation connected with batch heterogeneity, sampling and analysis.

6.3.4 Duplicate sampling (D)

The factor duplicate sampling (D) is a random factor that is nested within the factor batch. The nesting of this factor is caused by the differences between batches. The reasoning is comparable to the reasoning followed for the factor adjustment (A).

By taking samples at approximately the same time and place the repeatability of taking samples from a certain process phase can be estimated. The magnitude of this source of variation indicates how much variation is induced because of using double thick samples to analyse the contents of the complete steel bath.

6.3.5 Place of sampling (P)

In the tundish, two different places of sampling can be distinguished: just below the submerged entry nozzle and above an outlet. Differences between samples taken at these two places can occur due to heterogeneity in the batch, difficulties in sampling (i.e. inclusion of casting powder in the sample) and a

concentration gradient due to a batch transition. For the two other process phases, the place of sampling is kept as constant as possible.

The factor place of sampling (P) is included in the model as a fixed effect because it is of interest whether there exists a difference in concentration for samples taken from the two different places in the tundish.

6.3.6 Time of sampling (T)

The second factor dealing with heterogeneity of the batch is the time of sampling (T). A batch of steel flows through the tundish and mould within a certain amount of time. Taking samples at different points in time, an impression can be obtained of the gradient in concentration and the best time of sampling in terms of minimum variance. The time of sampling is included as a fixed effect to get an idea about differences in concentration measured in samples taken at different points in time.

6.3.7 Residual (R)

All variation not included in (explained by) the factors discussed in the former sections will be included in the residual variation. Among others, differences between process operators and differences in operating conditions are two of these sources of variation. An important third source of variation included in the residual variation is the heterogeneity of samples.

6.4 Experimental design

Step 3 For the experiment, two separate experimental designs were used. The first experimental design deals with those factors which are associated with sampling of the steel making process and the steel making process itself (batch, duplicate sampling, time of sampling, place of sampling). The second experimental design comprises those factors which deal with the analysis of the samples (adjustment and spectrometer). Excluding the factors of the analysis procedure from the first experimental design gives an opportunity to collect all samples before starting the chemical analysis. Separation in two designs is needed to randomize the samples over the levels of the factor adjustment. Within each adjustment period of eight hours, the instrumental drift is different. Analysing the samples in the same order as the sampling occurs could introduce systematic errors between analysis results because of this changing drift behaviour.

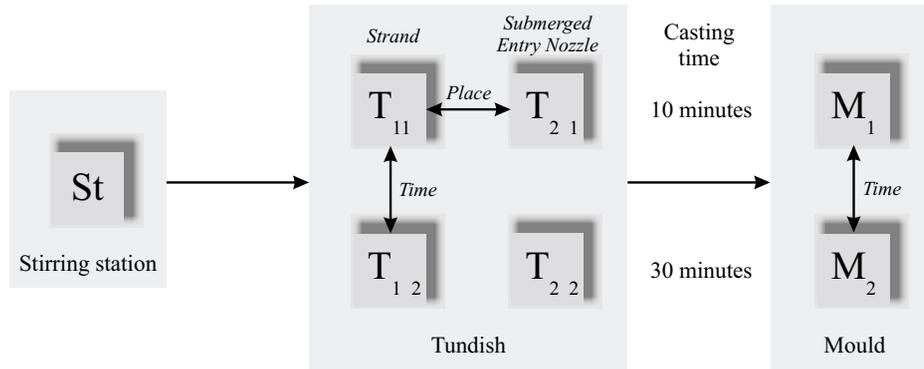


Figure 6.1: Experimental design for sampling the process phases stirring station, tundish and mould.

6.4.1 Experimental design for sampling

Three factors are included in the experimental design for sampling: place of sampling, time of sampling and duplicate sampling. From eight batches of the same type of steel, samples were taken according to the design in Figure 6.1.

Place of sampling (heterogeneity in place) is included for the samples taken from the tundish by taking samples just below the submerged entry nozzle and above one of the outlets of the tundish. For both tundish and mould, the factor time of sampling (heterogeneity in time) is included by taking samples at 10 and 30 minutes after starting to cast a certain batch of interest. For this experiment, two samples were taken each time when a sample had to be taken according to the experimental design. The duplicate samples were taken at approximately the same place and time.

6.4.2 Experimental design for analysis

For this experiment, the magnitude of two sources of variation in the analysis of steel are important to estimate: differences between spectrometers and adjustment. To achieve this, the analyses of the samples have to be divided over a number of spectrometers and a number of adjustment periods of these spectrometers. An experimental design containing four spectrometers and six adjustment periods per spectrometer has been chosen. Analysing the samples from eight batches according to a complete design would require 122 samples to be analysed in duplicate in at least two adjustments of the four available spectrometers. Clearly, such a design would require far too many analyses (1792). Therefore, an incomplete design was constructed in which balance was pre-

Table 6.2: Experimental design for analysis. Allocation of batch numbers to spectrometer and adjustment for samples taken from stirring station, tundish and mould. Each number in the experimental design stands for a batch from which samples were taken.

		Adjustment						
		Spectrometer	1	2	3	4	5	6
Stirring station	1	1	5	1	5	4	8	
	2	2	5	2	6	7	6	
	3	1	3	7	3	6	7	
	4	4	3	2	4	8	8	
Tundish	1	1	5	3	5	1	6	
	2	1	2	4	6	6	7	
	3	8	3	3	8	7	7	
	4	2	4	5	4	2	8	
Mould	1	1	4	4	5	7	7	
	2	2	2	6	5	6	5	
	3	1	3	1	2	7	8	
	4	8	3	4	3	6	8	

served by putting an equal number of observations in each cell [77, page 224] in which a cell is a combination of a spectrometer and an adjustment period.

The design, presented in Table 6.2 was constructed in such a way that each sample was analysed twice on the same spectrometer but during different adjustment periods and once on another spectrometer. To show this more explicitly, the samples taken from the stirring station from batch 4 are shown in boldface in the experimental design. It is important to notice that adjustments of different spectrometers are completely independent from each other.

Experimental design for analysis: stirring station

The design used for the samples taken from the stirring station is shown in Table 6.2 by the batch numbers in the row ‘Stirring station’. Per cell (intersection between spectrometer and adjustment), two (duplicate) samples from a certain batch occur. So, for the stirring station, in each cell, two (duplicate) samples are analysed. Both samples have to be analysed in duplicate (repeated measurements). For the stirring station, in total 4 analysis (2 measurements \times 2 duplicate samples) results are obtained from each cell shown in Table 6.2. Each sample occurs thrice in the design in order to estimate the effects of spectrometer and adjustment on the total variation.

Experimental design for analysis: tundish

For a certain batch, all tundish samples (T_{11} , T_{21} , T_{12} , T_{22}) are put in one cell in Table 6.2. This allows for an optimal estimation of the effects time of sampling and place of sampling in the tundish. Similar to the stirring station, the samples from the tundish have to be analysed three times at different combinations of spectrometer and adjustment period. The batch numbers in the row ‘Tundish’ in Table 6.2 show the experimental design for samples from the tundish. For this process phase, in total 16 analysis results are obtained from each cell in the experimental design for analysis (2 measurements \times 4 samples \times 2 duplicate samples).

Experimental design for analysis: mould

From the mould, two different samples (M_1 , M_2) are available in duplicate. This results in a total of four samples from the mould taken from one batch. Analysis of the four samples in one cell of the experimental design for analysis allows for an optimal estimation of the effect of heterogeneity and time effects. Like the samples taken from the stirring station and the tundish, each sample is included in the design three times at different combinations of spectrometer and adjustment periods. The experimental design for analysis of samples taken from the mould is shown in Table 6.2 by the batch numbers in the row ‘Mould’. For the mould, in total 8 analysis results are obtained from each cell shown in Table 6.2 (2 measurements \times 2 samples \times 2 duplicate samples).

6.5 Performing the experiments

Step 4

6.5.1 Sampling

From the three process phases, double thick samples were obtained according to the experimental design presented in Figure 6.1. For sampling, double thick samplers were used (Heraeus Electro-Nite, Belgium). Before analysis, the samples were judged visually on fitness for analysis. A complete set of samples (14 samples originating from 1 batch) was rejected if one (or more) of the samples showed irregularities. It should be noted that many of the rejected samples would have been used for process control under normal operating conditions. However, analysis results from samples with questionable quality can

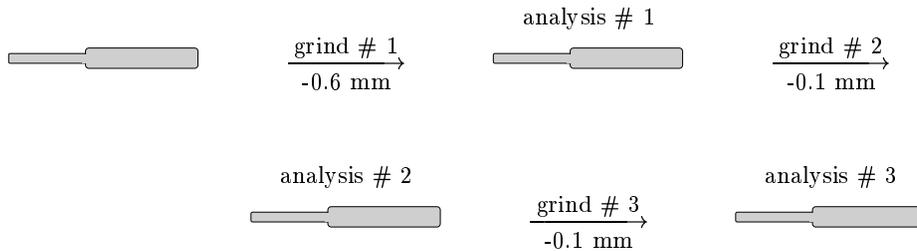


Figure 6.2: The double thick samples were analysed three times in a row with three grinding steps in between.

have a large influence on the estimations and therefore only samples without irregularities were used for the experiments.

Due to this restriction, sampling of more than 8 batches of steel was needed to obtain the required amount of 8 series of samples originating from 8 batches. Because of the selection procedure, the estimates for the factor sampling will be applicable to the ideal situation in which all sample obtained from the process are (visually) fit for analysis, and therefore are an underestimation of the sampling errors in normal operating conditions.

6.5.2 Analysis

Before analysis, the samples were ground on a Herzog HB2500 T belt grinder with NORTON 60-grit, Zirconium treated. Each sample was ground three times (Figure 6.2). The first grinding procedure removed approximately 0.6 mm from the sample surface while the consecutive two grinding procedures only removed approximately 0.1 mm from the sample surface to remove the spots created by sparking the samples.

The analyses were performed according to the experimental design shown in Table 6.2. Details of the four spark optical emission spectrometers are summarized in Table 6.3. The samples are handled by a robot arm for three spectrometers.

Per element, in total 672 analysis results (concentrations) were obtained from the experiments (112 samples \times 3 analyses per sample \times 2 measurements per analysis).

Within an adjustment period of eight hours, the analyses were performed approximately 2 hours after cleaning and adjusting the spectrometers. It will be shown in Chapter 8 that intensities obtained within the first hour after cleaning the spark stand are less stable than intensities obtained later on. Therefore, within an adjustment period of eight hours the analysis scheme

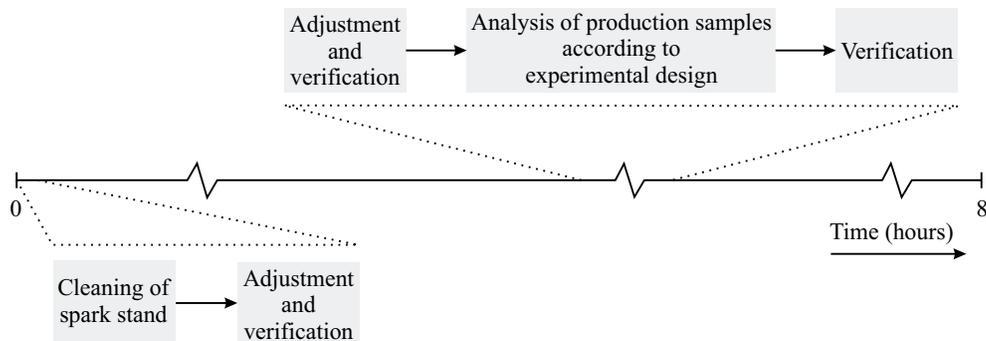
Table 6.3: Instrumental details of the four spectrometers used in the experiment.

Spectrometer	Brand	Manual/Automatic analysis
OES1	ARL S.A. OE 3460	Automatic
OES3	OBLF QSN 750R	Automatic
OES8	ARL S.A. OE 3460	Automatic
OES9	ARL S.A. OE 3460	Manual

presented in Figure 6.3 was used. Normally, the adjustment at approximately 2 hours after cleaning the spark stand is not performed. However, in this case it was needed because sometimes experiments were started two hours after cleaning the spark stand and in other cases it could be three hours. The extra adjustment was needed to make sure that the initial stage was the same within each adjustment period.

6.6 Estimation of the effects

Step 5 The data obtained from the chemical analyses were first evaluated to remove possible outliers. Statistical analysis of the data was performed with SAS® V6.12 for Windows®. The variance components (random effects) in the models shown in equations 6.1 through 6.3 and the standard errors of the variance components were estimated by means of restricted maximum likelihood (REML, Chapter 5). In some cases, a negative variance can be obtained. Because negative variances have no meaning, these variances are set

**Figure 6.3:** Schematic presentation of one adjustment period of eight hours during which analyses were performed.

to 0 and the errors of these estimates are not calculated (represented as '-').

The magnitude of the fixed effects (mean squares) and their significance were estimated by means of least squares (LS, Chapter 5).

6.7 Interpretation and discussion

Step 6 From the large amount of results obtained with REML and LS estimations, typical results are presented in this section. For elements with similar variations, the results of only one representative element is shown in detail. Besides the estimates of the random effects, also the standard errors of the estimates are reported. The standard errors of the estimates have rather high values due to the fact that these are based on asymptotic theory. The asymptotic theory describes how an estimator will behave in case an infinite large random test is performed. Consequently, for limited sample size, asymptotic theory gives approximate variances.⁸⁰ The standard errors of the estimates provide only a rough guide to the estimates' precision with such a small sample.⁸⁸

6.7.1 Carbon

For carbon, differences between results obtained from different spectrometers contribute most to the total variation apparent in the final analysis results (Figure 6.4 and Table 6.4). Both adjustment and sampling have less influence on the total variation. The residual variance, which contains all variation not explained by the other sources of variation in the model, turns out to have higher values for both samples taken from the tundish ($214 \cdot 10^{-8}$) and the mould ($291 \cdot 10^{-8}$) in comparison to the residual variation estimated for the stirring station ($55.8 \cdot 10^{-8}$). Heterogeneity of samples taken from the process phases tundish and mould could cause this problem. Sampling at the stirring station is automated partly and sampling is more easy at this process phase. The high environmental temperatures and the flow of the steel could cause problems in filling of the sample chamber, resulting in heterogeneous samples taken for the tundish and mould. Although the temperatures are even higher at the stirring station, sampling at the stirring station is easier because of the half automated sampling procedure.

The standard errors (S.E.) of the estimated variance components have been summarized in Table 6.4 along with the magnitude of the variance components ($\hat{\sigma}^2$). The standard errors presented in Table 6.4 indicate the level of confidence of the estimates of the variance components presented in Figure 6.4.

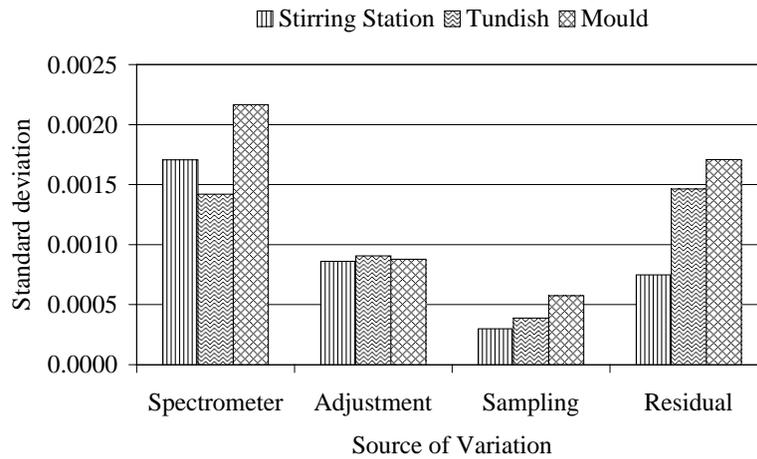


Figure 6.4: Contribution of four sources of variation to the total variation apparent in analysis results obtained for carbon (C). The estimates are presented as standard deviations.

Table 6.4: Estimates of the concentrations, variances ($\hat{\sigma}^2$) and standard errors of the estimated variance components for carbon (C).

Process phase	Concentration	$\hat{\sigma}^2$ ($\cdot 10^{-8}$); Standard Error ($\cdot 10^{-8}$)			
		Spectrometer	Adjustment	Sampling	Residual
Stirring station	0.0433	291;261	73.7;34.4	8.7;9.1	55.8;9.8
Tundish	0.0427	202;185	82.3;37.6	14.7;11.9	214;16.2
Mould	0.0438	469;411	76.5;44.7	33.4;29.0	292;32.7

The fixed effects (place and time of sampling) appear to be of minor importance for carbon compared to the residual variation (Table 6.5). So, for carbon no significant difference in concentrations could be found in samples taken at different places or at different points in time from tundish and mould.

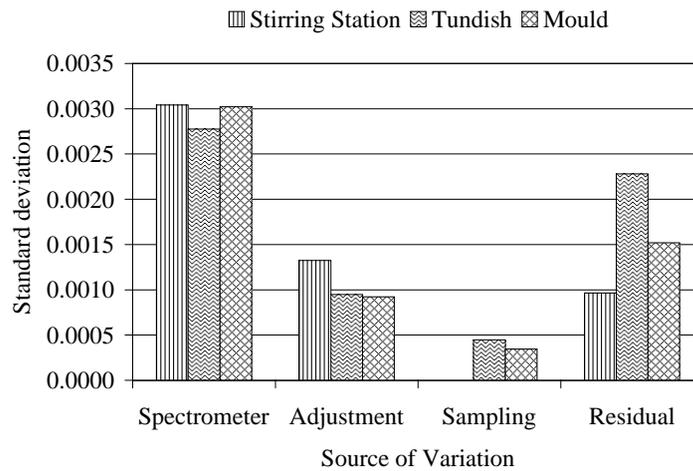
6.7.2 Manganese

For manganese, just as for carbon, the contribution of the differences between spectrometers to the total variation is relatively large. This holds for samples taken from the stirring station and the mould. For samples taken from the tundish, the contribution of the residual variation on the total variation plays an important role as well (Figure 6.5).

The magnitude of the variance components and the standard errors of the estimated variance components are presented in Table 6.6. No standard error

Table 6.5: Fixed effect estimates for carbon (C). Least squares estimates together with F-values and p-values.

		Carbon				
Process phase	Source	d.f.	SS ($\cdot 10^{-8}$)	MS ($\cdot 10^{-8}$)	F-value	p-value
Tundish	Time	1	0.12	0.12	0.00	0.98
	Place	1	22.4	22.4	0.10	0.75
	Residual	350	75018	214		
Mould	Time	1	81.4	81.4	0.28	0.60
	Residual	159	46418	292		

**Figure 6.5:** Contribution of four sources of variation to the total variation apparent in analysis results obtained for manganese (Mn). The estimates are presented as standard deviations.

is given for the variance component sampling in the stirring station because the corresponding variance component was negative and therefore set to 0.

From the results in Table 6.7 it can be seen that both place and time of sampling have a significant influence at least in the range of the 95% confidence interval. The residual MS is also high for samples taken from the tundish and mould. This result is probably caused by heterogeneity of manganese in the steel bath. Further investigation on steel with other product specifications is needed to test whether a gradient of manganese concentration exists.

Table 6.6: Estimates of the concentrations, variances ($\hat{\sigma}^2$) and standard errors of the estimated variance components for manganese (Mn).

Process phase	Concentration	$\hat{\sigma}^2$ ($\cdot 10^{-8}$) ; Standard Error ($\cdot 10^{-8}$)			
		Spectrometer	Adjustment	Sampling	Residual
Stirring station	0.221	926;806	175;77.3	0;-	92.6;15.4
Tundish	0.221	771;657	89.5;47.9	20.2;21.0	520;39.3
Mould	0.221	913;770	85.1;44.5	12.0;15.8	231;25.9

Table 6.7: Fixed effect estimates for manganese (Mn). Least squares estimates together with F-values and p-values.

Manganese						
	Source	d.f.	SS ($\cdot 10^{-8}$)	MS ($\cdot 10^{-8}$)	F-value	p-value
Tundish	Time	1	2013	2013	3.87	0.050
	Place	1	4601	4601	8.85	0.003
	Residual	350	182009	520		
Mould	Time	1	1452	1452	6.29	0.013
	Residual	159	36721	231		

6.7.3 Phosphorus

The influence of differences between spectrometers is less dominant for phosphorus. The variance component adjustment has an important contribution to the total variation for samples taken from the stirring station and the mould. As can be seen from the results presented in Figure 6.6, this is not the case for samples taken from the tundish.

The higher contribution of the spectrometer differences for samples taken from the tundish can not be explained at the moment and further research is needed. It should be noted that also the residual variation has higher values for samples taken from the tundish in comparison to samples taken from stirring station and mould. Disturbances during sampling in the tundish may be the cause of this increased residual variation. The standard errors of the variance components are summarized in Table 6.8.

Both time and place of sampling appear to have a significant influence ($p < 0.05$) on the concentration for samples taken from the tundish (Table 6.9). This means that a concentration gradient might exist in the tundish in both time and place. Besides differences between samples taken from different places and at different points in time, also differences within a sample are rather high judging the considerable residual variation for the tundish (Table 6.8). Differences between samples can be considered as heterogeneities on a macro

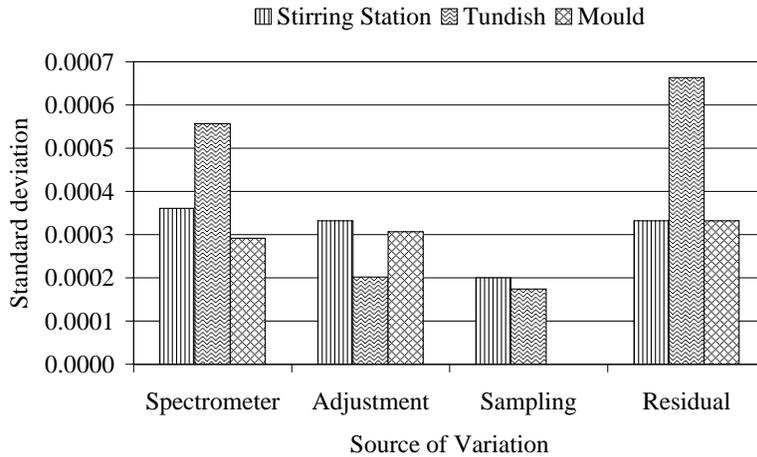


Figure 6.6: Contribution of four sources of variation to the total variation apparent in analysis results obtained for phosphorus (P). The variation is presented in terms of standard deviation.

Table 6.8: Estimates of the concentrations, variances ($\hat{\sigma}^2$) and standard errors of the estimated variance components for phosphorus (P).

Process phase	Concentration	$\hat{\sigma}^2$ ($\cdot 10^{-8}$) ; Standard Error ($\cdot 10^{-8}$)			
		Spectrometer	Adjustment	Sampling	Residual
Stirring station	0.0068	13.4;13.7	11.1;5.4	3.5;2.7	10.8;1.9
Tundish	0.0070	31.5;27.3	4.1;2.7	3.0;2.4	44.4;3.4
Mould	0.0074	8.5;9.7	9.4;4.2	0;-	11.4;1.2

scale and these heterogeneities are probably caused by concentration gradients within the process phase. High residual variations on the other hand are probably caused by a combination of heterogeneities on a micro scale within the process phase and diffusion of molecules within the sample before solidification is complete. Research on steel with another composition should reveal whether this conclusion is also true for other concentrations.

6.7.4 Sulphur

The estimates for the variance components for sulphur have been summarized in Figure 6.7. For sulphur, the adjustment is an important source of variation just like for phosphorus. In the case of sulphur however, the contribution of the variance component adjustment is of less importance in samples taken from the mould whereas for phosphorus, the contribution was of less importance for

Table 6.9: Fixed effect estimates for phosphorus (P). Least squares estimates together with F-values and p-values.

		Phosphorus				
	Source	d.f.	SS ($\cdot 10^{-8}$)	MS ($\cdot 10^{-8}$)	F-value	p-value
Tundish	Time	1	359	359	8.09	0.005
	Place	1	233	233	5.26	0.022
	Residual	350	15527	44.4		
Mould	Time	1	24.1	24.1	2.04	0.16
	Residual	159	1876	11.8		

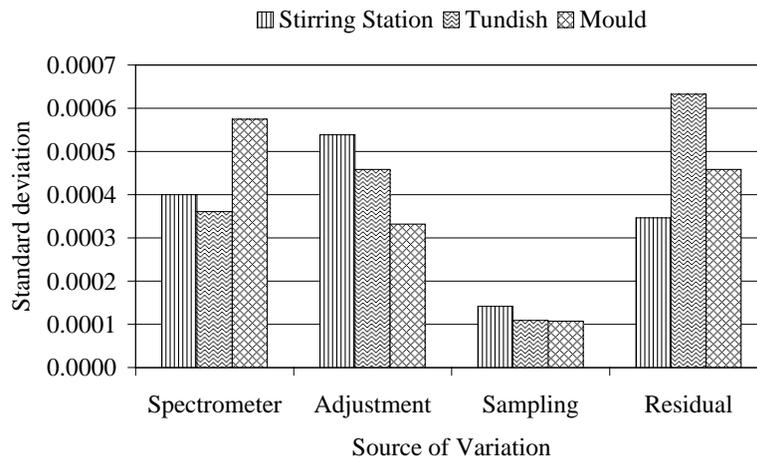


Figure 6.7: Contribution of four sources of variation to the total variation apparent in analysis results obtained for sulphur (S). The variation is presented in terms of standard deviation.

samples taken from the tundish (Figure 6.7).

This observation could purely be due to the estimation variance (the standard errors of the estimations are presented in Table 6.10) but the results from both phosphorus and sulphur show a trend in which adjustment plays an important role in the build-up of the total variation.

A possible cause for this behaviour is instrumental drift. Preliminary results from another experiment show that the drift within the spectrometers appears to be element specific (see Chapter 8). When drift appears to have a large influence, methods like Kalman filter⁸⁹⁻⁹⁴ and adaptive filtering⁹⁵ can be used to reduce the influence of drift on the variation in the analysis results.

Table 6.10: Estimates of the concentrations, variances ($\hat{\sigma}^2$) and standard errors of the estimated variance components for sulphur (S).

Process phase	Concentration	$\hat{\sigma}^2$ ($\cdot 10^{-8}$) ; Standard Error ($\cdot 10^{-8}$)			
		Spectrometer	Adjustment	Sampling	Residual
Stirring station	0.0124	15.7;20.2	28.9;13.6	2.2;2.1	12.1;2.1
Tundish	0.0124	13.0;15.1	20.8;9.1	1.2;1.4	39.9;3.0
Mould	0.0129	32.6;30.3	11.1;5.6	1.2;1.4	20.6;2.3

Table 6.11: Fixed effect estimates for sulphur (S). Least squares estimates together with F-values and p-values.

Sulphur						
	Source	d.f.	SS ($\cdot 10^{-8}$)	MS ($\cdot 10^{-8}$)	F-value	p-value
Tundish	Time	1	443	443	11.12	< 0.001
	Place	1	51.5	51.5	1.29	0.26
	Residual	350	13955	39.9		
Mould	Time	1	42.2	42.2	2.05	0.15
	Residual	159	3273	20.6		

From the results obtained for the fixed effects time of sampling and place of sampling (Table 6.11) it can be concluded that only the time of sampling in the tundish is of importance for sulphur.

6.7.5 Chromium

The estimates for the variance components for chromium have been summarized in Figure 6.8. It is clear that the differences between spectrometers have a large influence on the build-up of the total variation in the analysis results. In contrast to most other elements, the residual variation is of minor importance and the variation due to adjustment almost equals the residual variation. So it seems that mainly the differences between the spectrometers influence the variation found in the analysis results of chromium. This result indicates that chromium is divided homogeneous throughout the sample.

The concentrations found in the samples and the standard errors of the estimated variances are presented in Table 6.12. The difference in concentration between tundish and mould (0.018%) and stirring station (0.017%) is noticeable but this appears to be not significant. Moreover it should be noticed that the concentration of chromium is monitored but not steered for the type of steel under investigation.

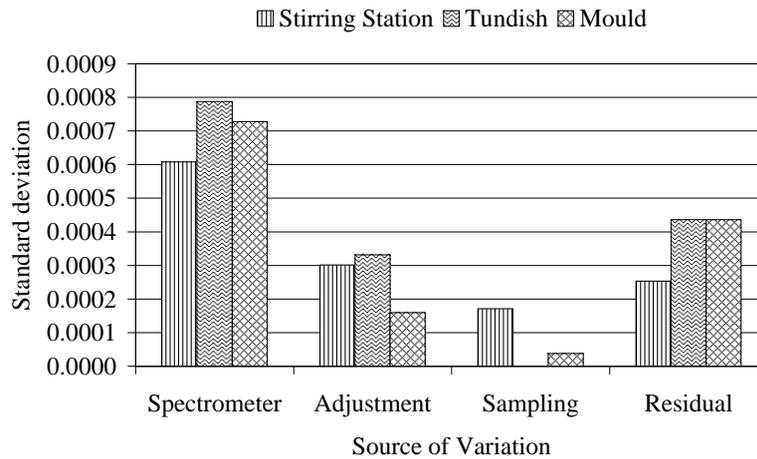


Figure 6.8: Contribution of four sources of variation to the total variation apparent in analysis results obtained for chromium (Cr). The variation is presented in terms of standard deviation.

Table 6.12: Estimates of the concentrations, variances ($\hat{\sigma}^2$) and standard errors of the estimated variance components for chromium (Cr).

Process phase	Concentration	$\hat{\sigma}^2$ ($\cdot 10^{-8}$) ; Standard Error ($\cdot 10^{-8}$)			
		Spectrometer	Adjustment	Sampling	Residual
Stirring station	0.0168	37.3;33.2	9.1;4.2	2.9;2.0	6.4;1.1
Tundish	0.0181	62.4;53.2	11.3;4.9	0;-	18.7;1.4
Mould	0.0180	53.1;44.8	2.5;1.9	0.15;0.9	19.5;2.1

Table 6.13 shows the estimates for the fixed effects. A significant difference in time of sampling is found for samples taken from the mould while for samples taken from the tundish, only place of sampling has a significant influence on the concentration. Especially the difference for samples taken at different points in time from the mould is large (4.8%). It is interesting to know which place and time of sampling are optimal for process control. This will be further discussed in Section 6.7.7.

6.7.6 Tin

The results for tin show some anomalies (See Figure 6.9 and Table 6.14 for the estimates of the variance components and Table 6.14 for the standard errors).

The concentrations of tin are low but the results obtained for this element are

Table 6.13: Fixed effect estimates for chromium (Cr). Least squares estimates together with F-values and p-values.

		Chromium				
	Source	d.f.	SS ($\cdot 10^{-8}$)	MS ($\cdot 10^{-8}$)	F-value	p-value
Tundish	Time	1	16.0	16.0	0.84	0.36
	Place	1	1495	1495	78.49	< 0.001
	Residual	350	6666	19.1		
Mould	Time	1	867	867	44.51	< 0.001
	Residual	159	3097	19.5		

still of interest. This is the only element for which sampling has an important influence on the total variation. This is especially the case for samples taken from the tundish. The reason why the sampling variance is that large for tin could be a difference in sampling method. For each process phase the same type of sample (double thick, see Section 4.2 on page 44) was used but certain differences between sampling probes existed.

The sampling chamber is closed with a small metal cap. This cap has to melt before steel can flow into the sample chamber. The cap is used in order to prevent slag and other material floating on the liquid steel bath from entering the sample chamber. The metal cap contains a small amount of tin. The tin apparent in the metal cap causes an increased variance for samples taken from

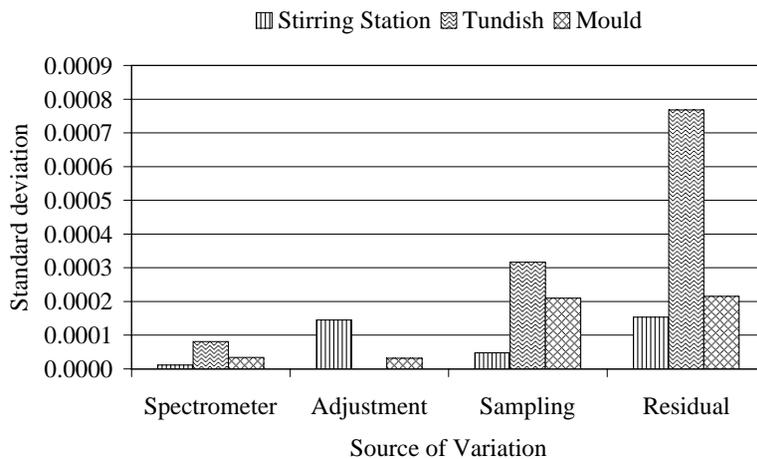
**Figure 6.9:** Contribution of four sources of variation to the total variation apparent in analysis results obtained for tin (Sn). The variation is presented in terms of standard deviation.

Table 6.14: Estimates of the concentrations, variances ($\hat{\sigma}^2$) and standard errors of the estimated variance components for tin (Sn).

Process phase	Concentration	$\hat{\sigma}^2$ ($\cdot 10^{-8}$) ; Standard Error ($\cdot 10^{-8}$)			
		Spectrometer	Adjustment	Sampling	Residual
Stirring station	0.0016	0.013;0.98	2.1;1.1	0.23;0.32	2.4;0.42
Tundish	0.0029	0.66;1.2	0;-	10.1;6.3	58.6;4.3
Mould	0.0018	0.11;0.3	0.10;0.28	4.4;2.4	4.6;0.52

the tundish. Further research should reveal the source of the extra variation. Also, it should be investigated whether this behavior exist for steel with other product specifications as well.

The concentration of tin is important to the process engineer. The concentration of this element is monitored but the differences found in this research are of no concern for the type of steel investigated here. The other sources of variation are not discussed here because the concentration of tin found in the sample is low.

6.7.7 Sampling location and time

From the tundish and mould, samples have been taken at different points in time (10 and 30 minutes). From the tundish also samples have been taken at two different locations (above one of the outlets and below the submerged entry nozzle (SEN)). In the previous sections the effects P (place) and T (time) have been included in the models. However, it is also possible to exclude the factors time and place from the models of tundish and mould (equations 6.2 and 6.3 respectively). Thus, for each place and time, a model like the one used for the stirring station (equation 6.1) can be used in order to estimate the residual variation for each type of sample individually. The results of these estimations are reported in Tables 6.15 and 6.16.

The results in Table 6.15 clearly show that the residual variation is the highest in samples taken from below the SEN at 30 minutes after starting to cast a new ladle of steel into the tundish (T_{22}). The lowest variation is found in most cases in samples taken from the tundish above the outlet (T_{11} and T_{12}). The increased variation at the SEN can possibly be explained by extra turbulence at the outlet of the steel ladle through which casting powder is mixed with the steel.

Samples taken at 10 minutes and at 30 minutes from the mould appear to be similar to each other (Table 6.16). Some differences in residual variation are found for the elements carbon, silicon, and aluminium where the sample

Table 6.15: Estimates for the residual variation and concentration corresponding to samples taken from the tundish (T_{11} , T_{21} , T_{12} , T_{22}).

Element	Residual variation, $\hat{\sigma}^2$ ($\cdot 10^{-8}$) (concentration (%))							
	T_{11}		T_{12}		T_{21}		T_{22}	
	outlet(10 min)		outlet(30 min)		SEN(10 min)		SEN(30 min)	
C	131	(0.043)	131	(0.043)	113	(0.043)	214	(0.043)
Mn	236	(0.221)	306	(0.221)	273	(0.221)	851	(0.224)
P	10	(0.007)	29	(0.007)	12	(0.007)	27	(0.008)
S	14	(0.013)	18	(0.013)	23	(0.012)	35	(0.013)
Si	65	(0.005)	110	(0.005)	67	(0.005)	232	(0.005)
Al	360	(0.049)	328	(0.049)	293	(0.048)	345	(0.049)
Cu	8	(0.011)	8	(0.011)	6	(0.011)	13	(0.011)
Sn	5	(0.003)	6	(0.003)	8	(0.003)	5	(0.003)
Cr	27	(0.018)	15	(0.018)	11	(0.018)	7	(0.018)
Ni	14	(0.023)	44	(0.023)	15	(0.023)	48	(0.022)
Mo	5	(0.002)	6	(0.002)	5	(0.002)	8	(0.002)

Table 6.16: Estimates for the residual variation and concentration corresponding to samples taken from the mould (M_1 , M_2).

Element	Residual variation, $\hat{\sigma}^2$ ($\cdot 10^{-8}$) (concentration(%))			
	M_1		M_2	
	10 min		30 min	
C	297	(0.044)	122	(0.044)
Mn	92	(0.221)	92	(0.221)
P	5	(0.007)	8	(0.007)
S	11	(0.013)	16	(0.013)
Si	92	(0.006)	33	(0.005)
Al	511	(0.048)	184	(0.048)
Cu	5	(0.011)	10	(0.011)
Sn	1	(0.002)	1	(0.002)
Cr	12	(0.018)	16	(0.018)
Ni	4	(0.023)	11	(0.023)
Mo	3	(0.002)	4	(0.002)

taken at 30 minutes is in favour because of a lower variance. Reduction of the heterogeneity over time may result in this variation reduction. For the samples taken from the mould at 10 and 30 minutes there exists no significant difference in concentration.

6.8 Conclusions

It should be noted that for this experiment only those samples have been selected which contained no irregularities on the surface. Therefore, the estimated sampling variations are only valid when samples are supplied to the laboratory of process control which have no irregularities on the surface of the sample.

Furthermore, the experiment described here concerns steel from only one specific constitution. Further research is needed in order to investigate whether the results obtained in this experiment are general or whether the estimated conclusions depend upon the type of steel under investigation.

From the results presented in the previous sections, the following conclusions can be drawn:

- Differences between spectrometers turned out to be an important source of variation for part of the total range of elements analysed in the experiment. The differences between results of chemical analyses obtained from different spectrometers are caused by differences in both hardware and software used in the spectrometers. In order to reduce the variation due to measurements, a standardisation procedure should be developed such that both deviations within spectrometers and deviations between spectrometers are corrected for.
- For phosphorus and sulphur, the drift apparent within a period of eight hours is an important source of variation (adjustment in the experiments). Methods like Kalman filters and adaptive calibration can possibly be used to reduce the influence of drift on the variation in the analysis results.
- Place and time of sampling appear to have significant influence on the variation for certain elements. The differences in concentrations are probably caused by concentration gradients in both time and place. When this conclusion holds for batches of steel with other product specifications as well, it is important to find the most representative place and time of sampling for each process phase.

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- Only for tin, a significant contribution to the variation due to sampling could be detected. This is only true for samples taken from the tundish. The variation is probably due to part of the sample probe which contains tin. The fact that this variation is apparent only in samples taken from the tundish is not fully understood yet and needs further research.

Chapter 7

Identification and quantification of sources of variation in the analysis of three different types of steel

7.1 Introduction

In the previous chapter, statistical results obtained for one type of steel have been presented. From experiments involving an investigation on the heterogeneity of steel samples it became clear that statistical results obtained from analyses of different types of steel do not necessarily need to be equal.⁹⁶ Hence, the results presented in the previous chapter obtained for one type of steel could be different for another type of steel. Using the statistical results from only one type of steel to design a strategy for variation reduction could result in better results for the investigated type of steel only. However, the accuracy of the analysis results for other types of steel might reduce when the strategy for variation reduction is not advantageous for those other types of steel.

To test whether the conclusions drawn from the results obtained in Chapter 6 can be generalized to other types of steel, further experiments have been performed on two other types of steel (type II and type III). The experimental set-up was the same as for type I steel, to make comparisons more easy. For the setup of the experiment the reader is referred to Chapter 6. In this chapter, the statistical analysis results of the three types of steel will be presented and discussed.⁸⁷

7.2 Results

The results of the statistical analyses are reported for the elements carbon, manganese, phosphorus, sulphur, chromium and tin. These are the same elements as described in the previous chapter. The estimates for the random effects and the fixed effects are reported separately. The most important and noticeable results are discussed.

7.2.1 Random effects

For the random effects, the relative standard deviation is presented in graphs for each of the three process phases stirring station, tundish and mould separately (Figures 7.1 through 7.6). The relative standard deviation (standard deviation divided by concentration) is presented to correct for the difference in concentrations between the three types of steel. Additional to the graphs, the results are presented also in tables in terms of variances accompanied by the standard error of the estimates (Tables 7.1 through 7.6).

7.2.2 Fixed effects

The fixed effects are presented in Tables 7.7 through 7.11. In the tables presenting the fixed effects, significance of the estimated effects is of importance. However, thoughtless acceptance of significance should be prevented. The amount of degrees of freedom available for estimating the residual mean squares and the mean squares (MS) due to the effects should be taken into account. A small number of levels (2) were included for the fixed effects time and place of sampling while the number of degrees of freedom for the residual MS is a multiple of this number. Due to the large amount of degrees of freedom, available for calculating the residual variation, other factors can easily be picked out as being statistically significant.

To bring the true significance into perspective, the concentrations measured at the different places and points in time should be taken into account as well. A fixed effect model without effects of time and/or place was applied to the samples of both tundish and mould (equation 6.1). This results in estimates of residual variations and mean concentrations for the different samples taken from the tundish and mould. The results of these estimations are presented in Table 7.12 (Tundish) and Table 7.13 (Mould).

7.3 Conclusions

The variance component contributing most to the total variation in the analysis results of steel samples is the spectrometer or rather, the differences between spectrometers. The differences are caused by differences in both hardware and software in the spectrometers. Reduction of these differences may well be accomplished by means of standardisation of both hardware and software. It is possible that the differences increase and decrease in time because of instrumental drift over a long period of time. This assumption can be tested by performing long term experiments on several machines by analysing one sample at regular time intervals within the adjustment period.

Besides the other interesting sources of variation that are mentioned in the conclusions of Chapter 6 already, the increased concentrations of tin in samples taken from the tundish for type I steel is seen for type II and III steel as well. Although the increase of the concentration is small, this result shows that experiments used in this experiment are powerful tools for finding sources of variation.

Time and place of sampling have to be chosen carefully for certain elements. It is hard to decide which time and place of sampling should be chosen for optimal process control. The best choice would probably be to take samples from places in the process where the disturbance of the production process is kept to a minimum. The concentrations found in samples taken from the different process phases stirring station, tundish and mould are comparable (except for tin). Samples can be taken with the least effort from the stirring station and therefore sampling from this process phase is preferred.

For practical reasons, preference for an other place of sampling may occur. Samples taken from the mould may be more representative for the cast product because small changes (which are not detectable by spark OES) in, for example, the carbon concentration can occur. The choice of the optimal place and time of sampling is therefore always a compromise between practical and statistical reasons.

The conclusions drawn in the previous chapter still holds in majority. Many of the variance components estimated for type II and III steel are similar to those of type I steel and therefore, improvement of the analysis results for one type of steel should be beneficial for all three (and even more) types of steel. It should be noted that these conclusions hold only for the elements taken into account in these statistical analyses.

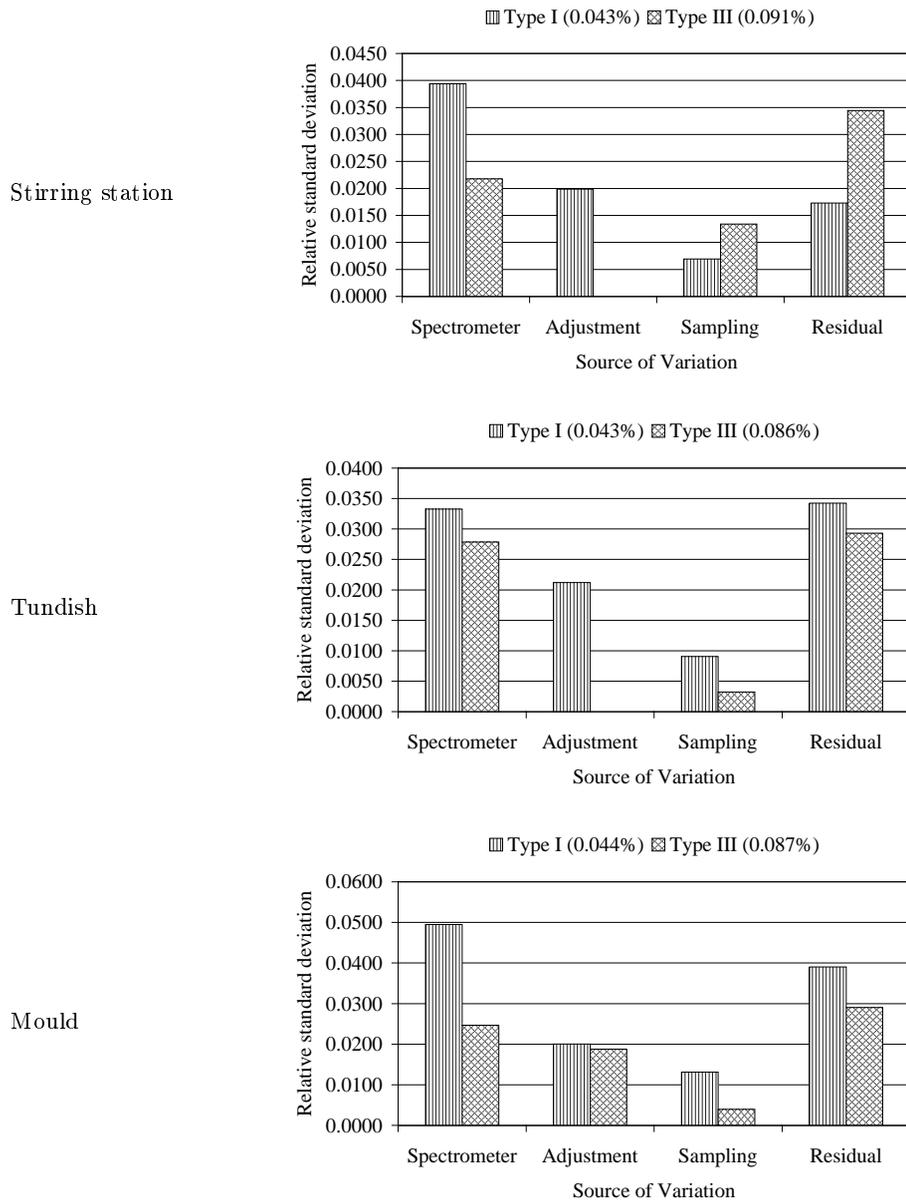


Figure 7.1: Contribution of four sources of variation to the total variation apparent in analysis results obtained for carbon (C). The variation is presented per process phase in terms of relative standard deviation.

Table 7.1: Variance components estimates ($\hat{\sigma}^2$) for carbon (C) obtained by means of Restricted Maximum Likelihood together with the asymptotic standard errors (S.E.). Results from type II steel have been omitted from the results because of the low concentrations for carbon in this type of steel.

Carbon		Spectrometer		Adjustment		Sampling		Residual	
	Mean	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE
Type I steel	mass %	$\cdot 10^{-8}$	$\cdot 10^{-8}$						
Stirring station	0.043	291	261	74	34	8.7	9.1	56	9.9
Tundish	0.043	202	185	82	38	15	12	214	16
Mould	0.044	469	411	77	45	33	29	292	33
Carbon		Spectrometer		Adjustment		Sampling		Residual	
	Mean	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE
Type III steel	mass %	$\cdot 10^{-8}$	$\cdot 10^{-8}$						
Stirring station	0.091	390	378	0	-	148	175	974	166
Tundish	0.086	577	491	45	33	7.7	17	639	48
Mould	0.087	464	465	269	136	12	33	644	72

Random effects: carbon

Figure 7.1 shows the statistical results obtained for carbon for two types of steel. The results for type II steel have been omitted because of the low concentrations for carbon in this type of steel. For low concentrations, the spark OES is not used. The standard errors of the estimates for the other two types of steel are presented in Table 7.1. These standard errors are large for reasons explained in Section 6.7 and therefore, the trend of the results shown in Figure 7.1 is more important than the exact numbers. From these results it can be concluded that samples taken from the stirring station for type III steel are less reproducible (high sampling variance) and more heterogeneous (high residual) than samples taken from type I steel. Furthermore, the differences between spectrometers are much less for type III steel except for samples taken from the tundish. The (absolute) variance due to differences between spectrometers is similar for both types of steel in both stirring station and mould.

The sampling variance is of minor importance and therefore, sampling induces no significant amount of variation to the analysis results for carbon.

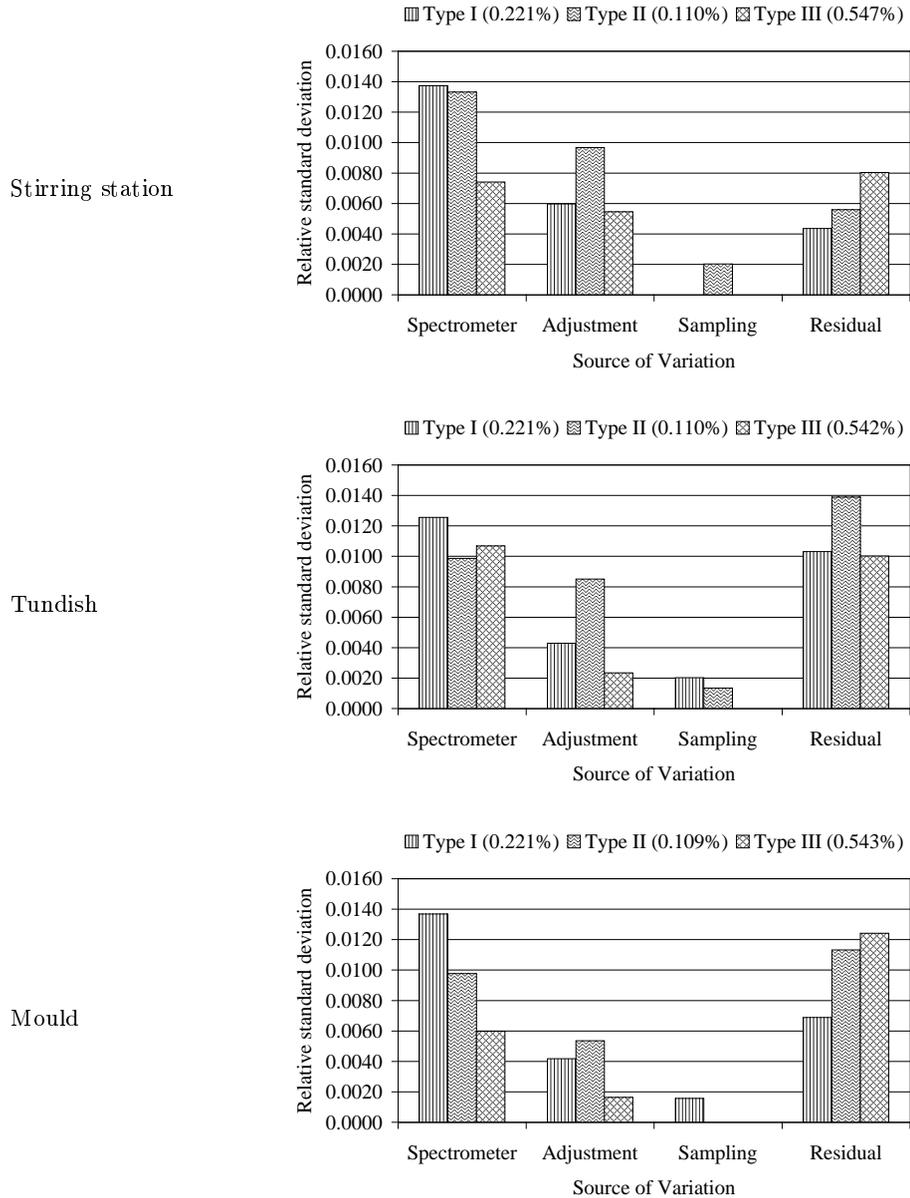


Figure 7.2: Contribution of four sources of variation to the total variation apparent in analysis results obtained for manganese (Mn). The variation is presented per process phase in terms of relative standard deviation.

Table 7.2: Variance components estimates ($\hat{\sigma}^2$) for manganese (Mn) obtained by means of Restricted Maximum Likelihood together with the asymptotic standard errors (S.E.).

Manganese		Spectrometer		Adjustment		Sampling		Residual	
	Mean	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE
Type I steel	mass %	$\cdot 10^{-8}$	$\cdot 10^{-8}$						
Stirring station	0.221	926	806	175	77	0	-	93	15
Tundish	0.221	771	657	90	48	20	21	520	39
Mould	0.221	913	770	85	45	12	16	231	26
Type II steel		Spectrometer		Adjustment		Sampling		Residual	
	Mean	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE
Type II steel	mass %	$\cdot 10^{-8}$	$\cdot 10^{-8}$						
Stirring station	0.110	216	206	114	48	5.2	5.9	38	6.7
Tundish	0.110	117	121	87	39	2.2	6.0	232	18
Mould	0.109	113	105	34	21	0	-	152	16.6
Type III steel		Spectrometer		Adjustment		Sampling		Residual	
	Mean	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE
Type III steel	mass %	$\cdot 10^{-8}$	$\cdot 10^{-8}$						
Stirring station	0.547	1641	1639	887	564	0	-	1926	341
Tundish	0.542	3351	2829	161	136	0	-	2947	220
Mould	0.543	1056	1018	79	262	0	-	4550	498

Random effects: manganese

The statistical results for manganese are presented in Figure 7.2 and Table 7.2. It is clear from the results that sampling does not contribute much to the total variation. The results also show that the residual variation is an important source of variation for samples taken from the tundish and the mould. This implies that samples taken from these process phases are more heterogeneous than samples taken from the stirring station in case of manganese. For all three process phases, the differences between spectrometers is an important source of variation. Compared to the contribution of differences between spectrometers, adjustment has no main influence on the variation in the analysis results.

For manganese, the relative standard deviations of the three types of steel are comparable to each other with differences between spectrometers being the most contributing factor. A reduction in the differences between spectrometers would therefore be beneficial for all three types of steel.

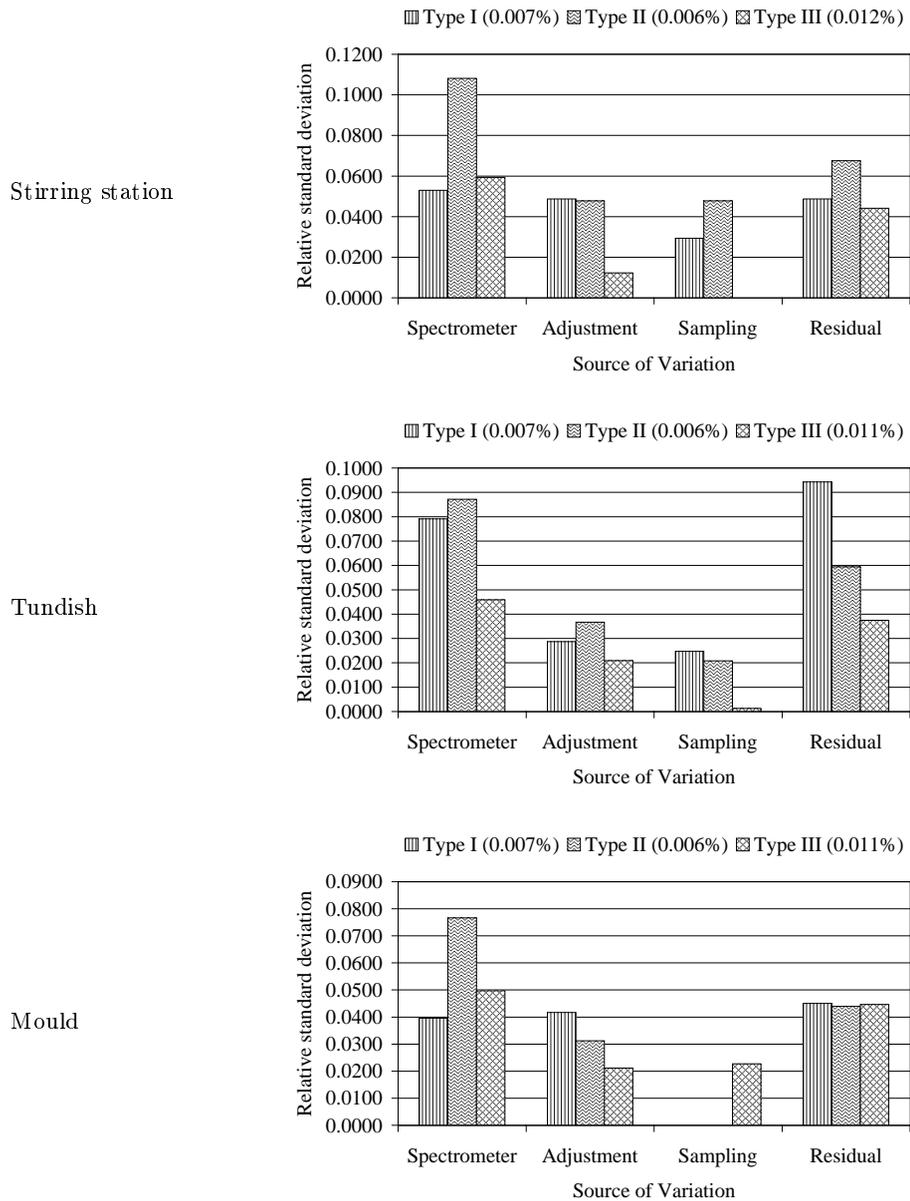


Figure 7.3: Contribution of four sources of variation to the total variation apparent in analysis results obtained for phosphorus (P). The variation is presented per process phase in terms of relative standard deviation.

Table 7.3: Variance components estimates ($\hat{\sigma}^2$) for phosphorus (P) obtained by means of Restricted Maximum Likelihood together with the asymptotic standard errors (S.E.).

Phosphorus		Spectrometer		Adjustment		Sampling		Residual	
	Mean	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE
Type I steel	mass %	$\cdot 10^{-8}$	$\cdot 10^{-8}$						
Stirring station	0.0068	13	14	11	5.4	3.5	2.7	11	1.9
Tundish	0.0070	31	27	4.1	2.7	3.0	2.4	44	3.4
Mould	0.0074	8.5	9.7	9.4	4.2	0	-	11.4	1.2
Type II steel		Spectrometer		Adjustment		Sampling		Residual	
	Mean	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE
Type II steel	mass %	$\cdot 10^{-8}$	$\cdot 10^{-8}$						
Stirring station	0.0059	41	36	8.2	4.9	7.7	5.2	16	2.9
Tundish	0.0061	28	24	5.0	2.3	1.6	1.1	13	1.0
Mould	0.0061	22	19	3.7	1.8	0	-	7.2	0.8
Type III steel		Spectrometer		Adjustment		Sampling		Residual	
	Mean	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE
Type III steel	mass %	$\cdot 10^{-8}$	$\cdot 10^{-8}$						
Stirring station	0.0116	47	41	2.4	3.8	0	-	26	4.5
Tundish	0.0113	27	23	5.6	2.6	0	-	18	1.4
Mould	0.0112	31	28	5.6	3.5	6.5	4.3	25	2.8

Random effects: phosphorus

The statistical results for phosphorus are presented in Figure 7.3 and Table 7.3. These results indicate that differences between spectrometers are the main source of variation for phosphorus. The residual variation also is rather high, indicating that individual measurements performed on single samples differ considerably. Of all three process phases, the relative standard deviations for samples taken from the mould have the lowest values.

Relative to the spectrometer variance, the variance component adjustment is an important source of variation for type I steel only for samples taken from the stirring station and the mould. For the other two types of steel and for type I steel in the tundish, adjustment contributes less to the total variation. This inequality is not expected because the analyses have been performed under the same circumstances. The results indicate that this source of variation is of lesser importance.

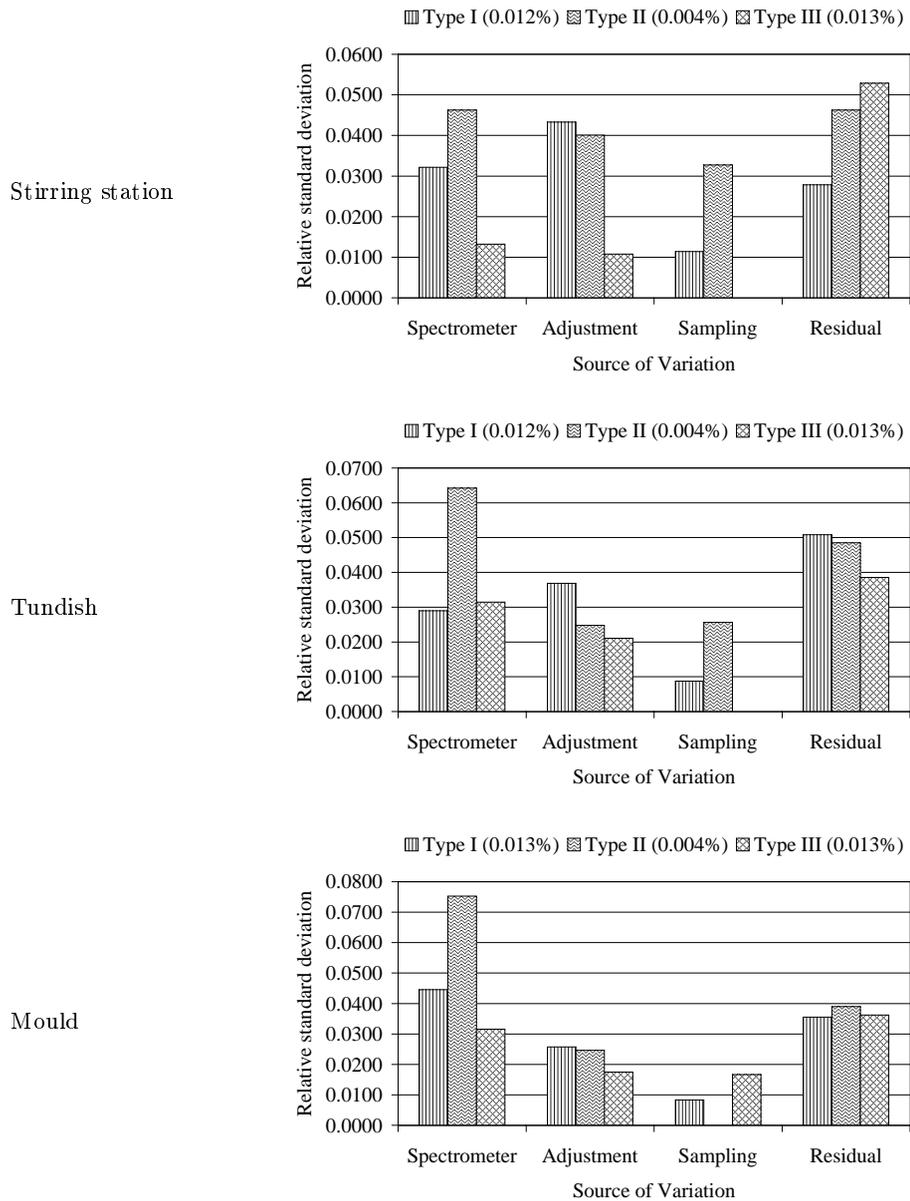


Figure 7.4: Contribution of four sources of variation to the total variation apparent in analysis results obtained for sulphur (S). The variation is presented per process phase in terms of relative standard deviation.

Table 7.4: Variance components estimates ($\hat{\sigma}^2$) for sulphur (S) obtained by means of Restricted Maximum Likelihood together with the asymptotic standard errors (S.E.).

Sulphur		Spectrometer		Adjustment		Sampling		Residual	
	Mean	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE
Type I steel	mass %	$\cdot 10^{-8}$	$\cdot 10^{-8}$						
Stirring station	0.0124	16	20	29	14	2.2	2.1	12	2.1
Tundish	0.0124	13	15	21	9.1	1.2	1.4	40	3.0
Mould	0.0129	33	30	11	5.6	1.2	1.4	21	2.3
Type II steel		Spectrometer		Adjustment		Sampling		Residual	
	Mean	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE
Type II steel	mass %	$\cdot 10^{-8}$	$\cdot 10^{-8}$						
Stirring station	0.0043	4.2	4.4	3.0	1.6	1.5	1.1	3.9	0.7
Tundish	0.0045	8.2	7.1	1.2	0.6	1.3	0.8	4.7	0.4
Mould	0.0044	11	9.4	1.2	0.6	0	-	3.0	0.3
Type III steel		Spectrometer		Adjustment		Sampling		Residual	
	Mean	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE
Type III steel	mass %	$\cdot 10^{-8}$	$\cdot 10^{-8}$						
Stirring station	0.0131	2.9	6.1	1.8	6.2	0	-	48	8.3
Tundish	0.0127	16	15	7	3.5	0	-	24	1.8
Mould	0.0127	16	16	4.9	3.0	4.4	3.1	21	2.4

Random effects: sulphur

The statistical results for sulphur are presented in Figure 7.4 and Table 7.4. From the results presented in Chapter 6 it was concluded for type I steel that adjustment is an important source of variation for sulphur in case of samples taken from the stirring station and the tundish. Compared to the other sources of variation, this applies to types II and III as well. However, the main contributing variance component is the residual error which might be caused by heterogeneity in the sample. The reason why the variance component adjustment contributes much to the total variation may be explained by the fact that this element is not measured relative to iron and therefore suffers more from instrumental drift than elements that are measured relative to iron.

From the other two sources of variation, differences between spectrometers contributes considerable to the total variation. The sampling variance forms no serious problem to the accuracy of the measurements.

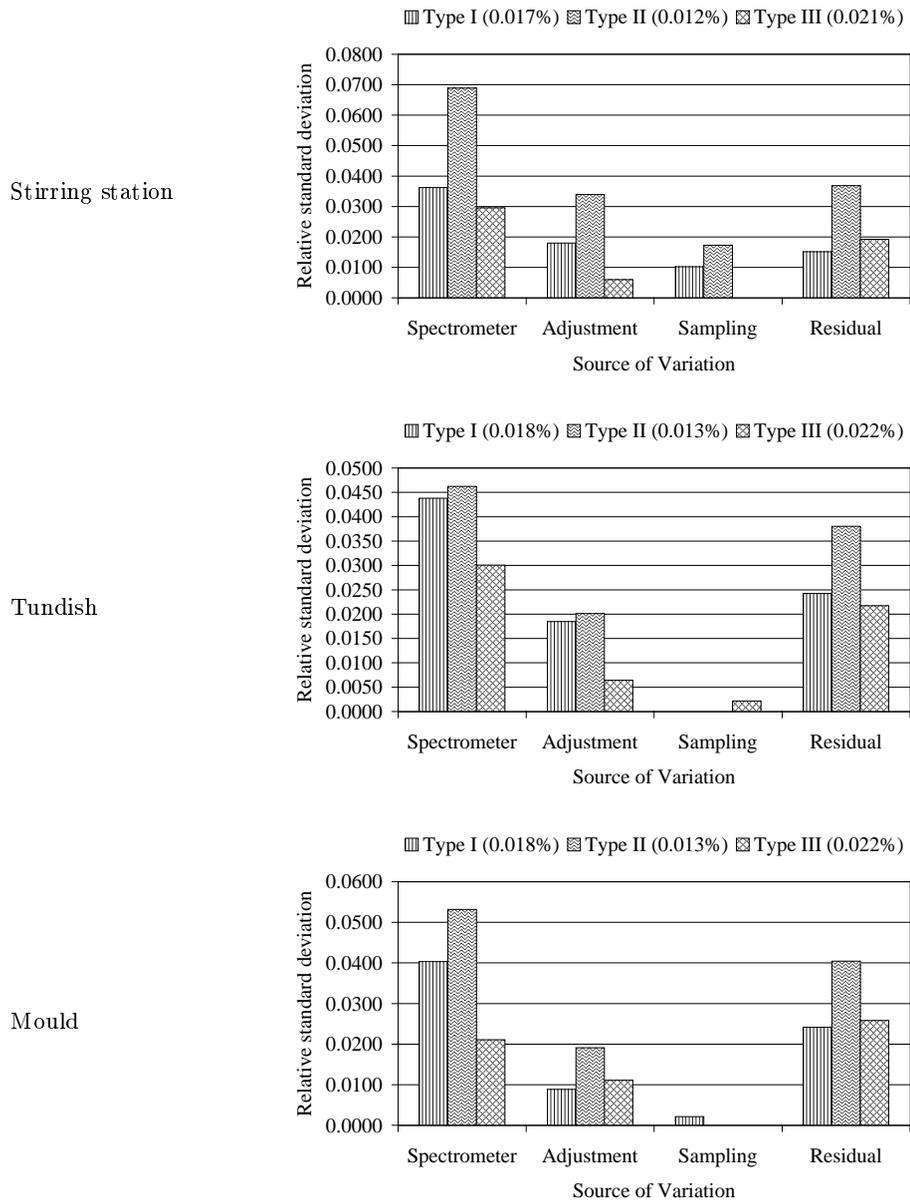


Figure 7.5: Contribution of four sources of variation to the total variation apparent in analysis results obtained for chromium (Cr). The variation is presented per process phase in terms of relative standard deviation.

Table 7.5: Variance components estimates ($\hat{\sigma}^2$) for chromium (Cr) obtained by means of Restricted Maximum Likelihood together with the asymptotic standard errors (S.E.).

Chromium		Spectrometer		Adjustment		Sampling		Residual	
	Mean	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE
Type I steel	mass %	$\cdot 10^{-8}$	$\cdot 10^{-8}$						
Stirring station	0.017	37.3	33.2	9.1	4.2	2.9	2.0	6.4	1.1
Tundish	0.018	62.4	53.2	11.3	4.9	0	-	18.7	1.4
Mould	0.018	53.1	44.8	2.6	2.0	0.1	0.9	19.5	2.2
Type II steel		Spectrometer		Adjustment		Sampling		Residual	
	Mean	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE
Type II steel	mass %	$\cdot 10^{-8}$	$\cdot 10^{-8}$						
Stirring station	0.012	69.7	62.5	16.6	8.5	4.4	3.9	19.8	3.5
Tundish	0.013	33.6	29.0	6.4	3.1	0	-	22.7	1.7
Mould	0.013	44.7	39.2	5.8	3.6	0	-	25.8	2.8
Type III steel		Spectrometer		Adjustment		Sampling		Residual	
	Mean	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE
Type III steel	mass %	$\cdot 10^{-8}$	$\cdot 10^{-8}$						
Stirring station	0.021	38.4	32.8	1.6	2.4	0	-	15.5	2.7
Tundish	0.022	44.4	37.1	2.0	1.4	0.2	0.6	23.5	1.8
Mould	0.022	22.5	21.4	6.1	4.1	0	-	33.0	3.6

Random effects: chromium

Figure 7.5 and Table 7.5 present the statistical results for chromium. For the element chromium, the variance component spectrometers is the most contributing factor to the total variation. Type II steel has a high relative standard deviation indicating that low chromium concentrations can be measured less accurately. Both the variance components sampling and adjustment contribute relatively little to the build-up of the total variation. The residual variation is of some concern but this variation is reduced by a factor $\sqrt{2}$ under normal operating conditions because of repeated measurements.

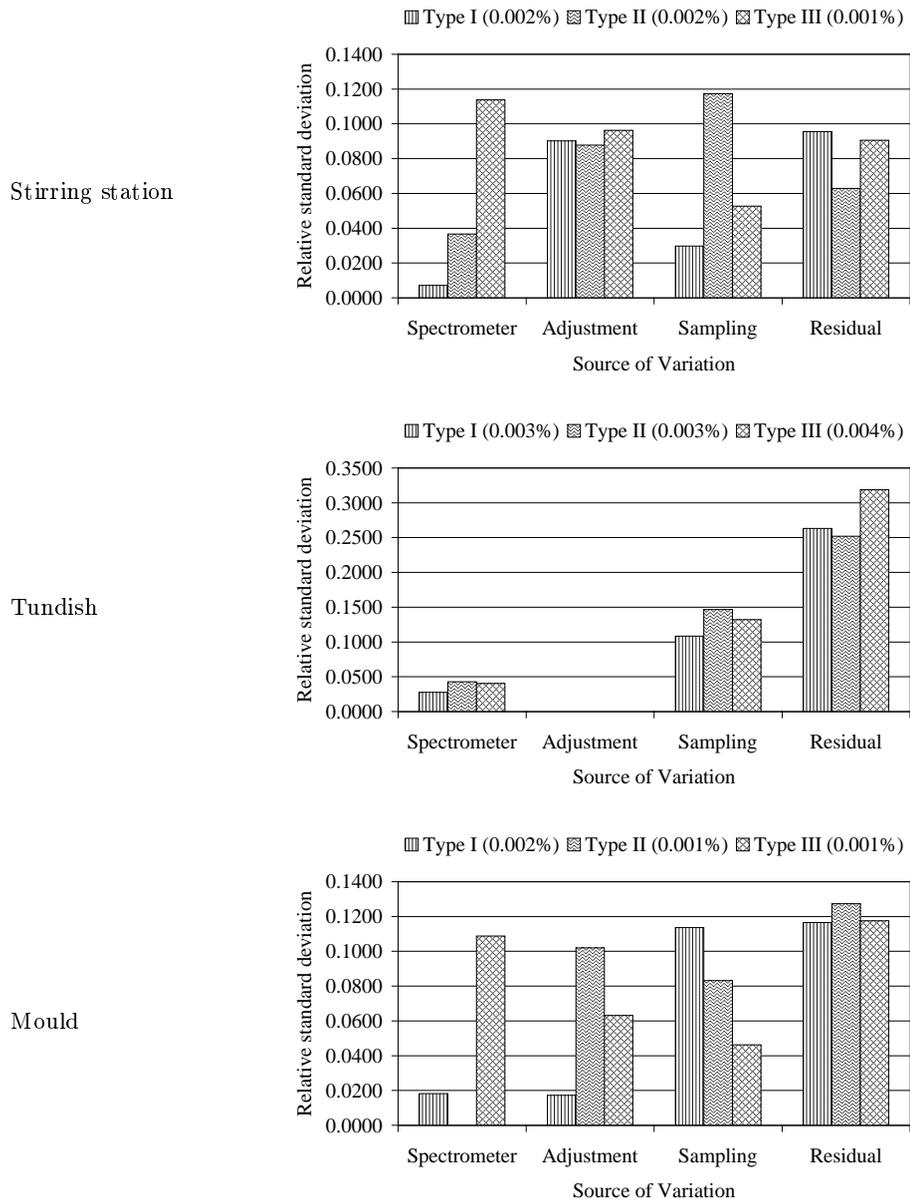


Figure 7.6: Contribution of four sources of variation to the total variation apparent in analysis results obtained for tin (Sn). The variation is presented per process phase in terms of relative standard deviation.

Table 7.6: Variance components estimates ($\hat{\sigma}^2$) for tin (Sn) obtained by means of Restricted Maximum Likelihood together with the asymptotic standard errors (S.E.).

Tin		Spectrometer		Adjustment		Sampling		Residual	
	Mean	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE
Type I steel	mass %	$\cdot 10^{-8}$	$\cdot 10^{-8}$						
Stirring station	0.0016	0.01	1	2.1	1.4	0.2	0.3	2.4	0.4
Tundish	0.0029	0.7	1.2	0	-	10.1	6.3	58.6	4.3
Mould	0.0018	0.1	0.3	0.1	0.3	4.4	2.4	4.6	0.5
Type II steel		Spectrometer		Adjustment		Sampling		Residual	
	Mean	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE
Type II steel	mass %	$\cdot 10^{-8}$	$\cdot 10^{-8}$						
Stirring station	0.0016	0.3	0.9	1.9	0.9	3.4	1.8	1.0	0.2
Tundish	0.0032	1.9	2.4	0	-	22.0	12.3	64.9	4.8
Mould	0.0013	0	-	1.7	0.7	1.2	0.7	2.7	0.3
Type III steel		Spectrometer		Adjustment		Sampling		Residual	
	Mean	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE	$\hat{\sigma}^2$	SE
Type III steel	mass %	$\cdot 10^{-8}$	$\cdot 10^{-8}$						
Stirring station	0.0013	2.3	2.4	1.6	0.8	0.5	0.4	1.5	0.3
Tundish	0.0035	2.1	3.2	0	-	21.7	13.5	127	9.5
Mould	0.0015	2.6	2.5	0.9	0.2	0.5	0.4	3.0	0.3

Random effects: tin

The statistical results for tin are presented in Figure 7.6 and Table 7.6. The increased level of tin in samples taken from the tundish as reported in Chapter 6 for type I steel is found in types II and III steel as well. The results shown in Figure 7.6 and Table 7.6 are only of interest because of the increased concentrations in samples taken from the tundish compared to the other process phases and the relative high level of the residual variation. The results can only be explained if tin is added to the sample. As mentioned before (Chapter 6), the metal cap on the sample probe, that is used to prevent material floating on top of the liquid steel from entering the sample holder, might be the source of the extra tin found in the samples taken from the tundish. Upon inquiry with the producer of the sample probes (Heraeus Electro-Nite Intl. NV) it appeared that the metal caps are covered with a thin tin layer ($2.8 \text{ g}\cdot\text{m}^{-2}$) to protect the metal cap from corroding which may explain the results.

Table 7.7: Fixed effects estimates for carbon (C). Least squares estimates with F-values and p-values.

Carbon Type I steel	Mean mass %		d.f.	SS .10 ⁻⁸	MS .10 ⁻⁸	F-Value	p-value
Tundish	0.043	Time	1	0	0	0.00	0.98
		Place	1	22	22	0.10	0.75
		Residual	350	75018	214		
Mould	0.044	Time	1	81	81	0.28	0.60
		Residual	159	46418	292		

Carbon Type III steel	Mean (mass %)		d.f.	SS .10 ⁻⁸	MS .10 ⁻⁸	F-Value	p-value
Tundish	0.086	Time	1	13908	13908	21.77	<0.001
		Place	1	4	4	0.01	0.93
		Residual	350	223554	639		
Mould	0.087	Time	1	3	3	0.00	0.95
		Residual	159	102450	644		

Fixed effects: carbon

The variance analysis performed on type I steel has been repeated on type III steel and the results of these calculations are reported in Table 7.7. In Chapter 6 it was concluded that both time and place of sampling have no significant effect on the measured concentration. An important difference between both types of steel is the concentration being twice as high for type III compared to type I steel. Furthermore, the results show that only time of sampling has a significant effect for type III steel samples taken from the tundish. Taking a closer look at the raw data it appears that the analysis results for one sample shows some discrepancy with the other results. Because of the relative small amount of batches taken into account in this experiment, the analysis results obtained for this sample has a rather large influence on the statistical results.

The trend of the statistical results is more important than details and therefore, it can be concluded for carbon in general that time and place of sampling have no important influence on the levels of carbon found in both tundish and mould.

Table 7.8: Fixed effects estimates for manganese (Mn). Least squares estimates with F-values and p-values.

Manganese Type I steel	Mean mass %		d.f.	SS .10 ⁻⁸	MS .10 ⁻⁸	F-value	p-value
Tundish	0.221	Time	1	2013	2013	3.87	0.05
		Place	1	4601	4601	8.85	<0.001
		Residual	350	182009	520		
Mould	0.221	Time	1	1452	1452	6.29	0.01
		Residual	159	36721	231		
Manganese Type II steel	Mean mass %		d.f.	SS .10 ⁻⁸	MS .10 ⁻⁸	F-value	p-value
Tundish	0.110	Time	1	1145	1145	4.93	0.03
		Place	1	1251	1251	5.38	0.02
		Residual	350	81333	232		
Mould	0.109	Time	1	6686	6686	42.33	<0.001
		Residual	159	25115	158		
Manganese Type III steel	Mean mass %		d.f.	SS .10 ⁻⁸	MS .10 ⁻⁸	F-value	p-value
Tundish	0.542	Time	1	2262	2262	0.76	0.38
		Place	1	828	828	0.28	0.60
		Residual	350	1043490	2981		
Mould	0.543	Time	1	73	73	0.02	0.90
		Residual	159	744457	4682		

Fixed effects: manganese

The analysis of variance results for manganese are reported in Table 7.8. For steel of types I and II both time and place of sampling have a significant influence on the analysis result in the range of the 95% confidence interval ($p \leq 0.05$). For samples taken from batches of type III steel however, no significant influence of place or time of sampling can be detected. It seems that the time and place of sampling are only important for low concentrations of manganese. From the results presented in Table 7.8 it can be concluded that both time and place of sampling should be chosen carefully. A balanced decision about the best time and place of sampling for manganese can be made by comparing the analysis results with concentrations found in the cast product. The sample with concentrations that compare best to the concentrations found in the cast product should be chosen then.

Table 7.9: Fixed effects estimates for phosphorus (P). Least squares estimates with F-values and p-values.

Phosphorus Type I steel	Mean mass %		d.f.	SS .10 ⁻⁸	MS .10 ⁻⁸	F Value	Probability
Tundish	0.0070	Time	1	359	359	8.09	0.005
		Place	1	359	359	5.26	0.02
		Residual	350	15527	44		
Mould	0.0074	Time	1	24	24	2.04	0.16
		Residual	159	1876	12		
Phosphorus Type II steel	Mean mass %		d.f.	SS .10 ⁻⁸	MS .10 ⁻⁸	F Value	Probability
Tundish	0.0061	Time	1	0	0	0.00	0.98
		Place	1	2	2	0.17	0.68
		Residual	350	4719	13		
Mould	0.0061	Time	1	44	44	6.00	0.02
		Residual	159	1167	7		
Phosphorus Type III steel	Mean mass %		d.f.	SS .10 ⁻⁸	MS .10 ⁻⁸	F Value	Probability
Tundish	0.0113	Time	1	204	204	11.18	<0.001
		Place	1	73	73	4.03	0.05
		Residual	350	6390	18		
Mould	0.0112	Time	1	33	33	1.30	0.26
		Residual	159	3971	25		

Fixed effects: phosphorus

The results of the fixed effects presented in Table 7.9 indicate that for phosphorus both time and place of sampling have a significant influence on the analysis result. This is true for type I and type III samples taken from the tundish. For type II samples, the time of sampling in the mould is of importance.

A more detailed overview of concentrations found in the process phases at different times and places of sampling is presented in Table 7.12 and Table 7.13. The estimates in these tables show that the significancies are not caused by consistently high or low concentrations of phosphorus in samples taken from a certain place or at a certain point in time. Hence, differences between samples taken at different place and points in time occur, but a decision about the best place or time of sampling can not be taken based upon these results.

Table 7.10: Fixed effects estimates for sulphur (S). Least squares estimates with F-values and p-values.

Sulphur Type I steel	Mean mass %		d.f.	SS .10 ⁻⁸	MS .10 ⁻⁸	F Value	Probability
Tundish	0.0124	Time	1	443	443	11.12	<0.001
		Place	1	52	52	1.29	0.26
		Residual	350	13955	40		
Mould	0.0129	Time	1	42	42	2.05	0.15
		Residual	159	3273	21		
Sulphur Type II steel	Mean mass %		d.f.	SS .10 ⁻⁸	MS .10 ⁻⁸	F Value	Probability
Tundish	0.0045	Time	1	127	127	27.12	<0.001
		Place	1	20	20	4.20	0.04
		Residual	350	1641	5		
Mould	0.0044	Time	1	7	7	2.27	0.13
		Residual	159	473	3		
Sulphur Type III steel	Mean mass %		d.f.	SS .10 ⁻⁸	MS .10 ⁻⁸	F Value	Probability
Tundish	0.0127	Time	1	28	28	1.16	0.28
		Place	1	106	106	4.39	0.04
		Residual	350	8477	24		
Mould	0.0127	Time	1	18	18	0.86	0.36
		Residual	159	3350	21		

Fixed effects: sulphur

In Table 7.10 the statistical results for the fixed effects are presented for sulphur. The time of sampling in the tundish has a significant influence for both type I and type II batches of steel. Although these results are significant with a level of confidence >99%, the difference between samples taken at different points in time are not very large (1 to 2%) for the sulphur concentrations (Tables 7.12 and 7.13).

The high level of significance combined with the small deviations is caused by the high number of degrees of freedom which are available to estimate the residual variance compared to the amount of degrees of freedom available for the other effects. It should be kept in mind that statistical significance is not always equal to relevant difference.

Table 7.11: Fixed effects estimates for chromium (Cr). Least squares estimates with F-values and p-values.

Chromium Type I steel	Mean mass %		d.f.	SS .10 ⁻⁸	MS .10 ⁻⁸	F Value	Probability
Tundish	0.018	Time	1	16	16	0.84	0.36
		Place	1	1495	1495	78.49	<0.001
		Residual	350	6666	19		
Mould	0.018	Time	1	867	867	44.51	<0.001
		Residual	159	3097	19		
Chromium Type II steel	Mean mass %		d.f.	SS .10 ⁻⁸	MS .10 ⁻⁸	F Value	Probability
Tundish	0.013	Time	1	34	34	1.50	0.22
		Place	1	203	203	8.84	0.003
		Residual	350	8027	23		
Mould	0.013	Time	1	358	358	13.57	<0.001
		Residual	159	4189	26		
Chromium Type III steel	Mean mass %		d.f.	SS .10 ⁻⁸	MS .10 ⁻⁸	F Value	Probability
Tundish	0.022	Time	1	5408	5408	230.56	<0.001
		Place	1	3	3	0.11	0.74
		Residual	350	8209	23		
Mould	0.022	Time	1	3545	3545	106.12	<0.001
		Residual	159	5311	33		

Fixed effects: chromium

Table 7.11 presents the estimates for the fixed effects for chromium in the three investigated types of steel. The results show for all three types of steel that time of sampling is an important factor for samples taken from the mould. For all three types of steel, the significance of the effect is due to the low residual variance found in the chemical analysis results.

The mean concentrations found in samples taken from the mould 10 minutes and 30 minutes after starting to cast a new batch, do not show much difference (Table 7.13). Hence, a concentration gradient in time is not found in the mould for chromium.

Fixed effects: tin

The fixed effects for tin have been omitted from this section because the concentrations of this element are too low and even small differences in concentrations result in significant but not relevant effects.

Fixed effects: sampling location and time

A fixed effect model without effects of time and/or place was applied to the samples of both tundish and mould (equation 6.1). This results in estimates of residual variations and mean concentrations for the different samples taken from the tundish and mould. The results of these estimations are presented in Table 7.12 (Tundish) and Table 7.13 (Mould). In these tables both the residual variation ($\hat{\sigma}^2$) and the concentration (mass percentage between parentheses) are presented per element, sample, place and point in time.

In Chapter 6 it was concluded that samples from the tundish can best be taken above the outlet but the results for all three types of steel are not consistent to give such a recommendation in general. Furthermore, for samples taken from the mould, there exists no favourite time of sampling.

Besides picking the best time and place of sampling, the results from Tables 7.12 and 7.13 can be used to investigate whether effects that were identified as being significant in Section 7.2.2 result in different concentrations. If this is not the case, the significancy is not attributable to systematic differences between the different samples. The results show no consistently high or low concentrations for certain types of samples and therefore it can be concluded that there exists no concentration gradient in place nor time.

Table 7.12: Estimates for the residual variation and concentration corresponding to samples taken from the tundish (T_{11} , T_{21} , T_{12} , T_{22}).

Element	Type	Residual variation, $\hat{\sigma}^2$ ($\cdot 10^{-8}$) (concentration (%))			
		T_{11} outlet(10 min)	T_{12} outlet(30 min)	T_{21} SEN(10 min)	T_{22} SEN(30 min)
C	I	131 (0.043)	131 (0.043)	113 (0.043)	214 (0.043)
	III	132 (0.087)	184 (0.087)	270 (0.085)	155 (0.086)
Mn	I	236 (0.221)	306 (0.221)	273 (0.221)	851 (0.224)
	II	53 (0.109)	164 (0.110)	21 (0.110)	174 (0.110)
	III	1173 (0.542)	493 (0.542)	870 (0.541)	443 (0.542)
P	I	10 (0.007)	29 (0.007)	12 (0.007)	27 (0.008)
	II	14 (0.006)	3 (0.006)	3 (0.006)	3 (0.006)
	III	17 (0.011)	10 (0.011)	8 (0.011)	7 (0.011)
S	I	14 (0.013)	18 (0.013)	23 (0.012)	35 (0.013)
	II	2 (0.005)	1 (0.004)	1 (0.004)	2 (0.004)
	III	12 (0.013)	14 (0.013)	16 (0.013)	44 (0.013)
Si	I	65 (0.005)	110 (0.005)	67 (0.005)	232 (0.005)
	II	19 (0.005)	20 (0.005)	9 (0.005)	28 (0.005)
	III	13 (0.006)	46 (0.006)	139 (0.006)	30 (0.006)
Al	I	360 (0.049)	328 (0.049)	293 (0.048)	345 (0.049)
	II	89 (0.024)	203 (0.024)	480 (0.025)	258 (0.025)
	III	231 (0.041)	83 (0.041)	228 (0.041)	109 (0.041)
Cu	I	8 (0.011)	8 (0.011)	6 (0.011)	13 (0.011)
	II	4 (0.008)	4 (0.008)	4 (0.008)	5 (0.008)
	III	4 (0.011)	8 (0.011)	6 (0.011)	5 (0.011)
Sn	I	5 (0.003)	6 (0.003)	8 (0.003)	5 (0.003)
	II	3 (0.004)	3 (0.003)	2 (0.003)	3 (0.003)
	III	4 (0.004)	5 (0.003)	5 (0.004)	4 (0.003)
Cr	I	27 (0.018)	15 (0.018)	11 (0.018)	7 (0.018)
	II	15 (0.013)	15 (0.013)	8 (0.013)	19 (0.013)
	III	5 (0.022)	12 (0.022)	13 (0.022)	7 (0.022)
Ni	I	14 (0.023)	44 (0.023)	15 (0.023)	48 (0.022)
	II	26 (0.023)	5 (0.023)	7 (0.023)	9 (0.023)
	III	21 (0.023)	11 (0.023)	11 (0.023)	8 (0.023)
Mo	I	5 (0.002)	6 (0.002)	5 (0.002)	8 (0.002)
	II	4 (0.002)	5 (0.002)	4 (0.002)	4 (0.002)
	III	5 (0.002)	4 (0.002)	5 (0.002)	4 (0.002)

Table 7.13: Estimates for the residual variation and concentration corresponding to samples taken from the mould (M_1 , M_2).

Element	Type	Residual variation, $\hat{\sigma}^2 \cdot (10^{-8})$ (concentration(%))			
		M_1		M_2	
		10 min		30 min	
C	I	297	(0.044)	122	(0.044)
	III	265	(0.087)	607	(0.087)
Mn	I	92	(0.221)	92	(0.221)
	II	31	(0.108)	39	(0.109)
	III	539	(0.543)	1120	(0.543)
P	I	5	(0.007)	8	(0.007)
	II	8	(0.006)	3	(0.006)
	III	8	(0.011)	22	(0.011)
S	I	11	(0.013)	16	(0.013)
	II	2	(0.004)	2	(0.004)
	III	14	(0.013)	23	(0.013)
Si	I	92	(0.006)	33	(0.005)
	II	48	(0.005)	111	(0.005)
	III	32	(0.007)	26	(0.006)
Al	I	511	(0.048)	184	(0.048)
	II	149	(0.023)	219	(0.024)
	III	50	(0.039)	71	(0.040)
Cu	I	5	(0.011)	10	(0.011)
	II	4	(0.008)	4	(0.008)
	III	5	(0.011)	8	(0.011)
Sn	I	1	(0.002)	1	(0.002)
	II	2	(0.001)	1	(0.001)
	III	1	(0.001)	2	(0.001)
Cr	I	12	(0.018)	16	(0.018)
	II	15	(0.013)	8	(0.012)
	III	17	(0.023)	16	(0.022)
Ni	I	4	(0.023)	11	(0.023)
	II	10	(0.023)	5	(0.023)
	III	5	(0.023)	18	(0.023)
Mo	I	3	(0.002)	4	(0.002)
	II	4	(0.002)	3	(0.002)
	III	4	(0.002)	7	(0.002)

Chapter 8

Simulation of alternative calibration methods

8.1 Introduction

In Chapter 4 a description is given of the calibration method used for the spark optical emission spectrometers (spark OES) at the Hoogovens laboratories for process control. This method has been developed and changed time after time over the years due to new insights and the introduction of better instruments. As can be seen in the description of the calibration method, the calculation is a rather complex combination of different procedures. Although this method has been developed and improved over the years, other methods may be used to improve the accuracy and precision of the analytical results. However, before implementation, such methods need to be verified to certify the continuation of the steel making process. Implementation of an alternative method might result in further deviations thereby influencing the process control.

The experiments described in this chapter have been performed to test whether changes to the current calibration method may reduce the variations in the analysis results. The experiments concerned simulations in which alternative methods to calculate the concentrations from intensities were tested. Results for the elements carbon (C), manganese (Mn) and phosphorus (P) are presented in this chapter.

8.2 Alternative calibration methods

A number of changes applied to the standard calibration system are simple and need no prior explanation. Some simulations however, involve a more complex method called *dynamic calibration* which is a method developed by Müller et al.⁹⁵ Because of its complexity, this method will be explained in some more detail at this stage.

The dynamic calibration as described by Müller et al.⁹⁵ differs in two ways from the calibration method used by *Hoogovens Staal BV*. The first difference involves the way in which the adjustment parameters are calculated. The second difference is actually the part of the method that is referred to as dynamic calibration.

8.2.1 Moving average adjustment

For the calculation of the adjustment parameters α and β (see Section 4.5 on page 48), intensities from the last and from previous adjustment measurements are used. Adjustment measurements are performed at the normal points in time (directly after cleaning the spark stand) resulting in adjustment intensities $I_{o,h}$ and $I_{o,l}$ for each element. The method *moving average adjustment* uses current and prior adjustment measurements for the calculation of the adjustment parameters α and β . A moving average of the intensities is used for the calculations.

The last five and the last three measured intensities are used for respectively the low and the high intensities. In Figure 8.1 the moving average applied to the adjustment measurements is visualised. The mean intensities $\overline{I_{o,h,t}}$ and $\overline{I_{o,l,t}}$ are used to calculate the adjustment parameters α and β according to equations 4.2 and 4.3. According to Müller et al.,⁹⁵ the moving average is applied “to minimise the relative standard deviation of the error”.

8.2.2 Dynamic calibration

The second correction method is an adjustment working at concentration level. The correction is applied at regular intervals in between the normal process analytical measurements. For the dynamic calibration, samples from a set of n calibration samples are measured at regular intervals. These intervals are small (every 5 or 6 minutes) in case of a strong drifting signal. When only a weak drift is expected to occur, measurements for the dynamic calibration are performed only every 2-4 hours.

The concentrations of the elements in the calibration samples are obtained with reference methods that are more precise and accurate than spark OES.

$$\begin{array}{c}
 \overline{I_{o,h,t}} = \frac{1}{3} \sum_{i=0}^2 I_{o,h,t-i} \\
 \underbrace{I_{o,h,t-2} \quad I_{o,h,t-1} \quad I_{o,h,t}} \\
 \\
 \begin{array}{c}
 | \quad | \quad | \quad | \quad | \\
 \hline
 \text{time} \rightarrow \\
 \\
 I_{o,l,t-4} \quad I_{o,l,t-3} \quad I_{o,l,t-2} \quad I_{o,l,t-1} \quad I_{o,l,t} \\
 \underbrace{\hspace{10em}} \\
 \overline{I_{o,l,t}} = \frac{1}{5} \sum_{i=0}^4 I_{o,l,t-i}
 \end{array}
 \end{array}$$

Figure 8.1: Moving average applied to the intensities of adjustment samples as explained by Muller et al.⁹⁵ $I_{o,h,t-i}$ = measured intensity of the high setup sample at time $t-i$; $I_{o,l,t-i}$ = measured intensity of the low setup sample at time $t-i$.

The reference methods are far more laborious and therefore, are not fit for process control in the steel production process. The concentrations obtained with these reference methods are called certificate concentrations. The measured concentrations that are calculated with the calibration line are plotted against the certificate concentrations as shown in Figure 8.2.

At regular intervals, one of the n samples (randomly chosen) is analysed and the prior analysis result is replaced by the new one. Next a new calibration line is calculated for the samples by means of least squares resulting in parameters b_0 and b_1 . When the certificate concentrations are equal to the measured concentrations, $b_0 = 0$ and $b_1 = 1$ (see Figure 8.2). However, due to drift and instrumental noise, the newly measured concentrations are not equal to the certificate concentrations resulting in regression coefficients $b_0 \neq 0$ and $b_1 \neq 1$. The assumption made by Müller et al.⁹⁵ is that the obtained relation between measured concentrations and certificate concentrations as shown in equation 8.1 is valid for production samples as well. Therefore, equation 8.2 is used to correct measured concentrations of production samples.

$$c_{\text{calibration sample, measured}} = b_0 + b_1 \cdot c_{\text{calibration sample, certificate}} \quad (8.1)$$

$$c_{\text{production sample, corrected}} = \frac{c_{\text{production sample, measured}} - b_0}{b_1} \quad (8.2)$$

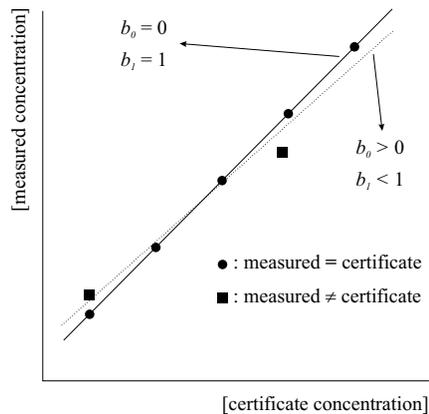


Figure 8.2: For the dynamic calibration, the measured concentrations are plotted against the certificate (true) concentrations. The parameters b_0 and b_1 relate the measured concentrations to the certificate concentrations.

For each element (e) measured on the spectrometer, a separate set of dynamic calibration parameters ($b_{0,e}$ and $b_{1,e}$) is estimated by means of least squares every time after analysing a calibration sample for the dynamic calibration. All n samples of the dynamic calibration set are analysed at a random order but the complete set of samples is analysed before a dynamic calibration sample is analysed again.

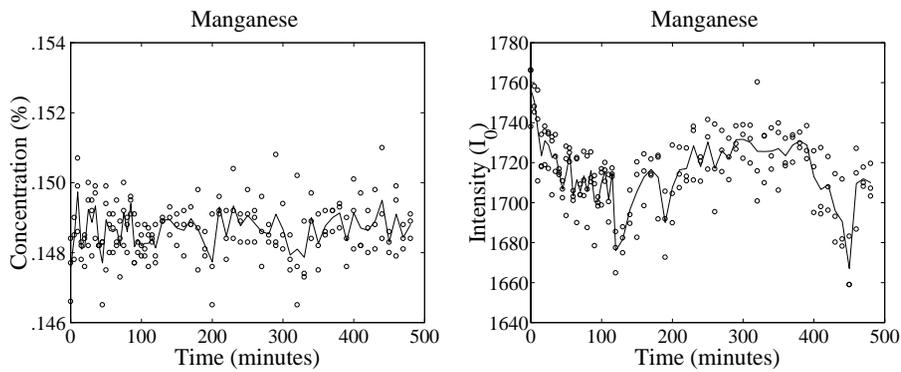
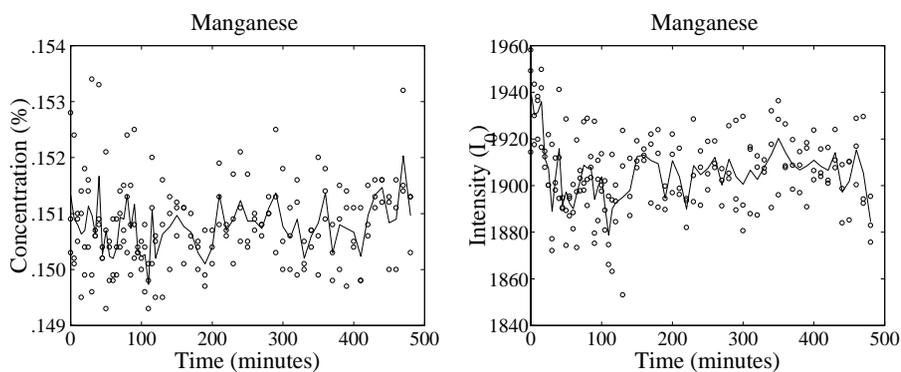
8.3 Drift experiment

To perform simulation experiments which have as much resemblance to the true situation as possible, measurements were carried out in which a verification sample was analysed repeatedly at predefined points in time. The sample was analysed according to the scheme presented in Table 8.1. At the start of the experiments, the interval of analysis was half the interval after 2 hours because the drift was expected to be more dominant in the early stage after cleaning the spark stand. This assumption appeared to be valid.

The obtained concentrations at each point in time were transformed to the original intensity (I_o , see Chapter 4). Figure 8.3 and Figures A.1-A.2 in Appendix A (page 143) show the concentrations and the raw intensities for each

Table 8.1: Analysis scheme of the drift experiment.

start (minutes)	end (minutes)	interval (minutes)	# analyses
0	115	5	24
120	480	10	37

**Figure 8.3:** Results of the first drift experiment for manganese (Mn). Obtained concentrations (left figure) and calculated intensities (right figure). \circ : individual measurements, - : mean of three measurements.**Figure 8.4:** Results of the second drift experiment for manganese (Mn). Obtained concentrations (left figure) and calculated intensities (right figure). \circ : individual measurements, - : mean of three measurements.

point in time at which the verification sample was analysed. For each point in time and element, three points are shown because each analysis consisted of three individual measurements. These experiments were performed twice. Figure 8.4 and Figures A.3-A.4 (page 143) show the results for the second experiment. Although the experiments were performed on the same spectrometer, with the same sample and under similar conditions, the results clearly show a systematic difference for the measured intensities. This indicates that there exists a necessity for the use of iron as an internal standard. Unfortunately, the intensities of phosphorus relate less to the intensity of iron and therefore this element is not measured relative to the internal standard iron.

The intensities of manganese and carbon (Figures 8.3, 8.4, A.1 and A.3) clearly show drift that is more or less absent in the presented concentrations of carbon and manganese. Because the intensities of carbon and manganese are divided by the intensities measured for iron, a rather good correction for the drift in the signal is obtained. Iron is used to correct for drift because there exists a strong correlation with the signals obtained for carbon and manganese. The intensities of phosphorus are not corrected by the intensity of iron because the strong correlation lacks for this element. As a result, the concentrations obtained for phosphorus still show some of the original drift occurring in the intensities.

The two series of measurements clearly show resemblance and it was concluded that the time series could best be described by means of a first order auto regressive model $AR(1)$. An $AR(p)$ model is able to describe a time series of order p . Equation 8.3 shows such a model:

$$y_t = \sum_{i=1}^p \theta_i y_{t-i} + \varepsilon_t \quad t = 1, \dots, n \quad (8.3)$$

where y_t is the signal y at time t , $\boldsymbol{\theta}$ ($\boldsymbol{\theta} = (\theta_1 \dots \theta_p) \in R^{1 \times p}$) is the coefficient vector of the model, p is the order of the model, n is the total number of observations and ε is an uncorrelated random number with zero mean and constant variance. With this model, the correlation between consecutive occurrences of signal y can be related to each other. Hence, signals y_t measured at a certain time t are correlated to signals y_{t-1} measured at time $t - i$ ($i = 1 \dots p$).

In the signals obtained for the current experiment, there also exists a correlation between different elements. In order to simulate such a multivariate time series, multivariate auto regressive models are needed. Equation 8.4 shows such a model

$$\mathbf{z}_t = \mathbf{w} + \sum_{i=1}^p \Theta_i \mathbf{z}_{t-i} + \boldsymbol{\varepsilon}_t \quad \boldsymbol{\varepsilon}_t = \text{noise}(\mathbf{C}) \quad t = 1, \dots, n \quad (8.4)$$

where \mathbf{z}_t is a m -dimensional vector of signals \mathbf{z} at time t , Θ ($\Theta := (\Theta_1 \dots \Theta_p) \in R^{m \times mp}$) is the coefficient matrix, p is the order of the model, n is the total number of observations and $\boldsymbol{\varepsilon}$ is an m -dimensional uncorrelated random vector with zero mean and covariance matrix \mathbf{C} . The m -dimensional parameter vector \mathbf{w} is included to allow for a nonzero mean of the multivariate signal \mathbf{z} .

The signals obtained in the drift experiments, can be described with a multivariate $AR(1)$ model as shown in equation 8.5.

$$\mathbf{z}_t = \mathbf{w} + \Theta \mathbf{z}_{t-1} + \boldsymbol{\varepsilon}_t \quad t = 1, \dots, n \quad (8.5)$$

In this model, the current m -dimensional signal \mathbf{z}_t is related to the prior signal \mathbf{z}_{t-1} by means of the coefficient matrix Θ ($\Theta \in R^{m \times m}$). The matrix Θ describes the variances within the signal of one element and the covariance between all elements contained in the m -dimensional vector \mathbf{z} . To find the coefficient matrix Θ and the intercept vector \mathbf{w} , ARFIT⁹⁷⁻⁹⁹ was used^a. ARFIT is a collection of MATLAB routines for the identification of multivariate $AR(p)$ models.

After building a model that represents the true results, signals can be simulated with the model and used for further experiments. In ARFIT, the simulated signal is accepted only after a certain period of time to obtain stable signals. This would result in flat signals, not similar to the true experiments. Therefore, the pre runs were omitted resulting in the signals presented in Figure 8.5. This figure shows the original and the simulated intensities for the elements carbon, manganese and phosphorus. Other elements were simulated as well but these elements were chosen to present the results of the experiments. As can be seen in the figures, the simulated signals show much resemblance to the true signals. Therefore, it was concluded that the model could be used for the experiments.

The signals simulated with the models presented in this section represent the signals in between two adjustments. Besides the measurements within

^aBoth ARFIT and a detailed description of the used MATLAB routines can be found on the Internet (<http://www.aos.princeton.edu/WWWPUBLIC/tapio/arfit/>)

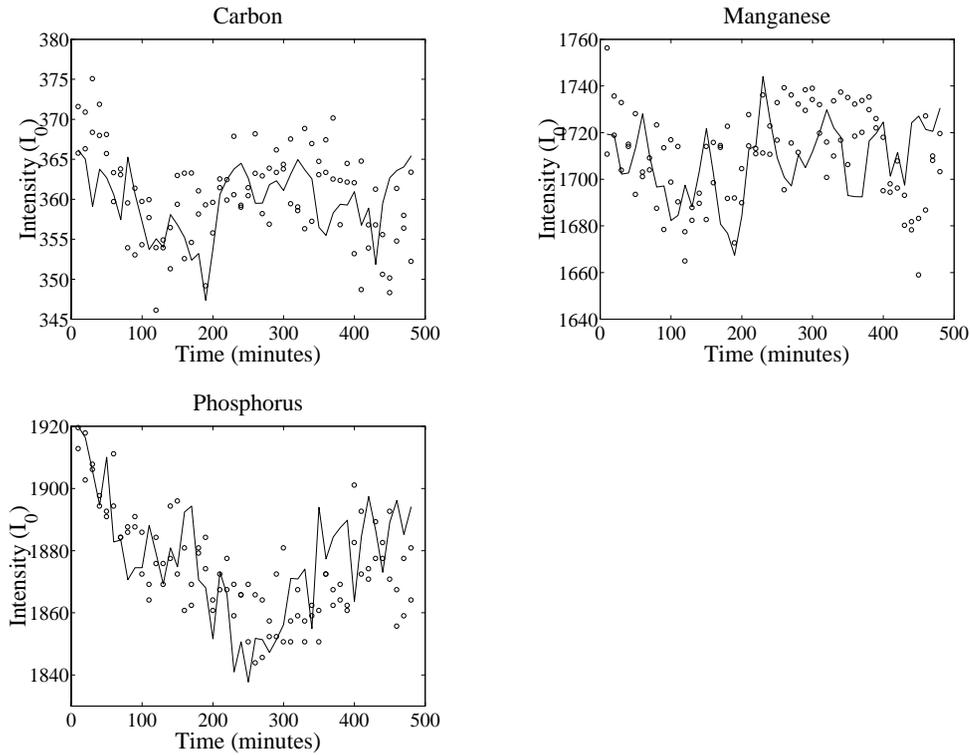


Figure 8.5: Comparison of measured (o) to simulated (-) signals. For the true analysis results, two concentrations are shown at each point in time.

an adjustment period, the adjustment measurements have to be simulated as well through simulations because those are an essential part of the calibration system.

During 92 successive adjustment periods, the measurements performed for adjustment of the spectrometer were recorded. The results of these measurements are presented in Figure 8.6 for manganese. The results for carbon and phosphorus are presented in Figures A.5 and A.6 in Appendix A. With similar calculations as explained for the verification measurements, a signal similar (first order AR(1) model) to the measured signal can be produced. The resulting simulations are included in Figures 8.6, A.5 and A.6 as well.

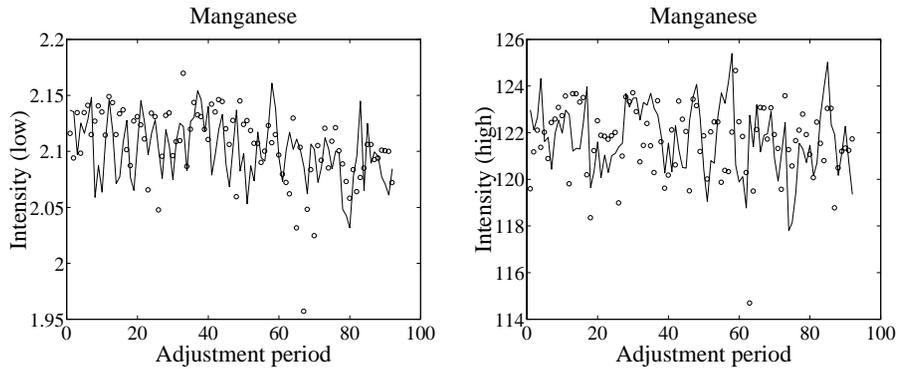


Figure 8.6: Measured (\circ) and simulated (-) adjustment measurements for manganese. Low adjustment intensity (left figure) and high adjustment intensity (right figure).

8.4 Setup of the experiments

The deviation of the measured intensity from the desired intensity can be described basically by two signals: the multivariate signal as explained by equation 8.5 and the deviation caused by cleaning the spark stand. Both deviations can be simulated which results in the signals presented in Figure 8.7. In this figure, five time series of eight hours with an interval of ten minutes are shown. Each signal applies to a different period of eight hours. The difference in offset is caused by simulating the disturbance of the intensity due to cleaning the spark stand. The drift that occurs over the eight hours simulates the disturbances that occur normally during such a period due to effects such as dust collected in the spark stand.

A third signal superimposed on the two deviations just explained is a noise signal. For regular analyses, one analysis of a sample needs two or three measurements performed on one sample. The results of these measurements are averaged and this results in an analysis result that is reported. Between the individual measurements, differences exist due to for example heterogeneity of the sample. To simulate these differences, noise is added to the signal. The relative standard deviation of the noise is set to 0.5% which is found to be a relevant amount of noise.

Summarizing, the total signal is disturbed by three sub signals: a multivariate auto correlated signal, a multivariate auto correlated signal for the adjustment and random noise. Of these three signals, the multivariate auto-

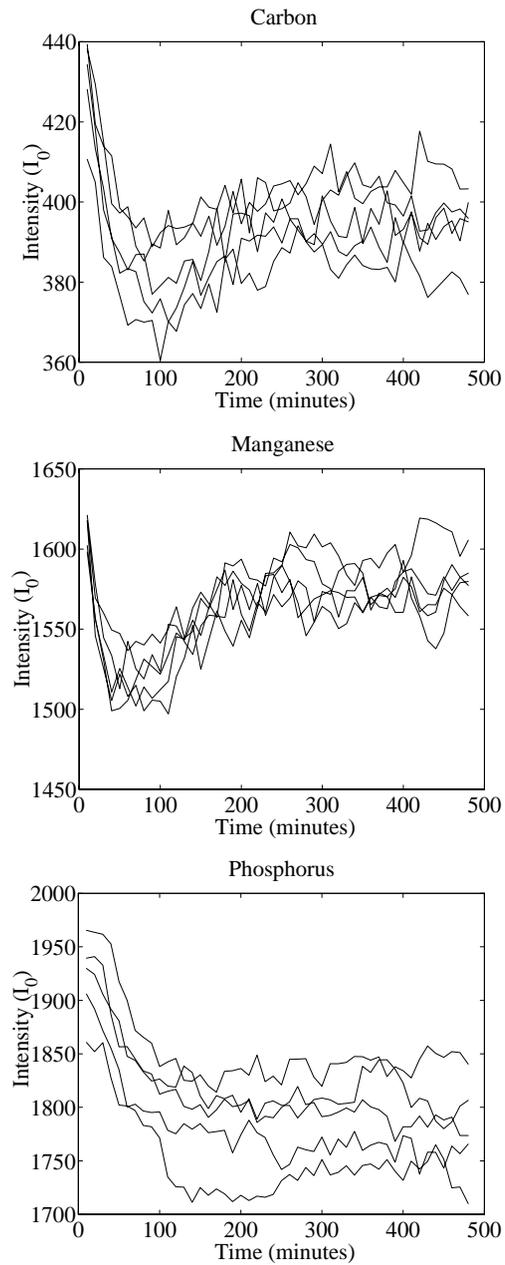


Figure 8.7: Simulated time series of 8 hour adjustment periods for the elements manganese, carbon and phosphorus.

correlated signal is equal within an adjustment period while the others are changing with time.

The intensities simulated with this model are processed with various calibration methods such as the dynamic calibration explained previously. For each simulation, measurements on one sample were simulated every 20 minutes. A total of 250 adjustment periods were simulated for each experiment. Within each experiment (9 experiments are presented in total) the simulated intensities were transformed to concentrations by means of the calibration methods under investigation. This results in 250 time series of concentrations measured during an adjustment period. At every point in time t , 250 concentrations were obtained when all the adjustment periods are put together. For each point in time two numbers were calculated: the total variation and the standard deviation. The standard deviation at time t is calculated with equation 8.6.

$$sd_{random,t} = \sqrt{\frac{\sum_{a=1}^{250} (c_{t,a} - \bar{c}_t)^2}{250 - 1}} \quad (8.6)$$

where $c_{t,a}$ is the measured concentration at time t during adjustment period a , \bar{c}_t is the mean concentration measured at time t over all the 250 adjustment periods and $sd_{random,t}$ is the standard deviation at point in time t . The standard deviations $sd_{random,t}$ show how the variation evolves in time within an adjustment period.

The second number (total variation, $sd_{total,t}$) is calculated with equation 8.7.

$$sd_{tot,t} = \sqrt{\frac{\sum_{a=1}^{250} (c_{t,a} - c_{true})^2}{250 - 1}} \quad (8.7)$$

where c_{true} is the concentration which would be found when no disturbances occur in the measured signal. For the experiments, the concentration measured directly after the adjustment is used because the instrument is assumed to be stable at that point in time. This results in the total variation being equal to the standard deviation at $t = 0$. The total variation $sd_{tot,t}$ is a function of the random error $sd_{random,t}$ and a systematic error $sd_{bias,t}$ (equation 8.8).

$$sd_{tot,t} = \sqrt{sd_{random,t}^2 + sd_{bias,t}^2} \quad (8.8)$$

Table 8.2: Setup of the simulations. The frequency of the dynamic calibration indicates how often a calibration sample is measured for the dynamic calibration. More details of the operating conditions are given in Section 8.5.

Simulation	Adjustment period (hours)	Moving average adjustment	Dynamic calibration	Frequency dynamic calibration (hour ⁻¹)	Disturbance (stepfunction)
1	8	on	off	-	0
2	8	off	on	1.5	0
3	8	on	on	1.5	0
4	4	on	on	1.5	0
5	16	on	on	1.5	0
6	8	on	on	3	0
7	8	on	on	1	0
8	8	on	on	1.5	2%
9	8	on	on	3	2%

The results of the simulations show both the total standard deviation ($sd_{tot,t}$) and the random error ($sd_{random,t}$) at each measured point in time t . Because of the relation shown in equation 8.8, the systematic error ($sd_{bias,t}$) directly follows from the difference between these two numbers. The design for each experiment is presented in Table 8.2.

8.5 Results

The results of the simulations are presented in graphs in which the results can be compared easily. The x axis shows the points in time and the y axis shows the measured variation (both total and random). In each simulation, the calibration method explained in Chapter 4 (standard method) and an alternative calibration method are compared to each other.

This section shows the results for the simulations. For each simulation, the results are presented in graphs as shown in Figure 8.8. Both the total variation ($sd_{tot,t}$) and the standard deviation ($sd_{random,t}$) are presented. Methods concerning the alternative calculations (moving average adjustment and dynamic calibration) are marked with crosses (x). The results for the standard method are marked with circles (o).

In some simulations, the total variation ($sd_{tot,t}$) is almost equal to the standard deviation ($sd_{random,t}$) for manganese. In this case, the results for the total variation and standard deviation can not be discriminated.

The first concentration measured in an adjustment period is assumed to be

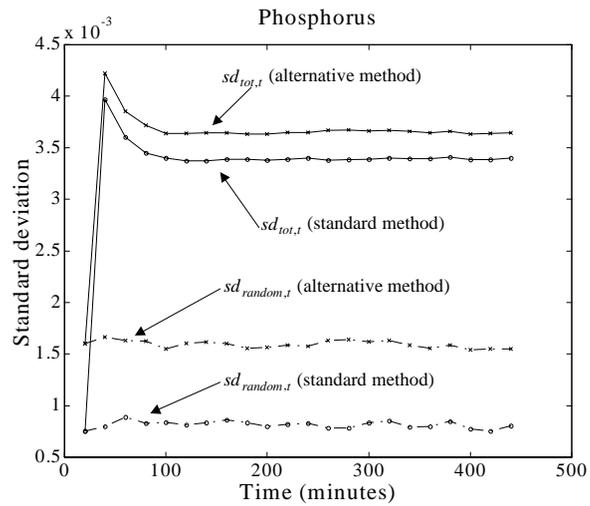


Figure 8.8: Results for an example simulation (solid lines: total variation ($sd_{tot,t}$); dashed lines: standard deviation ($sd_{random,t}$); circles (o): standard method; crosses (x): alternative method).

correct (c_{true}). So, at this starting point, the systematic error is 0 for each experiment and the total variation is equal to the random variation.

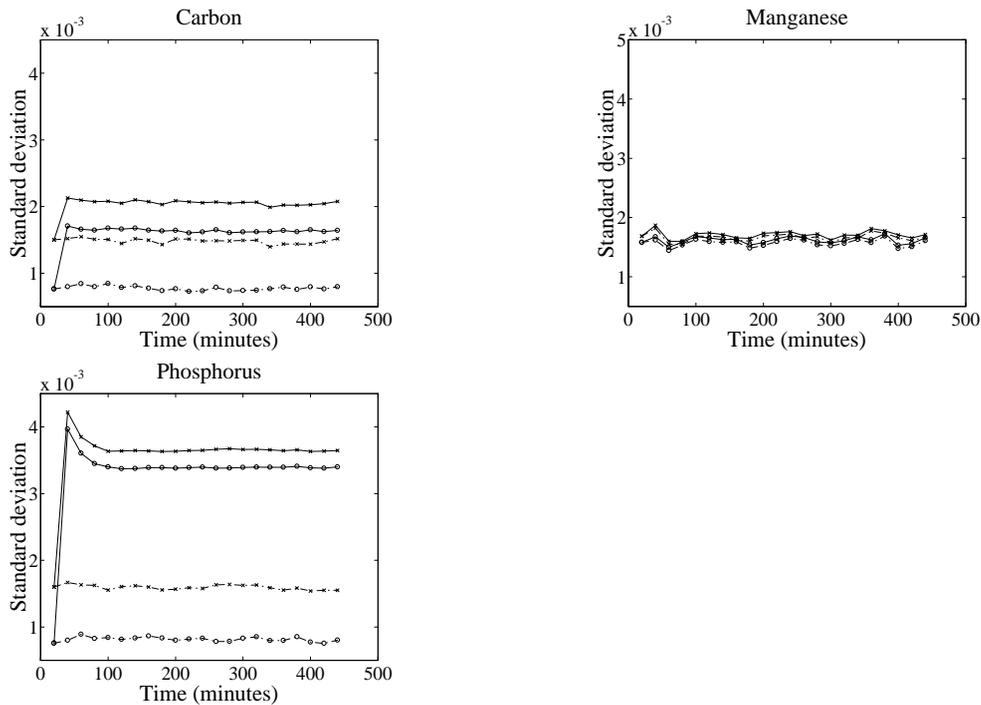


Figure 8.9: Results for simulation number 1 (solid lines: total variation ($sd_{tot,t}$); dashed lines: standard deviation ($sd_{random,t}$); circles (o): standard method; crosses (x): alternative method).

8.5.1 Simulation 1

In Figure 8.9 the result for simulation 1 are presented. In this first simulation, the only difference between the two methods is the application of the moving average adjustment. For both carbon and phosphorus, the standard deviations of the signal obtained for the alternative method are higher than those for the standard method. For manganese, there is no significant difference. For both carbon and phosphorus, there exists a strong increase of the systematic error in the first phase of the adjustment period (difference between solid and dashed line). This error is found in real experiments as well (Figures A.1 through A.4 in Appendix A). For manganese, the internal standard iron corrects for drift very well.

The signal stabilizes to a certain level inducing a certain amount of systematic error. For the moving average adjustment, measurements from a number of adjustment periods are averaged to obtain filtered adjustment intensities.

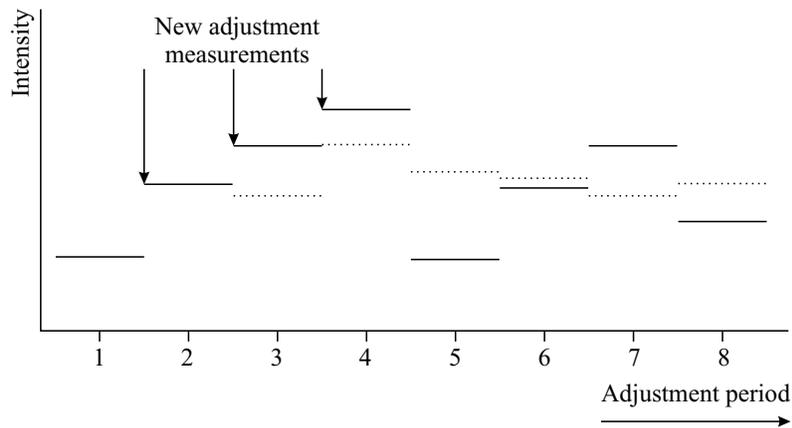


Figure 8.10: Example of the moving average adjustment signals (dashed line) compared to the adjustment signal of the standard method (solid line). The first two signals for the moving average adjustment signal have been omitted because at least three measurements are needed to start the moving average.

This system should work when the noise contributes more to the adjustment measurements than shifts in the signals of the instrument. The results obtained in the simulations imply that useful information is filtered from the adjustment measurements.

Figure 8.10 presents the intensities for the standard adjustment method and for the moving average adjustment for one of the adjustment samples. It shows that the adjustment intensities for the standard method fluctuate much more than the alternative method. If the fluctuations in the standard method would be caused by noise, the moving average adjustment should be able to correct for the fluctuation resulting in a more stable signal as shown in Figure 8.10. If, however, the less stable signal approximates the true signal better than the stable signal, information gets lost and therefore, a possibility of correcting for instrumental deviations is taken away.

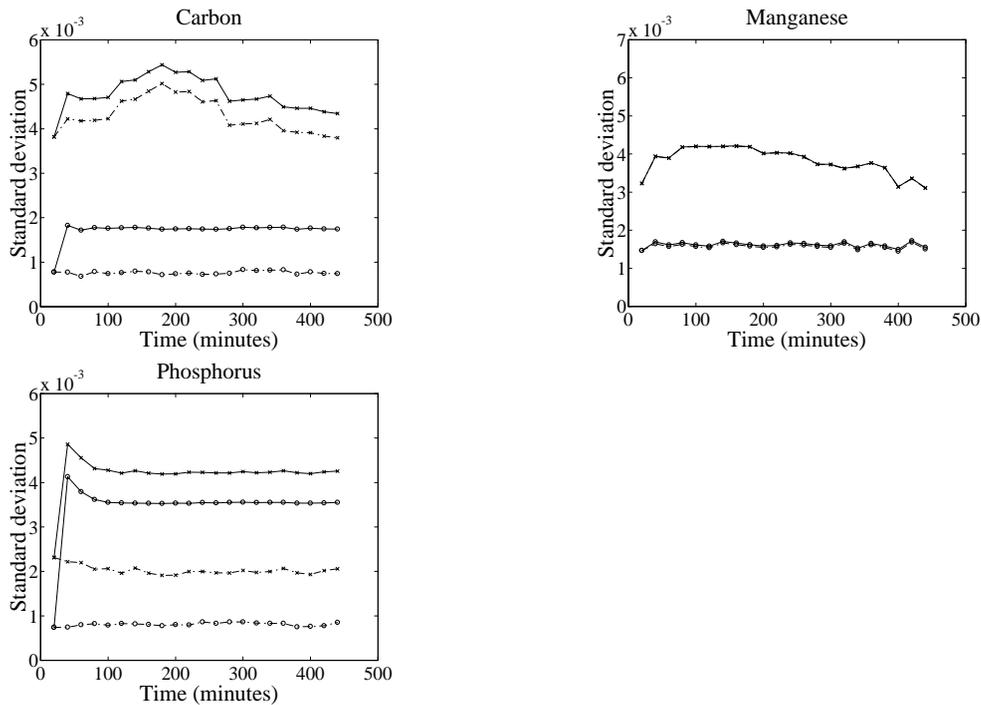


Figure 8.11: Results for simulation number 2. (solid lines: total variation ($sd_{tot,t}$); dashed lines: standard deviation ($sd_{random,t}$); circles (o): standard method; crosses (x): alternative method).

8.5.2 Simulation 2

The results for the second simulation (Figure 8.11) show that application of dynamic calibration to the standard calibration method results in an increase of the total variation for both carbon and manganese. The total variation for phosphorus is influenced by the dynamic calibration as well, but less. The variation found here, can be explained by two facts: i) each measurement performed for the dynamic calibration is a source of variation and ii) the dynamic calibration lags behind. Thus, the correction performed by the dynamic calibration parameters is not up to date because it is a moving calibration that contains drift behaviour over a certain period of time. Therefore, shifts that occur at time t still have influence after a certain period of time resulting in extra variation rather than a correction.

Compared to carbon and manganese, the results for phosphorus have a rather large systematic deviation for both methods. This is probably due to the fact

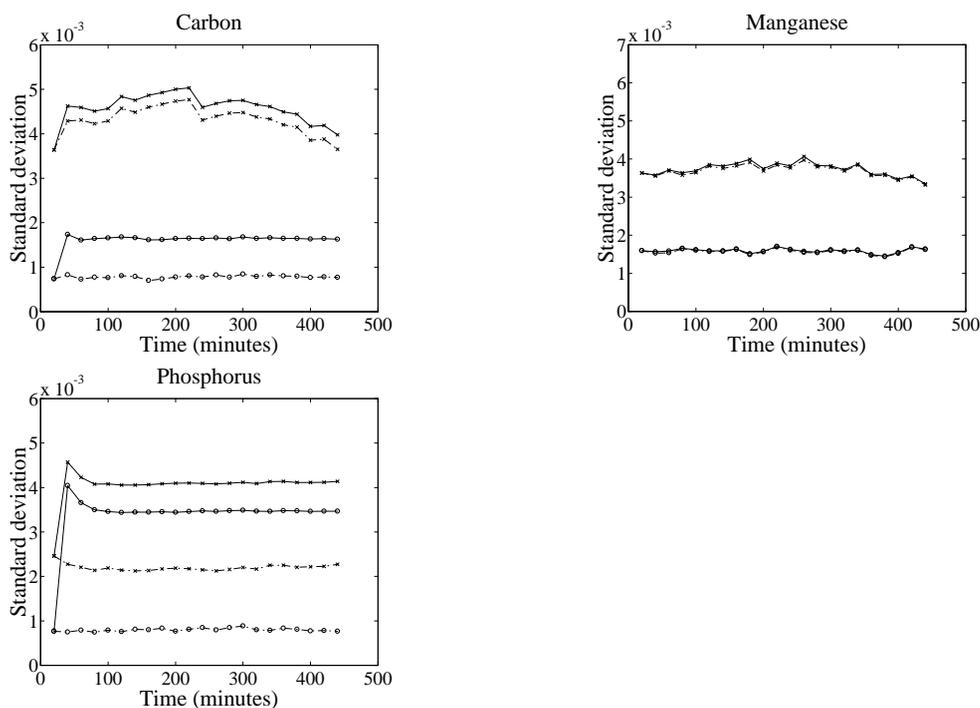


Figure 8.12: Results for simulation number 3. (solid lines: total variation ($sd_{tot,t}$); dashed lines: standard deviation ($sd_{random,t}$); circles (o): standard method; crosses (x): alternative method).

that the intensities of carbon and manganese are corrected by the intensity of the internal standard iron.

8.5.3 Simulation 3

In simulation 3 (Figure 8.12), both the moving average adjustment and the dynamic calibration have been used. The results of these simulations are not largely different from the results obtained in the second simulation. The only difference, however small, that can be seen is the decreased total variation for the alternative method compared to the results presented in simulation 2. For phosphorus, the differences between the standard and the alternative method in terms of total variation are not very large but still the standard method is the most favourite one. However, the difference is small compared to the variation induced by the correction methods (moving average adjustment and dynamic calibration) for the elements carbon and manganese.

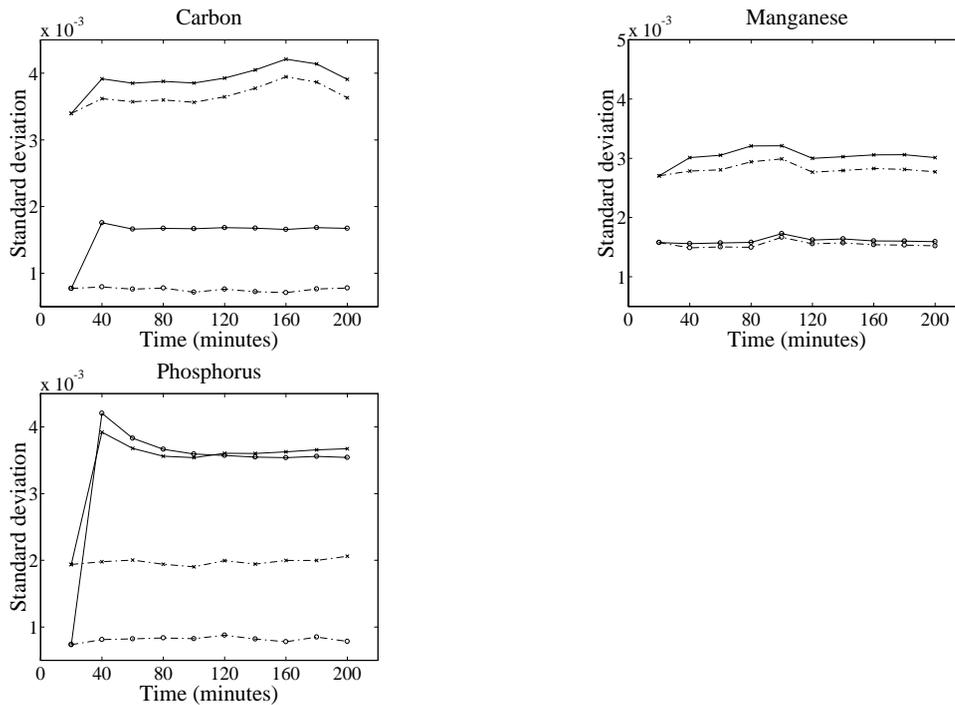


Figure 8.13: Results for simulation number 4. (solid lines: total variation ($sd_{tot,t}$); dashed lines: standard deviation ($sd_{random,t}$); circles (o): standard method; crosses (x): alternative method).

8.5.4 Simulation 4

Figure 8.13 shows the results obtained for simulation 4. The adjustment period was decreased from 8 hours to 4 hours in this simulation. For the standard method, this alteration does not induce any changes to the measured variations. For the alternative method however, the standard deviation has decreased compared to the experiment in which an adjustment period of 8 hours was simulated (simulation 3). In this shorter period, the moving average adjustment has more effect because within a shorter period of time, the effect of drift does not occur that strong compared to a situation where an adjustment period lasts longer.

For phosphorus, this results even in a situation where both methods have an equal total variation. This is caused by the fact that in this simulation the systematic error contributes less to the total variation for the alternative method.

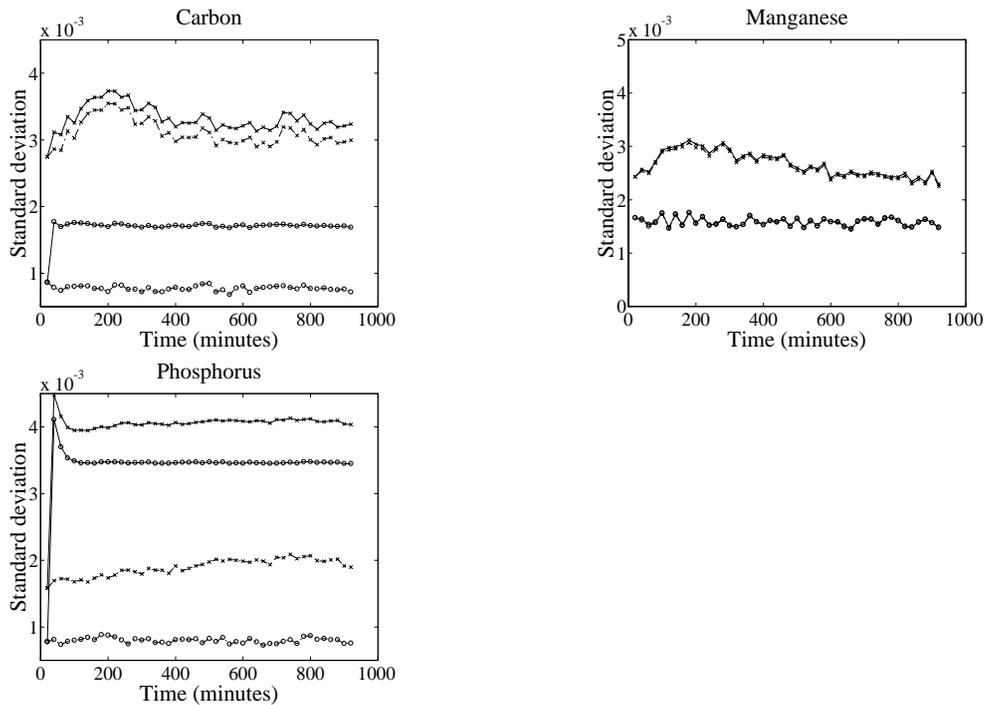


Figure 8.14: Results for simulation number 5. (solid lines: total variation ($sd_{tot,t}$); dashed lines: standard deviation ($sd_{random,t}$); circles (o): standard method; crosses (x): alternative method).

8.5.5 Simulation 5

The standard adjustment period of 8 hours has been extended to 16 hours in simulation 5. The results of this experiment are reported in Figure 8.14. The results for the standard method show that extension of the adjustment period from 8 to 16 hours should not induce any problems in terms of variation (compare Figures 8.12 and 8.14). However, before applying a longer adjustment period in practice, the validity of the model used in this experiment should be compared to experimental results obtained over a period of 16 hours. Results for the alternative method appear to be better in the beginning of the 16 hour adjustment period. For both carbon and manganese an increased variation is found after approximately 2 hours. After about 3 hours the variation is at the starting level again. This effect is probably due to the fact that after that amount of time, most of the dynamic calibration samples have been analysed in the new adjustment period.

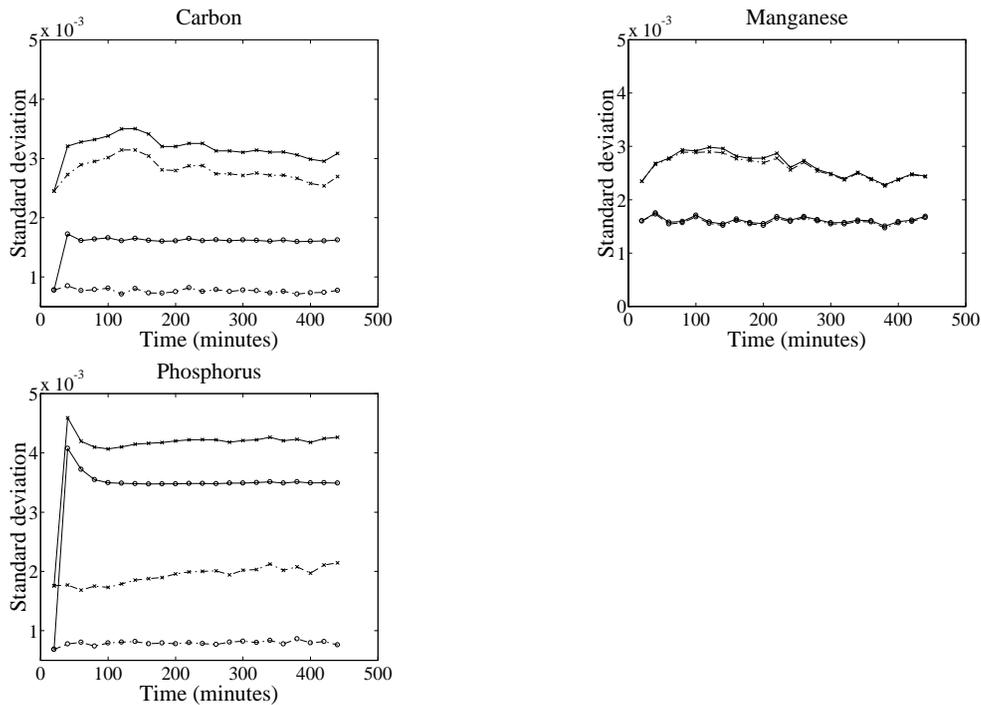


Figure 8.15: Results for simulation number 6. (solid lines: total variation ($sd_{tot,t}$); dashed lines: standard deviation ($sd_{random,t}$); circles (o): standard method; crosses (x): alternative method).

8.5.6 Simulation 6

For simulation experiment number 6, the frequency of analysing samples for dynamic calibration has been changed to once every 20 minutes. The results plotted in Figure 8.15 show that the increased frequency causes the standard deviation of the alternative method to decrease by approximately 25% for both carbon and manganese (compare to Figure 8.12).

For phosphorus, after an initial decrease, the variation starts to rise again. This increase is seen as well in other experiments but, as can be seen in the results of simulation 5, this effect stabilizes after 8 hours. Overall, an increased frequency of analysing dynamic calibration samples improves the results for the alternative method.

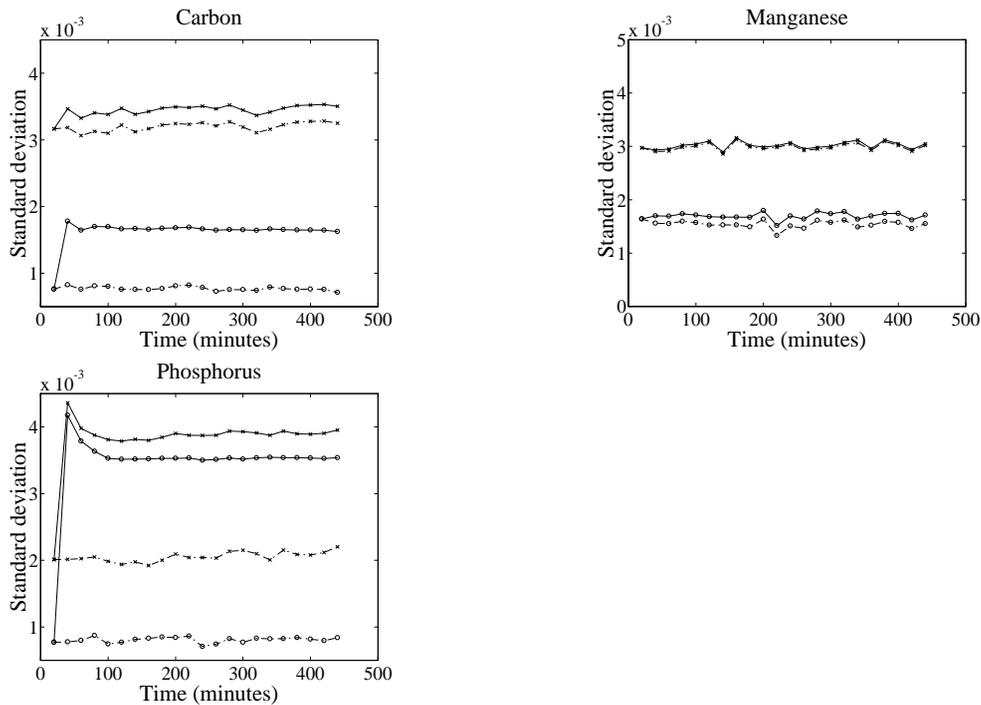


Figure 8.16: Results for simulation number 7. (solid lines: total variation ($sd_{tot,t}$); dashed lines: standard deviation ($sd_{random,t}$); circles (o): standard method; crosses (x): alternative method).

8.5.7 Simulation 7

The frequency of analysing dynamic calibration samples can be decreased as well. For simulation 7, the samples for the dynamic calibration have been analysed once every 60 minutes. The resulting variations (Figure 8.16) lie in between the results obtained for a frequency of once every 40 minutes (Figure 8.12) and once every 20 minutes (Figure 8.15). From these results it is clear that an optimum can be found and that there exists no linear relation between frequency of dynamic calibration and obtained variation.

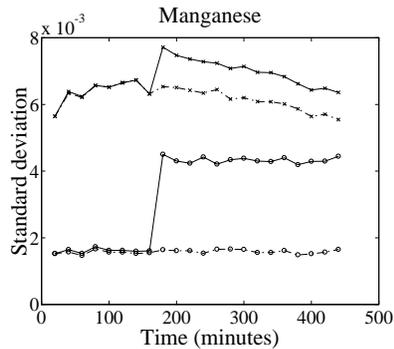


Figure 8.17: Results for simulation number 8 for manganese (Mn). (solid lines: total variation ($sd_{tot,t}$); dashed lines: standard deviation ($sd_{random,t}$); circles (o): standard method; crosses (x): alternative method).

8.5.8 Simulation 8

To test the robustness of both methods against sudden changes in the OES spectrometer, an experiment has been performed in which the signal (intensity) has been increased by 2% for manganese 180 minutes after adjusting the spectrometer. The resulting variations for manganese are reported in Figure 8.17.

The results for the alternative method show an increased variation but this is somewhat misleading. For each of the 250 simulations, a disturbance has been applied at the same moment (after 180 minutes). Because the dynamic calibration transfers results from previous measurements to the following measurements, the total variation increases by a certain amount. At the end of the adjustment period, the alternative method is still not back to normal and this results in an increase of the variation (memory effect). Under normal operating conditions, the disturbance would probably not take place very often.

Despite the above described problem, it is possible to conclude that the alternative method corrects for the disturbance after a certain period of time. The standard method lacks the correcting ability and therefore, a systematic error is introduced.

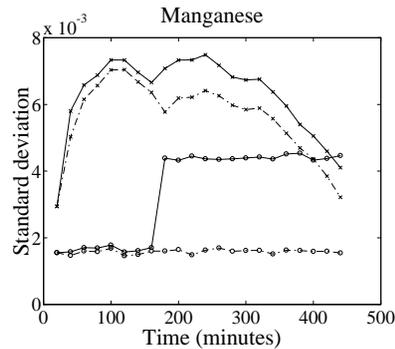


Figure 8.18: Results for simulation number 9 for manganese (Mn). (solid lines: total variation ($sd_{tot,t}$); dashed lines: standard deviation ($sd_{random,t}$); circles (o): standard method; crosses (x): alternative method).

8.5.9 Simulation 9

The results of simulation 9 are presented in Figure 8.18. For this simulation, the same experiment as in simulation number 8 has been performed with the only difference being that the dynamic calibration frequency has been increased from once every 40 minutes to once every 20 minutes. This results in a faster correction. The same effect of an increased variation over the whole time range is found here because the disturbance applied during adjustment period a still has an effect during adjustment period $a+1$. Although the alternative method shows better results after about 7 hours (Figure 8.18), the method is not applicable because the time period needed for correcting the problem is too long and too many samples other than production samples have to be analysed to keep the system running.

8.6 Conclusions

The simulations performed in this experiment have proven to be a powerful tool for testing alternative calibration methods. The tests could have been performed as well in the laboratory, using real instruments instead of the models used for the experiment but much more means (time, money, samples) would be needed. Besides that, the amount of simulations (250 per setting) exceeds the amount of means available for true experiments. An important issue in these kind of experiments is always that the models, used for simulating the signals, have to be accurate. The models used in this experiment were fitted with signals obtained from one instrument. Future experiments should

include models of signals obtained from other instruments as well.

The alternative method that was investigated in this chapter consists of two distinctive correction algorithms: moving average adjustment and dynamic calibration. Both algorithms worsen the results of the simulated signals compared to the standard method. With the application of the moving average adjustment, besides noise in the adjustment measurements, also important (drift) information may be removed, thereby inducing extra variation rather than reducing the variation (simulation 1). Addition of the dynamic calibration algorithm to the calibration system leads to unfavourable results as well (simulation 2). The extra variation in the signal of the alternative method has two possible causes. The first is the extra variation induced when measurements are performed for the dynamic calibration. The second cause might be the dynamic calibration lagging behind. Thus, the correction performed by the dynamic calibration parameters is not up to date because it is a moving calibration that contains drift behaviour over a certain period of time.

The alternative method is probably optimal for a certain type of drift. The results of simulations 8 and 9 show that a rather good correction is obtained when sudden upsets appear in the analytical signal. However, when the drift in the analytical signal is different from the signal that is optimal for the alternative method, poor results are obtained. It might be said that the correction algorithm contained in the alternative method *does not fit* the underlying drift that is present in the analytical signal under normal operating conditions.

Although dynamic calibration improves the results when sudden disturbances interfere with the signal, this correction involves many experiments to be performed. Therefore, it might be better to use verification samples to check whether the instrument is still stable. Verification is especially important when the adjustment period would be increased from 8 to 16 hours or maybe even longer. It would be wise to include checkups to certify the quality of the measurements over such a prolonged period of time.

Appendix **A**

Additional figures and tables

Table A.1: Details of the elements measured with spark OES. The used wavelenghts for the measurements may vary for different brands of spark OES.

Element	In plasma ^a	Wavelength (Å)	IP (eV) ^b	Order ^c
Fe	Fe ⁺	2730.73	7.870	1
C	C	1930.905	11.260	2
Mn	Mn ⁺	2933.06	7.435	1
P	P	1782.838	10.486	2
S	S	1807.311	10.360	2
Si	Si	2124.12	8.151	2
Al	Al	3944.006	5.986	1
Cu	Cu ⁺	2135.981	7.726	2
Sn	Sn ⁺	1899.91	7.344	1
Cr	Cr ⁺	2677.16	6.766	1
Ni	Ni ⁺	2316.04	7.635	1
Mo	Mo ⁺	2020.30	7.099	2
Nb	Nb ⁺	3194.98	6.880	1
V	V ⁺	3102.30	6.740	1
B	B	1826.41	11.814	2
Ti	Ti ⁺	3372.80	6.820	1
Ca	Ca ⁺	3968.47	6.113	1

^aThis column shows whether an element is present in the plasma as an atom or an ion.

^bThe ionisation potential (IP) indicates the amount of energy needed to free the less bound electron from an atom.

^cThe diffraction order indicates which order line is used for analysis. For boron, for example, the second order line is measured at 3652.82 Å (=2 × 1826.41 Å).

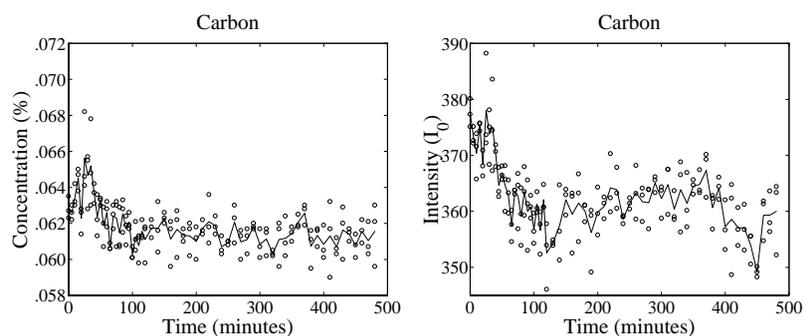


Figure A.1: Results of the first drift experiment for carbon (C). Obtained concentrations (left figure) and calculated intensities (right figure). \circ : individual measurements, - : mean of three measurements.

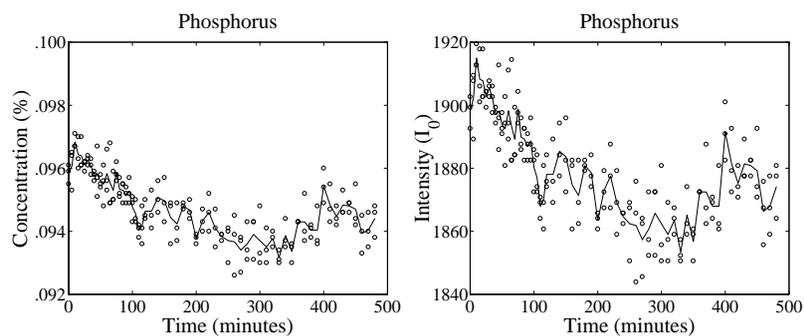


Figure A.2: Results of the first drift experiment for phosphorus (P). Obtained concentrations (left figure) and calculated intensities (right figure). \circ : individual measurements, - : mean of three measurements.

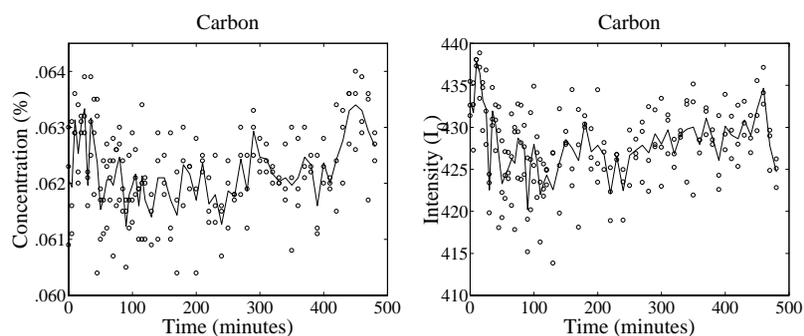


Figure A.3: Results of the second drift experiment for carbon (C). Obtained concentrations (left figure) and calculated intensities (right figure) \circ : individual measurements, - : mean of three measurements.

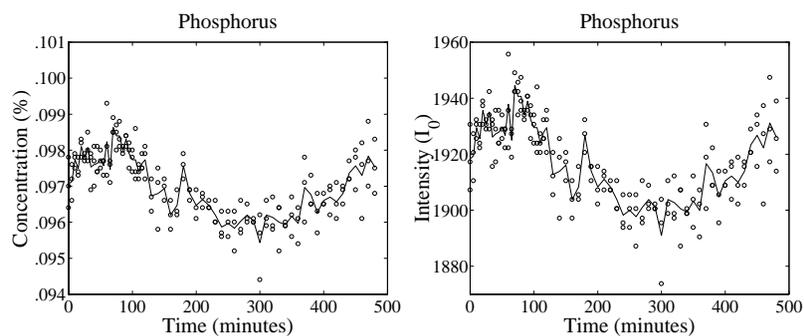


Figure A.4: Results of the second drift experiment for phosphorus (P). Obtained concentrations (left figure) and calculated intensities (right figure). \circ : individual measurements, - : mean of three measurements.

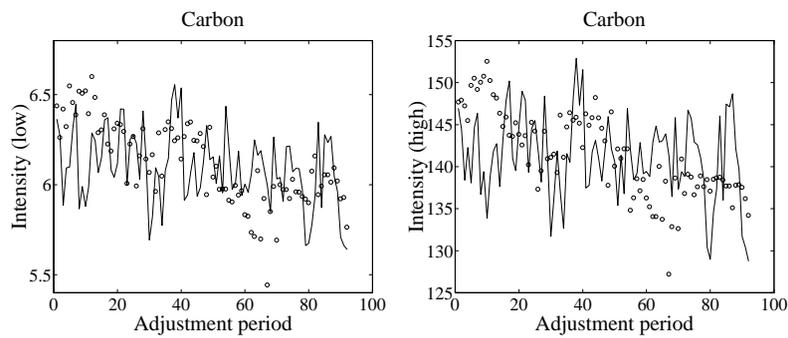


Figure A.5: Measured (\circ) and simulated ($-$) adjustment measurements for carbon (C).

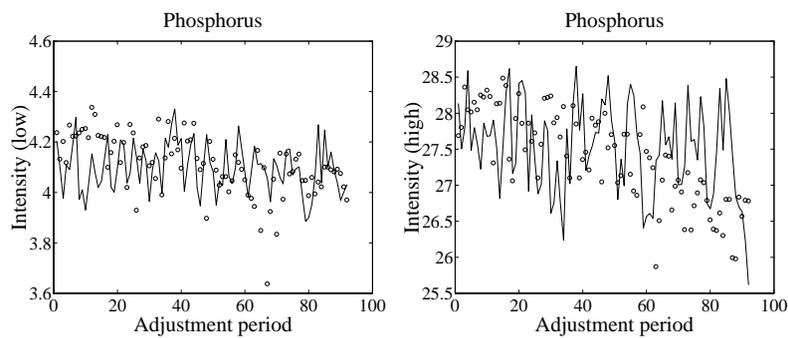


Figure A.6: Measured (\circ) and simulated ($-$) adjustment measurements for phosphorus (P).

Summary and future prospects

In production process environments, many sources of variation have an influence on the quality of the final product. To comply with product specifications, the production process has to be monitored and controlled. For process control, reliable analytical, preferably on-line, chemical measurements are needed. Analyses are subject to variation and therefore, analysis results never represent the true properties of a product.

When variation in the analysis results is a limiting factor for the optimal control of the production process, variation reduction is needed. Also, if clients request products with improved product specifications, process control needs to be optimised.

At the Dutch steel company *Hoogovens Staal BV*,^a research on the topic of variation reduction in the production, sampling and analysis of steel was initiated to ensure that concentrations of the elements in the final products comply with demands from clients, now and in the future. Although current demands give no rise to concern, effort has to be put in variation reduction in the analysis results because demands will become more and more stringent in the future.

^a*Hoogovens Staal BV* merged with *British Steel plc* in 1999 forming a new company called *Corus Group plc*. The research described in this thesis was performed before the two companies merged and therefore, only the Dutch steel company is mentioned.

The production of steel products such as soda cans and car parts is a complex process in which iron ore is reduced to metallic iron. Further refinery of the formed iron to steel is performed by carefully removing and adding certain elements such that finally the product meets certain quality standards. Chapter 2 describes the process of steel making in some detail to put the research presented in this thesis into perspective. The research concentrates on that part of the production process where liquid iron has been transformed to steel and is ready to be cast into moulds to form slabs of steel.

One method to improve the analyses is the development of more accurate and precise methods of analysis. Many researchers have searched for methods to improve process control in steel production. Several investigations involved the use of a laser as both a sampling and an excitation source. Others focused their research on in-situ analyses. In Chapter 3 an overview is given of studies that may give more insight in possibilities of improving process control in steel production. Laser based techniques possibly will replace the standard analysis methods in the future. Unfortunately, none of the reviewed papers indicate which sources of variation contribute most to the total variation in the analysis results. Therefore, it is unknown whether analysis methods with more accuracy and precision will improve process control substantially.

Besides improvement of the accuracy and precision of analytical methods, reduction of the response time by on-line analysis gets attention. Although interesting, these methods are still in their infancy. Newly developed techniques still cannot compete with the accuracy, precision and stability of standard methods.

Currently, spark optical emission spectroscopy (spark OES) is still the most favourite analysis method for analysing steel samples. The method is fast and both accuracy and precision meet the required conditions. With spark OES, solid steel samples are analysed and analysis results for the elements C, Mn, P, S, Si, Al, Cu, Sn, Cr, Ni, Mo, Nb, V, B, Ti and Ca are reported to the process engineer. A detailed description of the spark OES and the used samples is presented in Chapter 4.

The analysis results of the spark OES are used to monitor and control the chemical composition of the steel bath. As stated before, the customer demands are expected to become more and more stringent in the future and therefore, improvement of the analyses are needed. Replacing the spark OES with laser based analysis methods is one solution. Another method is improving the currently available methods of sampling and analysis. Such improvements can be performed by means of trial and error but this is not preferable because the model according to which the variation is build-up will be unknown. A strategic approach in which possible sources of variation are taken

into account gives a better insight in the structure of the total variation apparent in the final analysis result. Chapter 5 presents such a strategic method consisting of six steps, each to be performed consecutively. These steps are:

1. Identify and select factors that contribute to the total variation of the response factors.
2. Select a model that includes the factors chosen in step 1.
3. Design an experiment which is efficient for estimating the effects of the factors included in the model.
4. Perform the experiments according to the experimental design.
5. Estimate the effects of the factors included in the model on the total variation of the response factors.
6. Interpret and discuss the results of the estimations.

This strategy has been applied to the sampling and analysis procedure as used at the *Hoogovens Staal BV Laboratory for Process Control*.

Two chapters are devoted to the subject of identification and quantification of variation in the production, sampling and analysis of steel where the strategy introduced in Chapter 5 has been used. Chapter 6 describes the setup of the experiments and reports the results for one type of steel^b. To test whether results for one type of steel holds for other types of steel as well, Chapter 7 presents the results obtained for three different types of steel. From the experiments the following conclusions can be drawn:

- Differences between spectrometers are an important source of variation for part of the total range of elements analysed in the experiment. The differences between results of chemical analyses obtained from different spectrometers are caused by differences in both hardware and software used in the spectrometers. In order to reduce the variation due to measurements, a standardisation procedure should be developed such that deviations within spectrometers and differences between spectrometers are corrected.
- Another important source of variation is the drift apparent within a period of eight hours (adjustment in the experiments). Methods like Kalman filters and adaptive calibration may be used to reduce the influence of drift on the variation in the analysis results.

^bSteel can be produced in many different compositions. Steel with a certain composition, for instance composition 1, is called type 1 steel in this thesis.

- Place and time of sampling have to be chosen carefully for certain elements. A choice of the best time and place of sampling is hard to decide on. The best choice would probably be to take samples from places in the process phase where a minimum of disturbance to the production process will be caused.
- The concentrations found in samples taken from the different process phases are comparable for all elements except tin. The concentration of tin found in samples taken from the tundish are noticeably higher than in samples from the other two process phases. Only for tin, a significant contribution to the variation due to sampling could be detected. This is only true for samples taken from the process phase tundish. The variation is probably due to part of the sample probe which contains tin.
- Sampling is not a dominant factor. However, it should be noted that for this experiment samples have been selected which have no irregularities on the surface. Therefore, the estimated sampling variations are only valid when samples are supplied to the laboratory of process control which have no irregularities on the surface of the sample.

In Chapter 4 a description is given of the calibration method used for the spark optical emission spectrometers (spark OES) at the *Hoogovens Laboratories for Process Control*. This method has been developed and changed time after time over the years based on new insights and the introduction of better instruments. The calculation is a rather complex combination of different procedures. Although this method has been developed and improved over the years, other methods may be used to improve the accuracy and precision of the analytical results. However, before implementation, such methods need to be verified to certify the continuation of the steel making process. Implementation of an alternative method might result in further deviations thereby influencing the process control.

Chapter 8, finally, describes the results of simulation experiments that have been performed to test whether changes to the current calibration method can reduce the variations in the analysis results. The drift behaviour of the spark OES was simulated and the resulting intensities were used to simulate measurements. Results for the elements carbon (C), manganese (Mn) and phosphorus (P) show that the tested alternative methods do not improve the standard calibration method under normal operating conditions. The alternative method applies extra correction besides the corrections applied by the currently used method. Propagation of errors might explain the extra vari-

ation in the results when using the alternative method. If a perturbation is applied to the signal of the spectrometer, the alternative method appears to give better results than the standard method.

Future prospects

One of the characteristics of research is that further research is always a possibility and often needed. This is also the case for the research presented in this thesis. One of the conclusions was that the differences between results, obtained with different spark OES, are an important source of variation. Reduction of these results can result in better process control and therefore, further research is needed on this subject. Candidates for variation reduction can be found in development of drift correcting algorithms, application of laser ablation in stead of spark as excitation source, or usage of multivariate calibration methods.

Although the alternative algorithm presented in Chapter 8 appeared to be inapplicable for the reduction of the variation in the analysis results, correction algorithms should be investigated further. However, in such a research, the drift behaviour of various spark OES should be characterised first. With drift models characterising the drift, an ideal drift correcting algorithm can be build. The Kalman filter may be helpful in correcting the drift in the analytical signal.

Application of laser ablation for process control in steel analysis is possible when the fundamentals are understood and ablation can be controlled. Especially the coupling of laser ablation with techniques like ICP and MS is an interesting development and needs to be investigated further. Although the development of in-situ measurements with laser ablation encounters difficulties, further research in this direction is of importance as well because fast process control will be of importance when new steel production techniques like thin slab casting will be used.

For the analysis of steel samples with spark OES, univariate calibration methods are used although correlation in drift behaviour exists for certain elements. Multivariate techniques in calibration and in analysis of variance may be of use to improve process control and in variation reduction, respectively.

Samenvatting voor niet-ingewijden

Bij het staalbedrijf *Hoogovens Staal BV*,^c wordt het proces van staal maken continu verbeterd om zodoende steeds aan de eisen van klanten te kunnen voldoen. In het kader van dit verbeteringsprogramma is een onderzoek uitgevoerd naar de mogelijkheid om de chemische analyse van staal te verbeteren. De opzet, uitvoer en resultaten van het onderzoek zijn in dit proefschrift beschreven. Deze samenvatting is bedoeld voor lezers die niet bekend zijn met het onderwerp en toch iets meer willen weten over het uitgevoerde onderzoek.

Kwaliteit

In de huidige maatschappij speelt verbetering van kwaliteit een steeds belangrijkere rol. Zo wordt er veel gesproken over de kwaliteit van leven, over de kwaliteit van dienstverlening, maar natuurlijk ook over de kwaliteit van producten die we aanschaffen. Hier beperken we ons tot de kwaliteit van tastbare producten. Om te kunnen bepalen wat de kwaliteit van een product is, zijn metingen nodig die aangeven wat de eigenschappen van het product zijn. Bij een product als staal spelen eigenschappen zoals buigzaamheid en breekbaarheid een belangrijke rol. Voor het verkrijgen van staal met bepaalde eigenschappen, is het nodig om de concentratie van de verschillende elementen zoals ijzer, koolstof, mangaan en fosfor te controleren en, waar nodig, aan te passen. De resultaten van de metingen van de concentratie geven aan of het eindproduct al dan niet aan de gestelde eisen voldoet.

^c *Hoogovens Staal BV* is in 1999 samengegaan met *British Steel plc*. Samen vormen ze nu het bedrijf *Corus Group plc*. Het onderzoek, beschreven in dit proefschrift en uitgevoerd in opdracht van *Hoogovens Staal BV*, is uitgevoerd voordat de twee bedrijven samen gingen.

Naast de metingen aan het eindproduct zijn ook metingen tijdens het productieproces nodig om vast te stellen of het productieproces volgens wens verloopt. De meetresultaten tijdens het verloop van de productie geven een indicatie of er wijzigingen aan het productieproces nodig zijn om tot het gewenste eindproduct te komen.

Metten

Een vervelende eigenschap van metingen is dat de verkregen resultaten nooit exact de werkelijkheid weergeven. Het meten van bijvoorbeeld de buitentemperatuur is afhankelijk van factoren als de gebruikte thermometer en de persoon die de thermometer afleest. Als een groep mensen de buitentemperatuur opmeet, dan is de kans erg groot dat de meetresultaten verschillend zijn. Dit is het gevolg van verschillen tussen thermometers en fouten bij het aflezen van de thermometers. Het gemiddelde van de meetresultaten geeft een schatting van de werkelijke temperatuur. De afwijkingen tussen de afzonderlijke metingen geven aan hoe goed (kleine verschillen = weinig spreiding), of hoe slecht (grote verschillen = veel spreiding) de individuele metingen zijn. Behalve verschillen tussen de individuele metingen kan er ook nog een verschil bestaan tussen het gemiddelde van de metingen en de werkelijke waarde (systematisch verschil). Zowel de verschillen tussen de afzonderlijke metingen als het verschil tussen het gemiddelde en de werkelijke waarde kunnen een grote invloed op de processturing hebben.

Bij een productieproces kan de temperatuur in een reactievat een belangrijke factor zijn voor het leveren van een kwalitatief goed product. Wanneer in een dergelijk proces de temperatuurmeting een grote mate van spreiding of een systematisch verschil vertoont, dan is het moeilijk om te bepalen of de temperatuur in het reactievat de juiste waarde heeft. Door de meting van de temperatuur te verbeteren (optimaliseren) is het mogelijk om een kleinere spreiding en/of kleinere systematische afwijking in het meetresultaat te behalen. Een geoptimaliseerde meting geeft dan de mogelijkheid om het proces beter te sturen.

Spreidingsbronnen

Helaas is het niet altijd even duidelijk waar de spreiding in meetresultaten door veroorzaakt wordt. Meerdere soorten (bronnen) van spreiding zoals afleesfouten en afwijkingen van instrumenten resulteren in een totale spreiding. Doordat het eindresultaat van een meting een combinatie is van al deze soorten van spreiding, is het moeilijk om te bepalen welke bron van spreiding het grootste aandeel heeft gehad in het ontstaan van de spreiding. Het is

echter mogelijk om een schatting te maken van de grootte van de verschillende bronnen van spreiding. Dit kan door een proef op te zetten en uit te voeren volgens een proefopzet (experimental design). Analyse van de spreiding (ANOVA; analysis of variance) resulteert in het opsplitsen van de totale spreiding in de bijdragen van de verschillende bronnen van spreiding. De grootste bron(nen) van spreiding kan (kunnen) dan worden aangepakt om tot betere metingen te komen. Betere metingen wil zeggen: metingen met minder spreiding en dichterbij de werkelijke waarde.

Meerdere methoden voor verbetering

Bij de optimalisatie van de chemische analyse van staal kunnen verschillende methoden toegepast worden. In het onderzoek beschreven in dit proefschrift zijn drie wegen bewandeld om tot mogelijke verbeteringen te komen.

De eerste methode is het vervangen van bijvoorbeeld de momenteel gebruikte analysemethode door een andere methode die minder spreiding veroorzaakt in de analyseresultaten. Hiertoe is een inventarisatie van alternatieve methoden uitgevoerd. Uit dit onderzoek blijkt dat analysemethoden gebaseerd op lasertechniek mogelijk in de toekomst een belangrijke rol gaan spelen bij de chemische analyse van staal.

De tweede methode is een statistische analyse (ANOVA) van metingen die volgens een proefopzet uitgevoerd zijn. Hoofdstuk 5 geeft een aanpak in zes punten weer voor het opsporen en het bepalen van de grootte van bronnen van spreiding met als doel de totale spreiding te verminderen. Deze strategie is toegepast op een onderdeel van de productie, bemonstering en analyse van staal.

De derde methode tenslotte betreft het simuleren (nabootsen) van metingen met behulp van de computer. Simulaties vormen een krachtig hulpmiddel om de invloed van veranderingen aan metingen of berekeningsmethoden te bepalen. Simulaties worden vaak toegepast als experimenten in het werkelijke proces teveel verstoringen opleveren of als de metingen teveel tijd en geld kosten.

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