Quantifying sources of variation in process analytical measurements

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Publication date
2000

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.

[b]Steel 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.