Optimal process analyzer selection and positioning for plant-wide monitoring
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1. Selection and Positioning: Introduction

Theory of Process Analytical Chemistry

1.1 Introduction - How do plant managers make decisions regarding which process analyzers to buy and install for monitoring and controlling their processes? Should it be on-line, at-line or off-line instruments? Slow but accurate process GC's or fast but relatively imprecise NIR spectrometers? Often such decisions are made ad-hoc and based on limited research, because extensive development and long 'try-out' periods are considered as too expensive. However, there exists theory that can guide this decision-making: the Theory of Process Analytical Chemistry.

Process analytical chemistry is a rapidly growing field. For a large part this is due to the activities of the CPAC in Seattle (Washington, USA [1]), but other research groups have also focused their activities on performing process analytical measurements. The field is rapidly coming of age as indicated by special review articles devoted to process analytical chemistry. Moreover, at international analytical chemistry conferences, process analytical chemistry always deserves specialized sessions; there are even international conferences solely devoted to the subject.

A considerable number of process analytical chemistry papers discuss issues like calibration and standardization of process analyzers; building interfaces and equipment for on-line, in-line and in-situ monitoring; or sensor development for performing process analytical measurements. The reported figures of merit in these papers are often limited to precision (e.g. the root-mean squared error of prediction, RMSEP) and analysis time. However, precision and analysis time do not tell the whole story. Is a method that is more robust but also less precise than an alternative method to be preferred? What is an acceptable degree of precision given a certain process? Where in the process should one extract the sample or place the analyzer interface?

All the questions above are very important for the practical use of process analyzers. Answers to these questions can be found if process analytical measurements are formulated in one unifying theoretical framework. In
the chemical engineering literature the problem of optimal sensor location has attracted attention [2], but this work only takes into account some instrument specifications. In this thesis, a framework is presented which accounts for all instrument specifications. This framework is based on the measurability theory developed by Van der Grinten [3], [4]. The measurability theory has been expanded to include the problems mentioned above. In this introduction the theory will be explained using a case study. An in-depth explanation is given in earlier papers [5]-[7].

1.2 Case Study - A simulated case study is used for illustrative purposes. In this case study, the goal is to monitor conversion at the end of a styrene polymerization reactor. This example closely resembles industrial practice, dealing with a highly relevant reaction of sufficient complexity. Hence, it is a good example for illustrating our method. All calculations were validated using real experiments, reported elsewhere [7], [Chap. 4]. The example concerns the free radical polymerization of styrene. A simplified step-wise reaction scheme is given in Box 1.1. The reaction is performed in a tubular reactor (of one-meter length) as shown in Figure 1.1. The figure also shows some details on experimental conditions. The reactor tube is fed with a mixture of styrene monomer and initiator. The initiator concentration in the reactor feed shows small, unknown fluctuations around its nominal value. These fluctuations are considered as process disturbances and their influence on degree of conversion at the end of the reactor - how much styrene monomer has reacted to polystyrene - has to be monitored.

<table>
<thead>
<tr>
<th>Initialization</th>
<th>$I \rightarrow 2I^* + N_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chain initialization</td>
<td>$I^* + M \rightarrow I-M^*$</td>
</tr>
<tr>
<td>Propagation</td>
<td>$I-M^* + M \rightarrow I-M-M$</td>
</tr>
<tr>
<td>Termination</td>
<td>$I-M-M-M-M-I + M-I \rightarrow I-M-M-M-I$</td>
</tr>
</tbody>
</table>

**Box 1.1**

Four types of process analyzers are available for this monitoring task. Both a Size Exclusion Chromatograph (XSEC) [8] and a Near-Infrared
(NIR) spectrometer can be operated close to the reactor (at-line). The alternative is a Short-Wave Near-Infrared (SW-NIR) spectrometer, operated in on-line or in-line mode.

**Figure 1.1** Schematic drawing of the styrene polymerization reactor.

1.3 Post-Analysis Signal Reconstruction - The process analyzer measures the conversion (the 'process signal') at the end of the reactor. Due to the limitations of the process analyzer, continuous and perfect knowledge of this process signal is not possible: every analyzer has a limited precision and analysis time. Hence, we always have to do with a 'reconstructed signal': the process signal we can reconstruct using the measurements of our process analyzer.

The central theme of the Theory of Process Analytical Chemistry is signal reconstruction. Suppose that we would have a perfect instrument that would measure the conversion instantaneously without any error. The result is then the gray line in Figure 1.2. This represents the true process variation: the variation of degree of conversion in time that we are interested in.

Unfortunately, we do not have perfect instruments. Our instrument has a limited precision (indicated by a standard deviation $\sigma$) and we expect our measurements to be spread around the true value, e.g. $\pm 3\sigma$. This confidence interval is shown in Figure 1.2a by the gray markers.
We can reconstruct the signal in the best possible way by connecting all these measurements. This 'connection line' is the black line and this is the best reconstruction we can get post-analysis, that is, after collecting the last measurement results. If there is no systematic error in the measurements, the value of \(\sigma_i\) is an indication of the error we make in sampling the true signal. Obviously, the poorer the precision of the process analyzer, the greater the error in our reconstructed signal.

**Figure 1.2** The effect of different instrument imperfections on signal reconstruction: a) precision \(\sigma_i\), b) sampling frequency \(T_s\), c) sampling time \(T_g\), d) response correlation \(T_r\), e) delay time \(T_d\).

There are other contributions to the imperfection of process analyzers. Process measurements can only be performed at a limited frequency expressed as the sampling rate: the time in-between taking successive samples (indicated by \(T_s\)). Figure 1.2b shows the consequence of this limited sampling frequency. Likewise, the sampling itself is not instantaneous. It takes some time to collect ('grab') the sample from the process (indicated by \(T_g\)) and during this time, process variation is averaged. This is shown in Figure 1.2c. There might also be response correlation. This is carry-over in the detector response from one measurement to another (indicated by \(T_r\), the mean correlation time). The effect of this is shown in Figure 1.2d. Finally, the process analyzer can have a significant analysis time, \(T_d\). This causes a delay in the availability of the result and its effect is illustrated in Figure 1.2e. Of course, post-
analysis this delay can be counteracted by shifting the whole reconstructed signal to the left with a shift equal to the analysis time $T_d$. In reality, all these imperfections are present to some degree and affect the quality of the reconstructed signal. Moreover, we want to reconstruct the signal \textit{real-time}, while the process runs. Hence, we cannot interpolate and shift the reconstructed signal anymore, because at time $t$ the measurement at time $t+T_d$ is not yet available. The optimal process analyzer reconstructs the process signal \textit{real-time} and minimizes the distortion of the true process signal.

1.4 Real-time Signal Reconstruction - The problems of real-time signal reconstruction are visualized in Figure 1.3, where an off-line XSEC is used to measure the conversion. XSEC is an analytical technique based on Size Exclusion Chromatography where conversion ($X$) of a product is determined from the polymer and monomer peak areas in the exclusion chromatogram. Realistic values for this measurement are $T_i=T_0=0$, $T_d=T_f=20$ minutes with a precision of 0.17\% conversion [8].

![Figure 1.3 Real-time signal reconstructions of the degree of conversion: at-line XSEC.](image)

Suppose that a sample is taken at time $t$ minutes. Again, in practice the gray line (real process variation) is not known, but for the sake of argument the line is drawn in the figure. The analysis result of this sample becomes available at time $t+20$ minutes and has the value $A$, indicated by
a gray dot at time point \( t \). This value \( A \) is not exactly the process value at
time \( t \) because of the limited precision of the XSEC measurement. At time
point \( t+20 \) minutes another sample is taken from which the result
becomes available at \( t+40 \) minutes. The best guess for the process value
in-between time points \( t+20 \) and \( t+40 \) minutes is the measured value \( A \). 
This is indicated in the figure by the black bar in-between time points 
\( t+20 \) and \( t+40 \) minutes. In this way a real-time reconstruction of the
process values can be obtained and the black line indicates this.
Clearly, the reconstruction of the signal in real-time analysis is poorer
than a post-analysis reconstruction. This is the price we pay for
monitoring in real-time. To compare the quality of signal reconstructions
using different process analyzers, we need to have a measure of such a
quality.

1.5 Quality of Signal Reconstruction - We can express the quality of
signal reconstruction in a simple number, the measurability. Suppose we
know the true process value \( x_{\text{true}}(n) \) at time point \( n \) (in reality this true
value is never known, but conceptually \( x_{\text{true}}(n) \) exists). Then the variation
in \( x_{\text{true}}(n) \) can be expressed as a variance \( \sigma_{\text{true}}^2 \) around its target value \( \mu \),
which is the nominal operating point of the process. When the
measurements are performed at time points \( n=1,\ldots,N \), this variance \( \sigma_{\text{true}}^2 \)
can be calculated as:

\[
\sigma_{\text{true}}^2 = \frac{1}{N} \sum_{n=1}^{N} [x_{\text{true}}(n) - \mu]^2
\]  

(1.1)

where \( x_{\text{true}}(n) \) is the true process value (conversion in our example) at
time point \( n \). If the reconstructed signal value at a time point \( n \) is written
as \( x_{\text{rec}}(n) \), then the reconstruction error is \( x_{\text{true}}(n) - x_{\text{rec}}(n) \). The average
squared error over time interval \( N \) is thus:

\[
\sigma_{\text{error}}^2 = \frac{1}{N} \sum_{n=1}^{N} [x_{\text{true}}(n) - x_{\text{rec}}(n)]^2
\]  

(1.2)
and we want to minimize this $\sigma_{error}^2$. In theoretical studies, integrals are used to calculate $\sigma_{error}^2$ and $\sigma_{true}^2$ instead of summations, but the principle remains the same. It is easier to work with relative errors because $\sigma_{error}^2$ as such is a meaningless number. Hence, we define $M$ as

$$M = \frac{\sigma_{true}^2 - \sigma_{error}^2}{\sigma_{true}^2}$$ (1.3)

and this value $M$, called measurability factor, is always smaller than one. A value of one means that $\sigma_{error}^2 = 0$ and we are perfectly able to monitor the process signal. This will never happen in practice. A low value of $M$ means that $\sigma_{error}^2$ is relatively high and the measurements do not add much to the knowledge of the variation in the process variable. A value in-between 0.5 and 1 is considered acceptable [3].

1.6 Measurability of Conversion in the Example - Now we can apply the simple concept of measurability to determine objectively the performance of different process analyzers. In all cases the process analyzers are used to measure conversion in our polymerization example. The at-line XSEC, at-line NIR and on-line SW-NIR perform measurements at the outlet of the reactor, whereas the in-line SW-NIR performs its measurements somewhere along the reactor tube. The specifications and measurability factors of the different process analyzers are given in Table 1.1.

<table>
<thead>
<tr>
<th>Process Analyzer</th>
<th>$T_r = T_d$</th>
<th>$\sigma_i$</th>
<th>$M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>At-line XSEC$^*$</td>
<td>20 min</td>
<td>0.17%</td>
<td>$M_{XSEC} = 0.44$</td>
</tr>
<tr>
<td>At-line NIR</td>
<td>10 min</td>
<td>0.45%</td>
<td>$M_{NIR} = 0.72$</td>
</tr>
<tr>
<td>On-line SW-NIR</td>
<td>30 sec</td>
<td>0.63%</td>
<td>$M_{O-SWN} = 0.95$</td>
</tr>
<tr>
<td>In-line SW-NIR</td>
<td>30 sec</td>
<td>0.63%</td>
<td>$M_{I-SWN} = 0.98$</td>
</tr>
</tbody>
</table>

* All process analyzers are assumed to work with $T_i = T_d = 0$ and $T_r = T_d$ for simplicity.

- 7 -
From an instrumental performance point of view the four process analyzers in our example differ only in analysis time $T_d$ and precision $\sigma_i$. The XSEC - despite its high precision - is clearly to slow to monitor the degree of conversion of the present reaction in real-time (samples indicated by gray markers in Figure 1.3). The result is a poor signal reconstruction (black line). The measurability factor ($M_{XSEC} = 0.44$) is too low for practical purposes and the main reason is that the analysis time ($T_d$) and (thus) the sampling rate ($T_g$) are too long, causing serious delays in reconstruction.

![Figure 1.4 Real-time signal reconstructions of the degree of conversion: at-line NIR.](image)

At-line NIR gives a considerable improvement compared to the at-line XSEC. Figure 1.4 shows that the at-line NIR is faster than the at-line XSEC, but the precision of the at-line NIR is worse. This results in a measurability of 0.72 ($M_{NIR} = 0.72$). The on-line SW-NIR gives a much reduced analysis time without compromising too much on precision ($M_{SWN} = 0.95$).
The in-line SW-NIR process analyzer is positioned near the end of the reactor tube, which turns out to be the optimal location. The measurement results of the SW-NIR at this position are used to predict the degree of conversion in the reactor product (Figure 1.5). This prediction is made with the use of a process model. Calculating the optimal location and predicting conversion at the end of the reactor will be explained later. In-line SW-NIR performs slightly better than on-line SW-NIR, although the differences are small ($M_{1\text{-SWN}}=0.98$).

Eq. 1.3 uses the true process variation and reconstructed signal. In practice, we do not know this true process variation and have to calculate the $M$ value in a different way.

1.7 Calculating Measurability in the Design Phase - Fortunately, for calculating the measurability index we do not need to know the true process variation nor do we need to perform the actual measurements. All we need to have is a process model and knowledge about the behavior of realistic disturbances. Using this it is possible to calculate theoretical measurabilities. This is based an advanced method of error propagation.

Suppose that for a two-step analytical method it is known that step one has a precision of $\sigma_1^2$ and step two has a precision of $\sigma_2^2$. Then error propagation shows that the total analysis has a precision of $\sigma_1^2 + \sigma_2^2$. 

Figure 1.5 Real-time signal reconstructions of the degree of conversion: in-line SW-NIR.
assuming that the two steps are independent. This assessment can be made without actually performing the experiments. The only requirements are that i) we have to know the individual contributions ($\sigma_1^2$ and $\sigma_2^2$) and ii) we have to know a model ($\sigma_{\text{m}}^2 = \sigma_1^2 + \sigma_2^2$). Theoretical measurabilities are calculated by error propagation using a process model. The process model is based on the reaction mechanism shown in Box 1.1. The kinetics of these reactions are known and, hence, the whole polymerization process can be summarized as mass balances in the form of differential equations related to these reactions.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.6.png}
\caption{Figure 1.6 Illustration of the way that fluctuations in initiator (feed) cause variation in monomer concentrations and degree of conversion.}
\end{figure}

We want to monitor conversion at the outlet of the reactor. The disturbance in our example is uncertainty in the initiator concentration in the reactor feed. This external process uncertainty can be represented with variance $\sigma_{\text{AIBN}}^2$. We can propagate the variance of the initiator concentration through the reactor, as shown in Figure 1.6. Fluctuations in initiator concentration travel through the reactor as fluctuations in the monomer concentrations (governed by the reaction kinetics) and result in fluctuations in the monomer concentration and, hence, the conversion $X$ at the end of the reactor. Assuming a certain $\sigma_{\text{AIBN}}^2$, the expected fluctuation of $X$ can be calculated, which results in $\sigma_{X,\text{true}}^2$. This $\sigma_{X,\text{true}}^2$ is the
variation we can expect to be present at the outlet of the reactor. It is this variation that we want to monitor with our instrument(s).

Similar to the situation for process uncertainty $\sigma_{\text{ABN}}^2$, we can compute an expected performance of the process analyzer in measuring the conversion at the outlet by adding equations for the analyzer to the process model. Using appropriate values for the five instrument specifications $T_i$, $T_g$, $T_f$, $T_d$ and $\sigma_i$ (see Figure 1.2 and Table 1.1), a theoretical performance of the process analyzer can be determined. It is the task of process analytical chemists and instrument vendors to supply realistic values of such specifications (e.g. a $\sigma_i = RMSEP$ of 0.63% for the SW-NIR). Thus, we have i) the individual contributions $T_i$, $T_g$, $T_f$, $T_d$, $\sigma_i$ and ii) a model relating these contributions to the error of estimating the conversion. Next, we can perform error propagation to obtain the expected variance $\sigma_{X,\text{error}}^2$ of the estimation error of the conversion. The theoretical measurability is now:

$$M_{\text{theor}} = \frac{\sigma_{X,\text{true}}^2 - \sigma_{X,\text{error}}^2}{\sigma_{X,\text{true}}^2}$$

(1.4)

which is a similar definition as 1.3.

Figure 1.7 shows the theoretical measurability factors of equation 1.4 for in-line SW-NIR at different locations in the reactor tube ($\sigma_{\text{ABN}}^2 = 0.1 \times 10^{-3}$ mol$^2$L$^{-2}$). The theoretical process analyzer characteristics are those for the in-line SW-NIR instrument: $T_i = T_g$, $T_f = T_d = 30$ sec and $\sigma_i = 0.63\%$.

Performing the in-line SW-NIR measurement close to the reactor entrance would reduce the time needed to observe the process disturbances (because these initiator disturbances enter at the inlet), but the change in monomer concentration due to the disturbance in the initiator concentration is not very strong at the inlet. Performing the SW-NIR measurement at the reactor exit would result in a much larger signal (the disturbance has traveled through the system and the change in monomer concentration is attenuated), but then the disturbance is detected late. From Figure 1.7 we learn that in-line SW-NIR measurements in the first
part of the reactor tube yield insufficient information to predict the conversion. In-line SW-NIR in the second half of the reactor tube is much better suited for estimating the conversion in the reactor product. The best compromise for predicting the conversion at the exit is found close to the exit. For this optimum location, the in-line SW-NIR results of Figure 1.5 were calculated. The theory as explained above was tested with a real reactor. The results are reported elsewhere in this thesis and show a good agreement between the theoretical and practical measurabilities.

**Figure 1.7** The measurability factor for the SW-NIR analyzer as a function of the position along the reactor tube.

### 1.8 Extensions of the method

- The measurability index can be readily extended to include more than one process variable. Suppose that not only the conversion but also the molar mass distribution (e.g. $M_n$ and $M_w$) of the polymer are important. Polymer chain growth has a direct relation with styrene monomer conversion. By estimating the conversion from process analytical measurements we can also infer the $M_n$ and $M_w$ of the polystyrene product using a process model of our reactor system. Again, error propagation can be used, but now resulting in an uncertainty covariance matrix $\sigma_{\text{error}}$ of size 3x3 for conversion, $M_n$ and $M_w$. For the external process disturbances, the variation of the three process variables in the product stream is expressed in a covariance matrix $\Sigma_{\text{true}}$, also of size
3x3. The matrices $\Sigma_{\text{true}}$ and $\Sigma_{\text{error}}$ are natural extensions of $\sigma^2_\epsilon$ and $\sigma^2_{\epsilon,\text{error}}$, respectively. The measurability definition 1.4 can thus be generalized to

$$M_{\text{theor}} = \frac{\text{tr}(\Sigma_{\text{true}}) - \text{tr}(\Sigma_{\text{error}})}{\text{tr}(\Sigma_{\text{true}})} \quad (1.5)$$

where $\text{tr}(\cdot)$ means the trace of a matrix: the sum of its diagonal elements. This trace of $\Sigma_{\text{true}}$ and $\Sigma_{\text{error}}$ comes down to summing all variances of true and estimated conversion, $M_n$ and $M_w$, respectively. It is also possible to extent the approach to accommodate several measurements performed simultaneously, e.g., using an in-line SW-NIR along the reactor and a NIR at the end.

The measurability index constructed can be used to calculate the performance of competing process analyzer configurations already in the design phase of a process. Naturally, it can also be used for an existing process. Hence, the answer to the question posed in the beginning: plant managers can make a selection regarding which process analyzers to use by calculating their measurabilities!

1.9 Problems and Future Outlook - In this introduction we have presented a rudimentary overview of the theory of process analytical chemistry. For calculating the measurability index a fundamental model of the process has to be available. If a fundamental model is available, then this model contains estimated constants (e.g. kinetic constants). Such estimates carry some uncertainty and the consequences of this uncertainty on the calculated measurability have to be established.

The theory as presented in this thesis works for continuous processes. An extension of the theory of process analytical chemistry for batch processes is also pursued.

If the fundamental model is incomplete, then experiments can be run and so-called gray models can be built. These are hybrid models containing fundamental and empirical parts. The use of such models for calculating measurability indexes is still under investigation.
1.10 Thesis Summary - This thesis deals with optimal process analyzer selection and positioning for plant-wide monitoring. This part of the text – chapter 1 – gives a more popular overview, while the remaining parts go into detail on different aspects of the subject. The first choice a process analytical chemist (with the help of chemical engineers) has to make is: which of the often-large number of process variables are we going to measure? What constituent, at what position in the system should be sampled to attain the maximum amount of information on the process state in 'real time'? The answer to this question is found in the science of process dynamics, the subject of chapter 2. In this chapter simulations are used to define a number of deterministic selection criteria for optimal sensor selection and positioning. Besides the dynamics of a process, external disturbances and measurement characteristics are important in analyzer selection and positioning. In chapter 3 simulations are used to define a so-called stochastic selection criterion: the measurability factor. With this factor different instruments, at different positions, can be compared at a quantitative level. In defining the measurability factor the so-called process analyzer dynamics – formulating an abstract definition of sampling and analysis equipment – are introduced based on five criteria: precision, sampling frequency, sampling time, response correlation and delay time.

To verify the theory on process analyzer selection and positioning a lab-scale tubular reactor for bulk polymerization of styrene to polystyrene was constructed. On-line and in-line spectroscopic methods can be compared in the setup. The results of these experiments – presented in chapter 4 – confirm the link between theory and (laboratory) experiments. The last part of this thesis – chapter 5 – deals with styrene batch processes. In these systems the question changes: at which point on the batch trajectory should we perform a measurement to get the best estimate of the process state. In this chapter it is shown how the measurability factor can be used to answer this question. The chapter also gives some practical implications on the use of state observers for batch processes, using data from lab-scale experiments.