Optimal process analyzer selection and positioning for plant-wide monitoring

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Citation for published version (APA):
3. Selection and Positioning: Stochastic Grounds

Process analyzer location and performance assessment for optimal process monitoring in a tubular reactor

Abstract – The influence of process analyzer location and performance on plant-wide process monitoring is investigated. Process analyzer performance is evaluated using five uncertainty contributions to the estimation error: measurement error/uncertainty, analysis frequency, sample size/grab error, analyzer memory effect/response correlation and delay time. Both the choice of location and the performance characteristics of different process analyzers can be evaluated using a measurability factor $M$, ranging from zero to one, where one indicates perfect monitoring capabilities. Due to the unifying nature of the measurability factor, this factor can be used to make a rational decision between very different process analyzers. This allows for finding optimal process analyzer configurations for existing processes or for processes in the design phase. We use a tubular reactor simulation model for the partial oxidation of benzene to maleic anhydride to demonstrate the use of the measurability factor.
3.1 Introduction - An ever-increasing number of process analyzers is implemented in chemical industry. At the same time the diversity in techniques suitable for harsh process conditions – e.g. Chromatography, (Near)Infrared-, Raman- or (low field) nuclear magnetic resonance spectroscopy, mass spectrometry, flow injection analysis, ultrasonic analysis, to name just a few - grows steadily [34]. The implementation and operation of analytical in-process\(^1\) measurements is, however, still relatively expensive. The cost of purchase and maintenance often limits the number of analyzers that can be implemented for monitoring and/or control purposes. This naturally leads to the following three questions: what is the best location to place the limited amount of analytical instruments available, what is the best choice among the wide selection of process analyzers to monitor the process under observation and what is the added value of process analyzers as compared to more conventional, interferential measuring devices like temperature-, pressure-, flow-sensors?

In order to assess the performance of a process analyzer we identify five contributions to characterize the process analyzer, the *analyzer dynamics*. The first contribution is the uncertainty or error encountered in every real world measurement. The second contribution is the analysis frequency of the instrument, which determines the signal reconstruction capabilities. The third contribution is the uncertainty build-up introduced by collection a sample of sufficient size, the so-called grab error. The fourth contribution is memory effect or correlation between successive measurements. This phenomenon is often observed in ‘physical’ measurements like ion-selective electrodes, pH or conductivity, where responses are correlated over time. The fifth contribution is the delay time: the time passed between taking a sample and retrieving the analysis result. Separation based composition analyzers, e.g. require some time to analyze the sample before the result becomes available. These five contributions are used to characterize a process analyzer; describing the way an in-process measurement observes process variables.

\(^1\) The expression ‘in-process’ is an idiom for all off-line, at-line, on-line, in-line and non-invasive measurement techniques suited for ‘real-time’ monitoring and/or controlling of a process.
and presents them to e.g. the controllers. Additional instrumental characteristics could be considered, but the five mentioned above form a good representation of most analyzers.

In this chapter we model non-ideal measurements for estimating the entire state of a fixed bed tubular reactor simulation model for the catalytic partial oxidation of benzene to maleic anhydride. The state of this system is formed by the concentration and temperature profiles over the reactor tube. These state elements have to be determined from measuring one of the variables at one particular position. The optimal analyzer type and position are selected by minimizing the theoretical state estimation error in a Kalman filter. Using state estimation error as a criterion for optimization requires knowledge of the uncertainty in both the system and measurements. Many authors discussed the optimal sensor location problem using this same optimization criterion [24]-[32]. These authors however all work with relative simple sensors (typically temperatures), at the most dealing with measurement uncertainty and sample frequency in the optimization.

For process analyzers this is insufficient. The time delay introduced when performing an accurate Gas Chromatographic concentration measurement, e.g. might be competing with a fast but less accurate spectroscopic determination. These measurement - accuracy, sample frequency, delay time, etc. - characteristics must be incorporated to fairly assess the performance of different in-process applications. We do this by incorporating all dynamics (both plant and analyzer) in one system model, creating a so-called standard plant [36]. We explicitly model uncertainty caused by stochastic process disturbances and analyzer characteristics, showing their impact on optimal measurement type and location from a set of realizable configurations\(^2\). An alternative can be found in a deterministic analyzer selection criterion (focusing on the system dynamics, not using the stochastic process uncertainty) of optimal analyzer location based on the idea of degree of observability from system theory [5], [Chap. 1].

\(^2\) If we use the word the 'optimal' in this chapter we mean the best choice from the set of all possible process analyzers. The true 'optimal analyzer' would be infinitely fast and infinitely precise which are impossible specifications for practical and real measurements.
In the 1960’s P.M.E.M. van der Grinten developed ideas to quantify the performance of measurements and control actions by approximate first order dynamics and uncertainties [3], [37]. A short explanation of the theory developed by van der Grinten is given in Appendix 3.A. He introduced two scalar values called ‘meetbaarheidsfactor’ (measurability factor) and ‘regelbaarheidsfactor’ (controllability factor) that quantify how well a signal can be measured and how well a disturbance can be suppressed. The ideas only found limited application outside of the Dutch engineering community, possibly due to the language barrier ([38]; p.445). Only a few sources on this theory in the English language are available [3], [4], [39], [40].

The original theory of van der Grinten focuses on univariate, (simplified) first order descriptions of a process and a measurement and a fixed location. In this chapter we extend the five key ideas on measurement uncertainty and dynamics of van der Grinten to state estimation problems and define a measurability factor $M$ for the multivariate case, that is for the whole system. Moreover, we also consider the location of the analyzer in the optimization of the system’s measurability.

Process analyzer location and performance assessment as presented in this chapter can be seen as related to other research areas such as sensor failure and data reconciliation (see e.g. [41]). In this chapter we will however not address these important issues. Although an ever-increasing number of in-process analytical measurements is being installed, the implementation cost involved still not allows them to be treated like more regular sensors. In nearly all situations analyzers are used for key-information on process variables, and information ‘redundancy’ from these measurements is not really an issue yet. This justifies our focus on the specific instrument characteristics for process analyzers selection and positioning.

The remainder of the chapter is organized as follows. In the next section we develop the theory on different sources of analyzer dynamics and show their implementation in the Kalman filter. The third section contains a short description of the reactor simulation model used as an example. In the fourth section we present the result for the optimal process analyzer configuration problem (both instrument characteristics and location) for
the tubular reactor, and the last section is used to formulate conclusion based on the results.

3.2 Theory - Process model - In this chapter we model non-ideal measurements of a dynamic process and subsequently estimate the entire state of this system. The position of an analyzer for process monitoring or control in this chapter is shown in Figure 3.1. The process is influenced by a deterministic input (possibly modified by a regulator) and stochastic disturbances. This results in a certain process output. The analyzer measures one of the variables in the process and together with a filter tries to find the best estimate of the present state of the process. The estimated value is then used to adjust the regulator to achieve a desired process output.

![Figure 3.1](image)
The position of the analyzers in process monitoring and control.

The system and measurement dynamics and uncertainties can be captured in the well-known linear, time invariant state space format as follows [32], [33], [42]

\[
\dot{x}(t) = A_x x(t) + b_1 u(t) + b_2 w(t) \\
y(t) = c^T x(t) + v(t)
\]

(3.1a) \hspace{2cm} (3.1b)
Where \( x(t) \) (n x 1) is the state of the system at time \( t \), \( A_c \) (n x n) is the continuous time system matrix, \( b_i \) (n x 1) are input distribution vectors, \( u(t) \) is the deterministic input, and \( w(t) \) is the stochastic disturbance with distribution \( N(0,q(t)) \), where \( q(t) \) is the spectral density of \( w(t) \), \( y(t) \) is the measurement result, \( c \) (n x 1) is the output coupling vector, and \( v(t) \) is the stochastic measurement disturbance with distribution \( N(0,r(t)) \), where \( r(t) \) is the spectral density of \( v(t) \). For notational convenience we will only treat the theory for single channel inputs and measurements (SISO), the extension to the multiple inputs/outputs (MIMO) is however straightforward.

The discrete time solution for Eq. 3.1a - under zero order hold assumption for the inputs - is \( t = k\Delta t; \ t + \Delta t = (k+1)\Delta t \)

\[
x_{k+1} = e^{A_c \Delta t} x_k + \int_{t}^{t+\Delta t} e^{A_c (\tau + \Delta t - t)} d\tau b_1 u_k + \int_{t}^{t+\Delta t} e^{A_c (\tau + \Delta t - t)} d\tau b_2 w_k = A x_k + B b_1 u_k + B b_2 w_k
\]

(3.2a)

where integral \( B \) (n x n) is implicitly defined and \( w_k \) is the variance corresponding to the spectral density \( w(t) \) [32], [33], [42]. We further assume that measurements \( y_k \) are discrete observations (with sampling time \( \Delta t \)) from a system through the following equation

\[
y_k = c^T x_k + v_k
\]

(3.2b)

where \( v_k \) is the stochastic measurement disturbance with distribution \( N(0,r_k) \) and discrete time measurement variance \( r_k \).

In this chapter we adopt the concept of the standard plant [36]. The idea of this concept is to incorporate all dynamics (both plant and analyzer) in one system matrix \( A_c \) in Eq. 3.1. Augmenting the original plant system matrix with the dynamics representing the behavior of the analyzers creates the standard plant. The augmented states transform the true process variable selected for measurement to a new, modified variable
filtered by the process analyzer dynamics. This ‘virtual’ variable gives the signal retrieved from the analyzer. This procedure has the advantage that all dynamics present in system Eq. 3.1 (plant, measurement and possibly control) are captured in one model, merging all operations in one system matrix \( A_c \).

**Figure 3.2** Sampling of one process variable in the process. The sample is ‘processed’ by the analyzer, and the result is used to estimate the entire system state \( x(t) \) via a filter. The goal of the in-process measurement is to minimize the estimation error \( e(t) \) over all time \( t \).

**Process analyzer model** - Figure 3.2 zooms in on the process analyzer in a monitoring or control design. One of the state variables in the process is selected for measurement. This variable can e.g. be a concentration of one of the components. The variable under observation is in Figure 3.2 symbolized by element \( x^s(t) \) (x-signal or sampled variable) from the state vector \( x(t) \). The variable \( x^s(t) \) possesses certain dynamic behavior (symbolized by \( T_s \)) and variance/amplitude (\( \sigma_s^2 \)) due to the process disturbances. These dynamics and variances are intrinsic properties of the process. In the remainder of the chapter we focus on the stochastic disturbance input to the process in Eq. 3.1a, assuming that the deterministic input component \( u(t) \) is completely known.

The analyzer ‘processes’ the selected process variable and yields an estimated value on discrete time points as measurement outcome \( y_k \). This estimate is then fed to a filter that has two functions: invert the undesired signal processing by the analyzer, and estimate from this signal the
present state \( \hat{x}_k \) of the system under observation. This leads to an estimation error \( e_k = \hat{x}_k - x_k \), and the objective is to select the measurement and filter that minimize this estimation error. A small example in Appendix 3.B will help to illustrate the theory developed in this chapter [5].

To find the optimal in-process measurement configuration for estimating the state of a process we take six different aspects into consideration. The first one is the selection of the process/state variable and location to be sampled. This selection is guided by the amount of information a variable contains on the dynamics of the process under investigation, the availability of a suitable in-process instrument for monitoring in 'real-time' that variable at that location, and the matching of the process dynamics and analyzer dynamics. The variable selection is achieved by defining the appropriate measurement vector \( c \) in Eq. 3.2b.

The second aspect is measurement uncertainty \( \sigma_k^2 \) (Fig. 3.2), present in all physical and analytical measurements. Uncertainty in the analyzer outcome is approximated by the true quantity \( y_k(t) = c^t \chi_k \) plus additive white noise \( v_k \) with known distribution, typically determined during the calibration procedure or supplied by the instrument vendor

\[
\hat{y}_k = y_k + v_k \quad v_k \sim N(0, \sigma_k^2)
\]  

which is similar in form as the system measurement Eq. 3.2b.

The second source of error is the sampling frequency of the instrument, the error introduced by making discrete observations on the continuous time process with continuous time disturbances. This analyzer characteristic is symbolized by the time interval between successive sample \( T_f \) (where the sample frequency is \( 1/T_f \), Fig. 3.2), and its impact on signal reconstruction is again illustrated in Figure 3.3. We assume equidistant samples where the basis for switching from continuous time in Eq. 3.1 to discrete time in Eq. 3.2 is the period \( \Delta t \) between two successive
measurements. This parameter thus determines the time-period over which stochastic disturbance $w(t)$ in Eq. 3.1 is free to alter the system state before a new observation is done. The uncertainty about the state can only be reduced when this new measurement becomes available and a new state estimate is made.

For many instruments (e.g. spectrophotometers) there is a trade-off possible between the sample frequency and the measurement uncertainty in Eq. 3.2. If more time is taken per analysis, thereby increasing the signal-to-noise ratio, the measurement error can be reduced, at the cost of less frequent measurement outcomes.

*Figure 3.3* The effect of different process analyzer dynamics contributions on the observation of a variable for the outer world: $T_f$ sampling frequency, $T_g$ grab or sample, $T_i$ sensor response correlation and $T_r$ response delay. Markers indicate measurement points, (. .) is the true signal and (-) is the sensor response.

The fourth phenomenon is introduced by sample size or grab size. This component to the analyzer dynamics is named $T_g$ (Fig. 3.2). As an example one can think of a spectrophotometer averaging several spectra in a certain period of time to reduce the noise contribution in Eq. 3.2b. The mean spectrum with better signal-to-noise ratio can then e.g. be used to compute a concentration.

The expected value of a measurement taken over a short period of time is the average value over that time period. This expected value becomes available once the entire sample period has passed. Under the assumption that sampling or grab time is short compared to the dominant time
constants of the system we associate the measurement response with the mean time on this sampling time interval. Therefore we penalize the integration or sample time with a time delay of $T_g/2$ seconds. The effect of sample time or grab-size on signal reconstruction is illustrated in Figure 3.3. It is impossible to represent pure delays in the state space time domain notation in Eq. 3.1. A good approximation of pure delay for the problems presented in this chapter turns out to be a third order Padé approximation, shown here in the Laplace domain notation [38]

$$
\hat{y}(s) = e^{-\frac{T_g}{2}} y(s) + v(s) = \frac{-s^3 + \frac{24}{T_g^2}s^2 - \frac{120}{T_g^3}s + \frac{240}{T_g^4}}{s^3 + \frac{24}{T_g^2}s^2 + \frac{120}{T_g^3}s + \frac{240}{T_g^4}} y(s) + v(s) \quad (3.4)
$$

The concrete implementation of time delay in the state space time domain for the standard plant concept is illustrated by the example in Appendix 3.B.

The fifth component in process analyzer performance is the correlation between successive measurements. In many instruments there is significant carry over in the detector/signal response from one measurement to the next (e.g. pH Ion Selective Electrodes or Temperature Dependant Resistors), and this 'memory effect' can be modeled explicitly. In this chapter we assume exponentially first order correlation of the auto regressive form

$$
\hat{y}_{k+1} = e^{-\frac{T_c}{T_i}} \hat{y}_k + \sqrt{1 - e^{-\frac{T_c}{T_i}}} v_k \quad v_k \sim N(0, \sigma_y^2) \quad (3.5)
$$

where $T_i$ is the correlation time between successive measurements (Fig. 3.2) and the uncertainty $v_k$ is scaled to have equal magnitude as the uncertainty contribution in Eq. 3.3. The effect of sensor response correlation on signal reconstruction is illustrated in Figure 3.3. As can be seen it is effectively a convolution between the instrument dynamics and
the true underlying variable. The practical implementation is again shown in the example in Appendix 3.B.

The last component describing the performance of an in-process instrument is the delay time between sampling and the release of the result ($T_d$ in Fig. 3.2). A frequently encountered example of an analyzer with a significant time delay is a gas chromatograph for concentration measurements, where the different components in a sample first have to be physically separated before the analysis results can be determined. We again use a Padé approximation - similar to the one for sample size in Eq. 3.4 - to approach pure time delay

$$\hat{y}(s) = e^{-Ts} y(s) + v(s) = \frac{-s^3 + 12}{T_d^3} + \frac{60}{T_d^2} + \frac{120}{T_d} y(s) + v(s)$$

To stress the importance of the dynamics of in-process analyzers Figure 3.4 shows the 'time-profile' of a measurement. Only after a period equal to the delay time $T_d$ plus half the sample period $T_g$ the results become available, while the sample frequency $T_f$ determines how often a measurement outcome is retrieved. Optimal selection of instrument type and location must guarantee that sufficient information is left in the measurements to make a good 'real-time' estimate of the state of the system.

**Figure 3.4** Time schedule for an in-process measurement. ($\leftrightarrow$) indicate the different time spans, (..) designate the time point a measurement result is connected with.
State estimation with a Kalman filter - The filter used for state estimation of the standard plant model – as depicted in Figure 3.1 and 3.2 - in this chapter is the well-known Kalman filter [32], [33], [42]. It consists of two parts:

i) the state estimation time update (known as a priori estimate \( \hat{x}_k^- \)) between two successive measurements \( k \) and \( k+1 \), separated \( \Delta t \) seconds

\[
\begin{align*}
\hat{x}_{k+1}^- &= A\hat{x}_k^- + Bb_ku_k \\
P_{k+1}^+ &= AP_k^-A' + Q_k
\end{align*}
\]

(3.7a)

(3.7b)

ii) the state estimate measurement update/correction (known as a posteriori estimate \( \hat{x}_k^+ \)) using the measurement result at point \( k+1 \)

\[
\begin{align*}
k_{k+1} &= P_{k+1}^-c(c'P_{k+1}^-c + r_k)^{-1} \\
\hat{x}_{k+1}^+ &= \hat{x}_{k+1}^- + k_{k+1}(y_{k+1} - c'\hat{x}_{k+1}^-) \\
P_{k+1}^+ &= (I - k_{k+1}c)c'P_{k+1}^-
\end{align*}
\]

(3.8a)

(3.8b)

(3.8c)

where \( k_{k+1} \) is the Kalman filter gain, \( P_{k+1}^+ \) is the theoretical a posteriori estimation error covariance matrix, and \( Q_k \) is the positive semi-definite uncertainty distribution covariance matrix

\[
Q_k = \int_0^{\Delta t} e^{A\tau}(\tau+\Delta t-t)b_2 q(\tau)b_2' e^{A\tau}(\tau+\Delta t-t) d\tau
\]

(3.9)

The matrix \( Q_k \) represents the contribution of the system disturbance \( w(t) \) in Eq. 3.1 on the overall state estimation error in Eq. 3.7. Uncertainty \( w(t) \) - with a spectral density of \( q(t) \) - is 'injected' in the process with a system matrix \( A_c \). Uncertainty in Eq. 3.2a continuously builds up over the time period \( t \) to \( t+\Delta t \), the time between two discrete measurements in Eq. 3.2b. At these discrete measurement time-points all uncertainty can – for the hypothetical case of perfect measurements - be removed, but not before these points.
The Kalman filter as presented in Equations 3.7 and 3.8 is an unbiased, minimum variance and consistent estimator for the linear (or linearized) system in Eq. 3.1. If the system is observable and controllable, and if $Q_k$, $r_k$ and $A$ are bounded, the filter is asymptotically stable, meaning that all the eigenvalues of the matrix $A-k_c c'$ fall within the unit circle.

Notice that in the approach taken in this chapter the role of $Q_k$ - the constant term in the difference equation for the theoretical estimation error $P_k$ in Eq. 3.7b - is somewhat different than the one encountered in many other studies [2], [24], [26], [28]-[30], [35], [Chap. 4]. Here, we give $Q_k$ the role of describing the uncertainty propagation in the system for a period $\Delta t$ between two measurements, since this is of importance for the optimal process analyzer location problem addressed in this research. Known uncertainties for the system parameters in $A$ can also be accounted for by placing the appropriate values in the system uncertainty covariance matrix $Q_k$. In many applications this is done by (post-run) analysis, 'tuning' the diagonal elements in $Q_k$ to create a better fit between some reference values and the Kalman-predictions. In this chapter however we give guidelines for analyzer type and location selection in an early design stage of a process, which obviously excludes the use of post-run information. Known uncertainty in the system parameters can however be included in the system error matrix $Q_k$ if available.

Instrument selection and location are optimized by minimizing a sensible norm of the expected estimation error $P_k$ given by the algorithm in Equations 3.7 and 3.8. For linear time invariant systems this theoretical estimation error can be calculated $a$ priori by implementing Equations 3.7b, 3.8a and 3.8c. This means that the optimal analyzer type and location can be determined without any form of process simulations.

**Measurability factor** - From Eq. 3.9 we notice that - for a stable system matrix $A_k$ - there is an upper bound on the system uncertainty covariance matrix by $Q_k$ for $\Delta t \to \infty$ (the covariance matrix of uncertainty propagation through the system). This value for $Q_k$ corresponds with the maximum uncertainty in knowledge about the state of the process, corresponding to
the situation where no measurements what so ever are performed. When a analyzer/filter-combination is used to do an estimate, some of the uncertainty about the process state will be removed. The remaining uncertainty contribution after a measurement update is represented by the estimation error covariance matrix $P_k$ in Eq. 3.8c. The performance of a analyzer/filter pair can be judge by the size of this uncertainty residual.

Using this upper bound we can define a performance index for a particular in-process measurement configuration (Appendix 3.A)

$$M^2 = \frac{\text{trace}(Q_k) - \text{trace}(P_k)}{\text{trace}(Q_k)}$$

We will call the square root of this quantity the measurability factor. $M$ can vary between 0 and 1, where 1 means perfect knowledge about the state of the system after a measurement is taken (all uncertainty has been removed by the measurement and state estimate), while 0 indicates that a particular measurement configuration supplies no information about the state of the process\(^3\). The best analyzer type and location is taken as the one maximizing the measurability factor $M$. If the system is unstable there is no upper bound on the error covariance matrix.

The criterion to judge the performance of the analyzer/filter combination is the trace of the estimation error covariance matrix $P_k$ and the system uncertainty $Q_k$. This norm corresponds to the sum of estimation error variances, thereby giving variances for all variables equal weight.

In this chapter we will estimate all process variables from one measurement, and place equal weight on all errors through the trace criterion in Eq. 3.10. If installing more analyzers is feasible or if appropriate information is available alternative (weighted) selection criteria can be introduced placing heavier penalties on mismatch for certain process variables. There is no problem in introducing these alternative criteria in the proposed procedure of optimal instrument selection and positioning.

\(^3\) For an extremely poor choice of analyzer the trace of $P_k$ could theoretically exceed the trace of $Q_k$, giving a negative result for Eq. 3.10 and a negative value for the measurability factor $M$. 

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3.3 Tubular Reactor Model - The theory on analyzer selection developed in this chapter is illustrated with a simulation model of a fixed bed tubular reactor for the production of maleic anhydride by partial oxidation of benzene [5], [18], [19], [Chap. 2].

Three exothermic, irreversible gas phase reactions take place on a solid V₂O₅-MoO₃-P₂O₅ catalyst particles packed in a one-inch diameter tube:

\[ \text{C}_6\text{H}_6 + 4 \text{O}_2 \rightarrow \text{C}_4\text{H}_2\text{O}_3 + \text{CO} + \text{CO}_2 + 2 \text{H}_2\text{O} \quad (3.11a) \]
\[ \text{C}_6\text{H}_6 + 6 \text{O}_2 \rightarrow 3 \text{CO} + 3 \text{CO}_2 + 3 \text{H}_2\text{O} \quad (3.11b) \]
\[ \text{C}_4\text{H}_2\text{O}_3 + 2 \text{O}_2 \rightarrow 2 \text{CO} + 2 \text{CO}_2 + \text{H}_2\text{O} \quad (3.11c) \]

Reaction 3.11a is the desired path for the formation of maleic anhydride – the product – from benzene. Reactions 3.11b and 3.11c represent the undesired burning of reactant and product, respectively. The feed stream to the reactor is air mixed with approximately 0.9%(v/v) benzene. Because of the oxygen excess in the feed all reactions are assumed to be pseudo first order in the limiting reactant.

The two mass balances used in the model are molar flow benzene \( F_B \) (mol.s\(^{-1}\)) and molar flow maleic anhydride \( F_{MA} \) (mol.s\(^{-1}\)) in the fluid phase stream. The partial differential equations are given by Equations 3.12a and 3.12b (\( t \) denotes time; \( z \) indicates axial position in the reactor; \( v \) is linear gas velocity of 2.48m.s\(^{-1}\); \( D_{eff} \) is effective mass diffusion coefficient):

\[ \frac{\partial F_B(t,z)}{\partial t} = -v \frac{\partial F_B(t,z)}{\partial z} + D_{eff} \frac{\partial^2 F_B(t,z)}{\partial z^2} - k_1(t,z)F_B(t,z) - k_2(t,z)F_B(t,z) \quad (3.12a) \]
\[ \frac{\partial F_{MA}(t,z)}{\partial t} = -v \frac{\partial F_{MA}(t,z)}{\partial z} + D_{eff} \frac{\partial^2 F_{MA}(t,z)}{\partial z^2} + k_1(t,z)F_B(t,z) - k_2(t,z)F_{MA}(t,z) \quad (3.12b) \]

Two heat balances are included in the simulation, namely the temperature of the fluid phase \( T_f \) (K) and the temperature of the stagnant solid phase catalyst \( T_s \) (K). The corresponding (partial) differential equations are shown in Equations 3.12c and 3.12d (\( k_{eff} \) is effective heat diffusion...
coefficient; \( U_{f-w} \) is the fluid phase-wall heat transfer coefficient; \( U_{s-f} \) is the solid phase-fluid phase heat transfer coefficient; \( T_w \) is the reactor wall temperature; \( c_s \Delta H_x \) is a reaction enthalpy coefficient.

\[
\frac{\partial T_f(t,z)}{\partial t} = -v \frac{\partial T_f(t,z)}{\partial z} + k_{df} \frac{\partial^2 T_f(t,z)}{\partial z^2} - U_{f-w}(T_f(t,z) - T_w) - U_{s-f}(T_s(t,z) - T_f(t,z))
\]

(3.12c)

\[
\frac{dT_s(t,z)}{dt} = -U_{s-f}(T_s(t,z) - T_f(t,z)) + c_s \Delta H_s k_1(t,z) F_B(t,z) + c_s \Delta H_s k_2(t,z) F_B(t,z) + c_s \Delta H_s k_3(t,z) F_{MA}(t,z)
\]

(3.12d)

Figure 3.5 shows the steady-state concentration and temperature profiles over the reactor tube for three different benzene feeds. The boundary conditions used in the calculations are \( F_B(t,0) = \text{[feed]} \text{ mol.s}^{-1} \), \( F_{MA}(t,0) = 0 \text{ mol.s}^{-1} \) and \( T_f(t,0) = 733 \text{ K} \). Diffusion effects at the entrance and exit are neglected.

**Figure 3.5** a) molar flow benzene  b) molar flow maleic anhydride  c) fluid phase temperature  d) solid phase temperature; benzene feed 0.900 (-), 0.873 (..) and 0.927 %(v/v) (- -).
The non-linear partial differential equation system in Eq. 3.12 is rewritten in a linear, finite dimensional state space reactor model [5]. The first step is to divide the reactor length into \( m \) equidistant segments indicated by \( z_i \), where \( z_0 \) is the reactor entrance. For every grid-point \( z_i \) we define four (partial) differential equations from Eq. 3.12. In the next step, the first and second order differential terms in the partial differential equations on every grid-point are approximated by second order upwind and central difference terms. After this step, the original reactor model is transformed into a set of \( n = 4 \times m \) ordinary differential equations, two mass and two heat balances on all \( m \) grid-point over the reactor length ('Method Of Lines' approximation).

The last step is to linearize all non-linear terms in the reactor model. This is done by a first order Taylor-series approximation.

After these modifications we have transformed the original reactor model into \( n \) linear time invariant ordinary differential equations. They can then be organized in a state space model as shown in Eq. 3.1a. The state vector is organized in an alternating fashion \( \mathbf{x}(t) = [F_b(t,z_1), F_{\text{MA}}(t,z_1), T_i(t,z_1), T_s(t,z_1), F_b(t,z_2), \ldots , T_s(t,z_m)]' \). The band diagonal dynamic coefficients matrix \( \mathbf{A}_c \) has appropriate constants connecting the \( n \) linear differential equations for successive grid points. In our reactor model both the deterministic input \( u(t) \) and the stochastic input \( w(t) \) is benzene concentration in the feed stream. This system for our reactor model is asymptotically stable.

To simulate analyzers in the reactor the system measurement equation 3.1b is used. All the components of the analyzer dynamics are included in the augmented system matrix \( \mathbf{A}_c \) in accordance with the standard plant concept.
3.4 Results - To study the effect of process analyzer uncertainty and dynamics we introduce three kinds of measurements in our reactor simulation model presented in the previous paragraph [43], [44]. The first instrument is a fast but relatively inaccurate spectroscopic measurement of the benzene (B) or maleic anhydride (MA). The second analyzer is a fast gas chromatographic (GC) measurement of benzene or maleic anhydride. For this analyzer accuracy is increased at the cost of introducing delay time necessary to physical separate the different components in instrument. The third measurement is a thermal resistor sensor for the solid or fluid phase temperature in the reactor tube. This is an example of an instrument having significant correlation in the response. The specification of each instrument is specified in Table 3.1.

<table>
<thead>
<tr>
<th>Analyzer</th>
<th>$\sigma_i$</th>
<th>$T_0^*)$</th>
<th>$T_1^*)$</th>
<th>$T_f$</th>
<th>$T_d^*)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Spectrometer</td>
<td></td>
<td></td>
<td></td>
<td>0.05s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B: 0.045%(v/v)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MA: 0.030%(v/v)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) GC</td>
<td></td>
<td></td>
<td></td>
<td>5.00s</td>
<td>5.00s</td>
</tr>
<tr>
<td></td>
<td>B: 0.014%(v/v)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MA: 0.009%(v/v)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) Thermal resistor</td>
<td>1.5 K</td>
<td>3.0s</td>
<td>0.05s</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1

*) '-' means no significant contribution for the overall performance of this type of analyzer.

The disturbance on the system is a ten percent fluctuation of the nominal benzene feed flow of 0.9%(v/v). Using Equations 3.7, 3.8 and 3.9 the theoretical estimation errors for the different instruments are computed. The task of the Kalman filter is to estimate from the measurement outcome all state variables $x(t)$ in the reactor tube in Eq. 3.13. The measurability factors for the three process analysers specified in Table 3.1 placed at different location in the reactor tube are shown in Figure 3.6.
From Figure 3.6 and Table 3.1 we learn that the best performance for monitoring the benzene/maleic anhydride reactor is achieved by analyzer (a) – the fast but less accurate spectroscopic analyzer - measuring maleic anhydride at $z = 0.6-0.7$m. Instrument (a) also gives a good performance for benzene concentration analysis near the entrance, which is close to the source of disturbance for the reactor model, namely fluctuation in the benzene feed. The second observation is that estimation of the reactor state using analyzer (b) performs poor for both benzene and maleic anhydride analysis. The delay time $T_d$ of five seconds for this GC-analysis is simply too long for this process and the measurement thus contains hardly any information for real-time monitoring the system state. The third sensor (c) in the location $z = 0.4-0.7$ - sampling temperature of fluid or solid phase in the reactor tube - is a reasonable alternative for the use reactor state estimation, although not as good as the concentration measurement with analyzer (a).
If we look at Figure 3.6, together with the nominal reactor profiles plotted in Figure 3.5, we can draw some additional conclusions. The first one is that none of the instruments perform well in the last part of the reactor tube. Not much information on the dynamic behavior of the reactor system is available in the last half of the system, as is to be expected. A second observation is that the rather extreme 'hot-spot' plays a crucial role in the location. Temperature measurements are clearly dominated by its location, while the concentrations are indirectly influenced by the 'negative feedback' for the exothermic oxidation of benzene as can be observed in Figure 3.5a. Another observation is that all optimal positions have slightly moved towards the reactor entrance, as compared to deterministic selection criteria for optimal measurement location [5], [Chap. 2]. Two reasons can be identified: the interaction of analyzer and reactor dynamics, and the fact that the only disturbance for this particular example system was selected to be the uncertainty in the benzene feed at the reactor entrance. If alternative disturbances, possibly taking place at different positions in the reactor tube, where to be included in the process model the optimal measurement location might be altered.

3.5 Conclusions - In this chapter we have shown that the dynamic behavior of a process analyzer plays an important role in selection of the optimal in-process measurement type and location. Six contributions that are needed to specify the in-process analyzer performance have been identified: analyzer location, uncertainty $\sigma_i^2$, sample frequency $T_s$, sample/grab size $T_g$, response correlation $T_r$ and delay time $T_d$. Other important components in the success or failure of the process state estimation problem are the dynamics $T_s$ and amplitude $\sigma_i^2$ of the process variable selected for measurement.

In our case study – partial oxidation of benzene to maleic anhydride in a tubular reactor – the best analyzer is a fast spectroscopic measurement of the product and, to a lesser extent, the reactant. Gas chromatographic measurement of neither reactant nor product performed well, due to the relative large delay time associated with this instrument. Temperature measurement of fluid and solid phase also performed well in the 'hot-spot' region of the reactor tube.
The approach as formulated in this chapter – including all process analyzer relevant dynamics in the so called *standard plant*, and using the theoretical estimation error to compute the measurability factor – can serve to optimize new in-process measurement implementations. This optimization for analyzer type and position can be done in an early ('drawing board') stage of the process design cycle. By using analyzer specifications, retrieved e.g. from instrument vendors, analytical chemistry departments or earlier experiences, and a model of the process the theory developed in this chapter makes it possible to determine the feasibility of process state estimation and monitoring/control tasks. The measurability factor $M$ is a convenient scalar number to compare different in-process measurement configurations. The tools formulated in this chapter can be used to investigate the potential of in-process measurements.

3. Appendix - In this Appendix we will give an introduction to the ideas as presented by P.M.E.M van der Grinten on optimization of measurements and control schemes [3], [37]. We have changed some of the notation used in the original work in order to create a closer parallel with the work presented here.

Controlling is intervening in a situation on the basis of measurements [3]. Three possible sources for lack controller performance can be identified in this definition. I) The measurement may be in error due to sensor inaccuracies and sluggishness. II) The intervention may lose its effectiveness through over-determinacy or dynamically unfavorable regulator behavior. III) The static and dynamic characteristics of the system under control are insufficiently known. If a measurement is used for control, the accuracy and speed with which the result becomes available are of equal importance. If time is lost in the measurement, or sampling intervals are long, the systems status may have changed without this appearing in the sensor response. Intervention made on such a basis can never be fully correct.

Three dynamic operations are identified for the measured signal (denoted $w(t)$): the sample time or frequency $T_s$, the averaging or grab-size time
and the delay time $T_d$, needed to condition and process the sample (Fig. 3.4). A measurement error $v(t)$ is superimposed on the result.

In many practical applications a reconstruction filter is used to minimize error $e(t)$ between the sensor outcome and the true value. In evaluating the efficiency of the estimator only variations in the measured quantity $w(t)$ and the measuring error $v(t)$ are considered (systematic errors are not included). The definition 3.A1 is used to determine optimum efficiency

$$m^2 = \frac{\sigma_r^2 - \sigma_w^2}{\sigma_w^2}$$  \hspace{1cm} (3.A1)

where $m$ denotes the measurability factor ('meetbaarheidsfactor'), indicating what part of the signal is actually measured under optimal conditions ($m = 1$ is perfect reconstruction; $m = 0$ means no information at all).

Completely analogous we can define an efficiency factor for the control structure, again focusing on the changes of the variable about their nominal value. Variable $w(t)$ now represents the equivalent disturbance (summed effect of all disturbances on the process) in the point immediately before the measurement location. The goal of stabilizing control is to minimize the resulting error output $e(t)$. The controller efficiency is now derived as

$$r^2 = \frac{\sigma_w^2 - \sigma_r^2}{\sigma_w^2}$$  \hspace{1cm} (3.A2)

where controllability factor ('regelbaarheidsfactor') $r$ indicates the extent to which disturbances can be suppressed. Notice that $r$ can never exceed $m$. This means that besides e.g. sluggishness of the controller itself, the sensor performance can dominate the overall control performance.

Dynamics of stationary signal or time series $w(t)$ can be characterized by their auto-correlation function, which for many physical systems can be approximated by Markov processes.
\[ \varphi_{ww}(\tau) = E[w(t)w(t+\tau)] = \sigma_w^2 e^{-\tau / T_w} \quad \varphi_{ww}(0) = \sigma_w^2 \]  

(3.A3)

Equation 3.A3 can be seen as a prediction curve, characterized by the variance/amplitude \( \sigma_w^2 \) and the correlation time \( T_w \). The latter can be estimated already during the design stage by computing the largest time constant of the expected disturbances.

To achieve good control the overall delay time (sum of sensor and controller delay) must be smaller than the disturbance time constant: \( T_d < T_w \). This is illustrated in Figure 3A.1 for the case of optimal control. A disturbance \( w(t) \) will emerge as output error \( e(t) \) until time equals \( t = T_d \), after which the error is compensated for by the controller. From this observation and Eq. 3.A2 a controllability factor due to delay time is deduced

\[ r_d = e^{-T_d / T_w} \]  

(3.A4a)

For all other contributions to the overall measurement and control uncertainty similar equations can be derived. These are often simplifications of more complicated, statistically more thorough
descriptions. Here we present only the final results. For details on derivations, more complicated auto-correlation functions and process disturbances we refer to van der Grinten [3].

The contribution of sampling frequency is given by

\[ m_f = e^{-T_f/2T_w} \]  

(3.A4b)

The factor \( \frac{1}{2}T_f \) stems from the notion that information at the moment of sampling is complete, but immediately before the next sample the information is obsolete by a time equal to \( T_f \). Similar reasoning leads to an equation for the sample size error

\[ m_k = e^{-T_f/2T_w} \]  

(3.A4c)

Formulas can be derived for the measurement error with sensor error correlation \( T_v \) and the inverse controller response with inversion time \( T_{in} \)

\[ m_n \approx 1 - \frac{\sigma_v}{\sigma_w} \sqrt{\frac{T_v}{T_w}} \]  

(3.A4d)

\[ r_{in} = \frac{1 - T_{in}/T_w}{1 + T_{in}/T_w} \]  

(3.A4e)

The overall controllability factor can now be determined from the different contributions by the following equation

\[ r_{tot} = m_f m_k m_m m_d r_{in} \]  

(3.A4f)

Equation 3.A4f serves two purposes. The value of the overall controllability factor \( r_{tot} \) must be close to 1. As a rule of thumb values larger than 0.8 indicate good measurement/controller couples, while values below 0.5 indicate that control schemes are of little use. Equation 3.A4f gives us a quantity to directly compare various sensor/controller set-ups. The second advantage is that the overall uncertainty can be split.
up in separate contributions that can be optimized individually, with the aim of identifying (and ultimately removing) the bottleneck from a control structure or sensor implementation.

We would like to emphasize again that a more complete (English) treatment on the material as presented in this Appendix can be found in van der Grinten [3].

3.B Appendix - The autonomous system in Eq. 3.B1 serves as an example to study some of the influence of analyzer location and dynamics defined in the main text [5]

\[
\begin{align*}
\dot{x}(t) &= A_x x(t) + b_x w(t) = \\
&= \begin{bmatrix} -1 & 1 & 1.5 \\ 1 & -2 & 1 \\ 0 & 1 & -3 \end{bmatrix} \begin{bmatrix} x_1(t) \\ x_2(t) \\ x_3(t) \end{bmatrix} + \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} w(t) \\
x(0) &= \begin{bmatrix} 1 \\ 1 \\ 0 \end{bmatrix} \\
q(t) &= 0.1
\end{align*}
\]

(3.B1)

As can be seen from Eq. 3.B1 disturbances \( w(t) \) are 'injected' on the first state and are distributed over the other two states through the system dynamics in \( A_x \). The autonomous solution for the system plus the auto-correlation's \( \phi(x_i x_i) \) and cross-correlation's \( \phi(w,x_i) \) for a white noise feed pattern with distribution \( N(0,0.1) \) is shown in Figure 3.B1. The dynamics of state \( x_1(t) \) and \( x_2(t) \) show a clear system delay time for input uncertainty \( w(t) \).
On this system we define three ‘instruments’ with the specifications as shown in Table 3.B1.

![Figure 3B.1](image-url)

<table>
<thead>
<tr>
<th>Analyzer</th>
<th>$\sigma_i^2$</th>
<th>$T_g^*)$</th>
<th>$T_i^*)$</th>
<th>$T_r^*)$</th>
<th>$T_d^*)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_a$</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>0.1s</td>
<td>-</td>
</tr>
<tr>
<td>$B_b$</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>5.0s</td>
<td>5.0s</td>
</tr>
<tr>
<td>$B_c$</td>
<td>0.5</td>
<td>-</td>
<td>2.0s</td>
<td>0.1s</td>
<td>-</td>
</tr>
</tbody>
</table>

*) '-' means no significant contribution on the overall performance of this analyzer.

The specifications of the instruments imply the following characteristic features: $B_a$ is a moderately accurate instrument with a high sampling frequency, $B_b$ is a very accurate analyzer, but suffering from a large delay time (typically equal to the analysis time), and $B_c$ is a representative of many physical measurements with a moderate accuracy and a significant memory effect.

Implementation of $B_a$ is straightforward using the appropriate values in equations as presented in the theory section: sampling time $T_i$ forms the basis for going from the continuous system in Eq. 3.B1 to discrete observation, while $\sigma_i^2$ specifies the uncertainty in the measurement responses.
To implement the time delay of $B_b$, measuring e.g. the first state, the original system $A_c$ has to be augmented with three virtual states $x_4(t)-x_6(t)$ in accordance with Eq. 3.6 creating the standard plant

$$\dot{x}(t) = A_c x(t) + b_2 w(t) = \begin{bmatrix} -1 & 1 & 1.5 & 0 & 0 & 0 \\ 1 & -2 & 1 & 0 & 0 & 0 \\ 0 & 1 & -3 & 0 & 0 & 0 \\ 1 & 0 & 0 & -2.4 & -2.4 & -0.96 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} x_1(t) \\ x_2(t) \\ x_3(t) \\ x_4(t) \\ x_5(t) \\ x_6(t) \end{bmatrix} + \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} w(t)$$

$$y(t) = c' x + v(t) = \begin{bmatrix} -1 & 0 & 0 & 4.8 & 0 & 1.92 \end{bmatrix} x + v(t)$$

(3.82)

In Eq. 3.82 the parameters for the augmented part of the system form a companion canonical state space representation of the Padé approximation for time delay in Eq. 3.6.

To model the signal correlation in $B_c$, sampling e.g. state number two, system $B_1$ has to be augmented by one state $x_4(t)$ in accordance with Eq. 3.5

$$\dot{\tilde{x}}(t) = A_c \tilde{x}(t) + b_2 w(t) = \begin{bmatrix} -1 & 1 & 1.5 & 0 & 0 & 0 \\ 1 & -2 & 1 & 0 & 0 & 0 \\ 0 & 1 & -3 & 0 & 0 & 0 \\ 1 & 0 & 0 & -2.4 & -2.4 & -0.96 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} \tilde{x}_1(t) \\ \tilde{x}_2(t) \\ \tilde{x}_3(t) \\ \tilde{x}_4(t) \end{bmatrix} + \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} w(t)$$

$$y(t) = c' \tilde{x} + \sqrt{1-(e^{-1/T})^2} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \tilde{x}_1(t) \\ \tilde{x}_2(t) \\ \tilde{x}_3(t) \\ \tilde{x}_4(t) \end{bmatrix} + 0.8 v(t)$$

(3.83)

For these three analyzer types the uncertainty propagation from Eq. 3.9 is determined and the expected estimation error $P_k$ is computed from Equations 3.7 and 3.8. The measurability factor Eq. 3.10 for these the three analyzers in Table 3.81 for the system 3.81 are given in Table 3.82
The table shows that measuring the first state is favorable for every instrument [5]. It also shows that the best overall match between system and analyzer dynamics for state estimation is between $B_a$ and the first state. The last conclusion from this example is that if only state $x_3$ is available, $B_c$ is to be preferred.

<table>
<thead>
<tr>
<th>Analyzer</th>
<th>$x_1$</th>
<th>$x_2$</th>
<th>$x_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_a$</td>
<td>0.8</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>$B_b$</td>
<td>0.4</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>$B_c$</td>
<td>0.7</td>
<td>0.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>

*Table 3.B2*