# GRAF™ – AN INNOVATIVE GAS RETRIEVAL ALGORITHM FOR FOURIER TRANSFORM SPECTROSCOPY

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*ABB innovates with **a** new proprietary method to serve the industry of gas analysis and emission monitoring. From its long and successful collaboration to space programs for Earth observation, ABB adapts to industrial needs algorithms developed for atmospheric science and meteorological observations. Our goal: bring value to customers by improving performances, and simplifying modeling, calibration and maintenance processes.*

GRAF™ (Gas Retrieval Algorithm for Fourier transform spectroscopy) is a non-linear least-squares retrieval algorithm specialized for the prediction of gas concentrations from spectra measured by FTIR analyzers. It relies on well-known spectroscopic databases such as HITRAN [1], and gas cross-section databases like PNNL Infrared Spectral Library [2] to model absorbance spectra of gas mixtures. The gas concentrations are then predicted from FTIR measurements by comparison with synthetic spectra simulated from the databases, combined with innovative modeling of fundamental FTIR characteristics such as the Instrument Line Shape (ILS) [3,4].

Using reference databases for modeling provides many advantages:

- develop models faster, reducing the effort required by traditional calibration tools for measuring gas mixtures with concentrations that cover the model range;
- include interferents with minimum laboratory effort;
- minimize handling of hazardous gases;
- increase the transferability of the models by using a collection of spectra that do not contain instrument response, noise or artifacts, reducing the work required for the compensation of interferents (such as water vapor compensation);
- provide specialists with efficient tools to evaluate the feasibility of new applications;
- facilitate the adaptation of existing models to various application constraints, like changes of optical path length, pressure or temperature;
- improve global performance of the models.

Those comprehensive databases can be complemented with new spectral signatures obtained from lab measurement, when required.

GRAF™ consists of a suite of modeling tools: GRAF Modeler™ and GRAF Spec™, with a prediction kernel: GRAF Predictor™. These modeling tools help ABB application scientists computing calibration spectra from the databases and define the parameters of the models such as gas species, spectral bands, concentration ranges, interferent gases, optical path length of the gas cell, instrument characteristics, etc., and to generate calibration files.

## Prediction algorithm

The GRAF Predictor™, whether combined with modeling tools for re-processing measurements or embedded in ABB process analyzers for real time analysis, loads GRAF™ calibration files and GRAF™ models to build synthetic spectra of gas mixtures simulating the output of Fourier transform spectrometers. The predictor kernel fits those spectra to actual measurements in order to

determinate the value of the retrieval parameters (gas concentrations). The retrieval of gas concentrations with medium resolution spectrometers (typically from 0.5 to 4 $cm^{-1}$) requires inverse algorithms able to handle nonlinear variations of the parameters. The nonlinearity of the absorbance at a given wavenumber with respect to the gas concentration and other instrument parameters is moderate for gas applications. It arises mainly from the resolution function of the spectrometer that is significantly larger than the natural line width of gas absorption lines which is typically on the order of 0.1 $cm^{-1}$.

GRAF™ is based on nonlinear Bayesian inverse algorithm commonly used in atmospheric sounding [5] to minimize residuals between calibration spectra and measurements in order to retrieve gas concentrations. The attractiveness of Bayesian inverse methods resides in the underlying theory of probabilities. All parameters, whether measured or estimated, are described by probability distributions that constrict the parameters in a given range. The method provides descriptors for the estimations that can be easily understood, like the mean value that one takes as the actual value of a prediction, and standard deviation that is associated with a confidence interval. The availability of a confidence intervals for predictions is already a significant advantage of the Bayesian approach. But it includes also the cross-correlation of the parameters that describes how dependent estimated parameters are to each other. Furthermore, the probability theory provides simple ways to account for uncertainties like random errors (noise) inherent to measurements, as well as the range of the parameters. The distribution of the parameters in this technique is assumed to be Gaussian, which is convenient for its underlying theory, and representative of physical phenomena such as the noise in Fourier transform spectrometers.

Instrument modeling

In order to achieve transferability of the models and high reproducibility of the predictions over time, minimizing need for recalibration, GRAF™ characterizes the FTIR instrument line shape (ILS) specific to each system and configuration. This important parameter can be defined as the spectral response of an FTIR to a monochromatic source. Apart from the resolution function, the ILS describes the fundamental broadening of the spectral response due the optical components controlling the divergence of the beam modulated by the interferometer. This broadening increases proportionally to the wavenumber of the light source, being more important at high wavenumbers than at low wavenumbers, and cannot be reduced to a simple convolution. Using innovative and efficient algorithms [3,4], each new measurement is normalized in real-time taking into account specific ILS parameters of an analyzer, which is a preferred approach for continuous measurements.

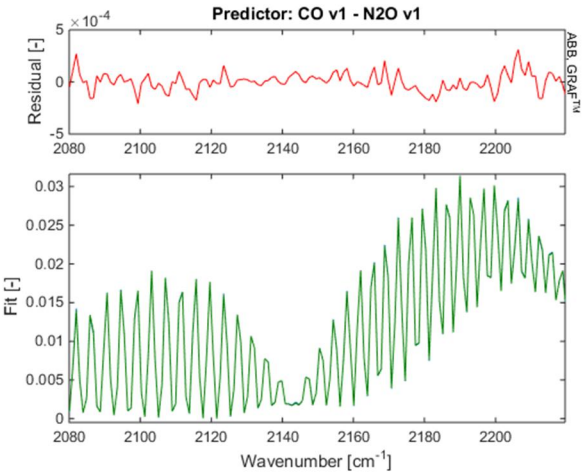


Figure 1: Prediction of $CO_2$ and $N_2O$ mixture. Absorbance spectra of measurement (green) and prediction (blue, not visible) are overlaid. Red curve shows spectral residual.

Figure 1 shows an example of the agreement obtained between a normalized absorbance spectrum measured with an ABB FTIR (green curve), and a simulated spectrum generated with

GRAF™ (blue curve, not visible) for a CO and $NO_2$ sample. The spectral residual is about 2 orders of magnitude lower than the spectra, which can hardly be differentiated on this scale.

## Diagnostics

The algorithm is complemented with diagnostics values to verify that spectral residuals of predictions are within expectations. Those diagnostics are useful to assess the quality of the predictions and raise warnings whenever interferents of unknown species may render predictions invalid. When warnings occur, spectral residuals can be further analyzed with GRAF™ modeling tools to identify unknown components or diagnose sampling issues.

Figure 2 shows the same prediction than Figure 1 when $N_2O$ is excluded from the model (considered as an unknown component). The spectral residual contains clear features of $N_2O$ signature around 2200 $cm^{-1}$.

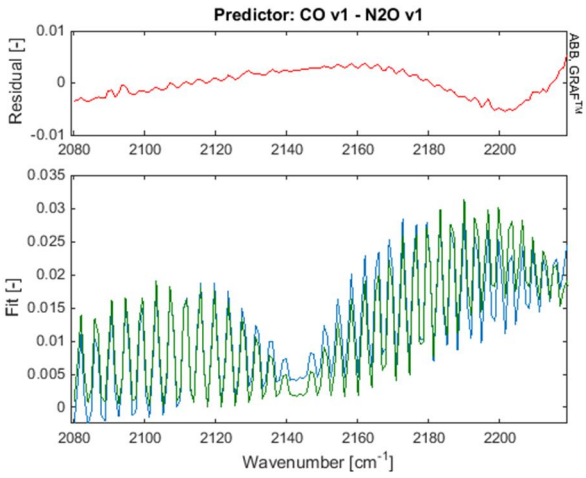


Figure 2: Prediction of $CO_2$ and $N_2O$ mixture, without modeling of $N_2O$. Absorbance spectra of measurement (green) and prediction (blue) are overlaid. Red curve shows spectral residual with $N_2O$ signature around 2200 $cm^{-1}$.

## Calibration and validation

Combustion emission monitoring is a demanding application where ppm and sub-ppm levels of pollutants must be monitored while interferents with strong absorption bands such as water vapor and $CO_2$ commonly reach concentrations of 30% and 15% in volume respectively. ABB process gas analyzers have now a simplified calibration procedure to compensate for prediction bias caused by those strong interferents. The calibration can now performed with a single measurement. Robustness to interferents has been intensely validated for typical industrial gases over wide ranges of concentrations, as well as linearity and limit of detection in presence of strong interferents. The transferability of the models and performances over different analyzers was also extensively tested and confirmed.

GRAF™ includes also a compensation method for the collision broadening effect, the natural broadening of the absorption lines that is dependent on the actual composition of the gas matrix. The natural width of the absorption lines of a molecule depends on the other molecules it is likely to collide. This effect becomes more apparent for gases with concentration ranging over a few percent of the total sample volume. This compensation also models the impact of changing ratios of components that do not have absorption bands in the infrared but affect species of interest, or interferents. For example, variation of $O_2$ in a combustion process may influence the interference of water vapor on other gas components if not taken into account.

## Conclusion

GRAF™ is changing the way of building gas calibration models and deploying FTIR analyzers. Our customers can now benefit from advance prediction algorithms, unique and innovative modeling of instrument characteristics as well as from the tremendous work of the spectroscopy community to build and maintain high quality gas databases.

## References


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