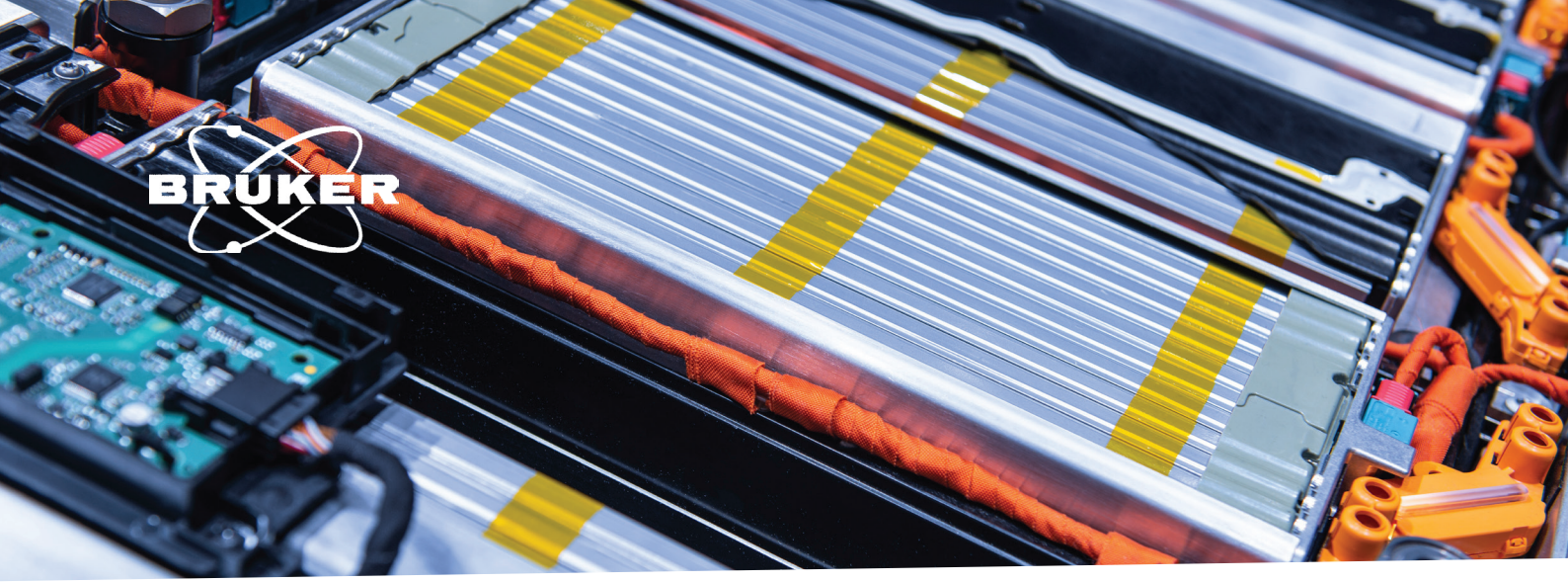


FT-IR based Gas Analysis of Battery Gases

Application Note M174

Introduction

Gas mixtures with IR-active components can be quantified quickly, accurately, and in real time with the use of Fourier-Transform Infrared (FT-IR) based Gas Analyzers. As the technique is not limited to specific analytes or applications – the systems can be basically employed for the quantification of any IR-active gas compound – new application fields open regularly. For instance, the instruments have been used in the automotive sector for emission monitoring of combustion engines for several years. Recently, driven by the worldwide mobility turnaround from fossil fuel to electric vehicles, the demand for the analysis of battery gases has dramatically increased.

Here we show how the Bruker Gas Analyzers of the MATRIX II-MG Series in combination with the unique Gas Analysis software OPUS GA and the spectral database can be adapted to new applications such as battery gas measurements.

Requirements on hard- and software for the analysis of battery gases

The analysis of battery gases is typically complex due to the presence of many IR-active compounds. Some of these compounds, like H_2O, CO_2, and CO, can be present in a rather high concentration, such that in most spectral regions the absorption lines of various compounds overlap. Moreover, new compounds of interest emerge because of the various new materials used in battery manufacturing.

Hence, for the unambiguous FT-IR based analysis of such complex gas mixtures, one needs:

a. An FT-IR spectrometer with high spectral resolution and wavenumber accuracy

b. A sophisticated quantification algorithm based on underlying physics models to efficiently manage spectral interference

c. The possibility to quickly incorporate reference spectra of new compounds of interest

Methods and Results

1. Flexible analysis and the extension of the spectral database

OPUS GA allows the calibration-free analysis of gaseous compounds employing non-device specific reference spectra stored in a spectral database. The quantification results are obtained via a non-linear fitting routine that fully accounts for interfering gases. Hence, OPUS GA is flexible as the quantification of new gases is achieved solely through selections in the software, e.g., choice of the respective reference spectrum and/or spectral region.

To investigate battery gases, it was required to extend the spectral database by the addition of quantitative reference spectra of the relevant compounds, such as phosphorous pentafluoride (PF_5) and phosphoryl fluoride (POF_3). For this purpose, two chemical reactions were conducted to obtain quantitative IR spectra of PF_5 and POF_3 (requirement **c**).

First, PF5 was synthesized by thermal decomposition of lithium hexafluorophosphate ($LiPF_6$) at 100 to 200 °C, i.e., $LiPF_6$ -> LiF + PF_5. Subsequently, a quantitative POF_3 spectrum was created by partial hydrolysis of PF_5 (PF_5 + H_2O -> POF_3 + 2 HF). Please note that for the acquisition of the desired quantitative PF_5 and POF_3 spectra, consideration of the IR signatures of H_2O, HF, SiF_4 and other side products was necessary.

2. Analysis of Battery Gases

Experiments with the MATRIX II-MG with a spectral resolution of 0.5 cm^{-1} and a wavenumber accuracy of better than 0.05 cm^{-1} (requirement **a**) were performed to analyze a battery gas. The calibration-free Gas Analysis software OPUS GA was employed to control the spectrometer and to quantify gas components emitted by the battery (requirement **b**). Figure 1 shows the relative transmission spectrum of gases emitted by a battery.

The isolated and dominant IR bands of C_2H_4 (≈ 950 1/cm), CO (≈ 2100 1/cm), CO_2 (≈ 2300 1/cm), CH_4 (≈ 2800 1/cm), C_2H_2 (≈ 3300 1/cm) and H_2O (≈ 3600 – 3900 1/cm) were used for a direct identification and quantification of these compounds. Additionally, many other compounds are part of the gas mixture, but their IR bands are not directly visible due to severe spectral interference.

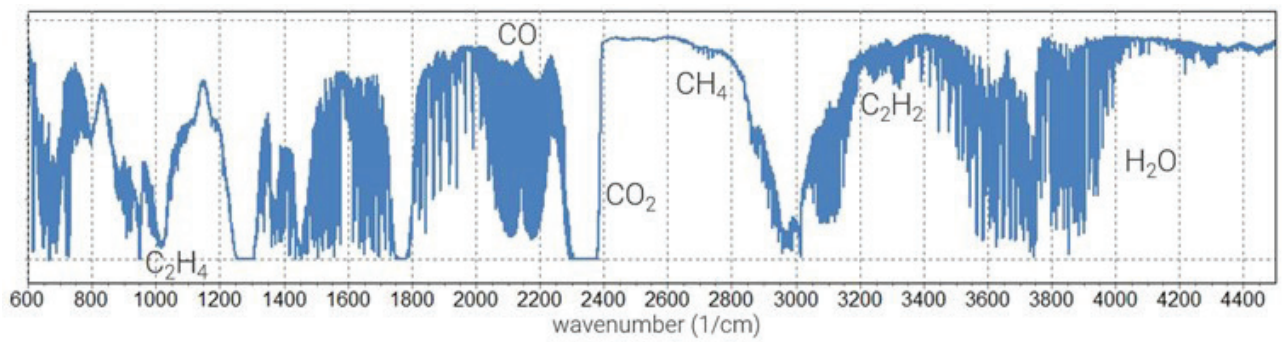


Fig. 1
Transmission IR spectrum of a battery gas and the IR bands of selected compounds.

However, because of the high spectral resolution of 0.5 cm^{-1} and efficient consideration of spectral interference, methanol (CH_4O), ethyl methyl carbonate ($C_4H_8O_3$) and phosphorous pentafluoride (PF_5) were found and quantified in the narrow spectral region from 980 – 1100 cm^{-1} (Figure 2). The measured IR spectra, where the contribution of interfering compounds was subtracted (black), and simulated IR spectra (red) show perfect agreement and the clear identification was possible (requirement **a**, **b**, and **c**). Among these gases, acetaldehyde (C_2H_4O), propylene (C_3H_6) and ethylene carbonate ($C_3H_4O_3$) were identified and quantified.

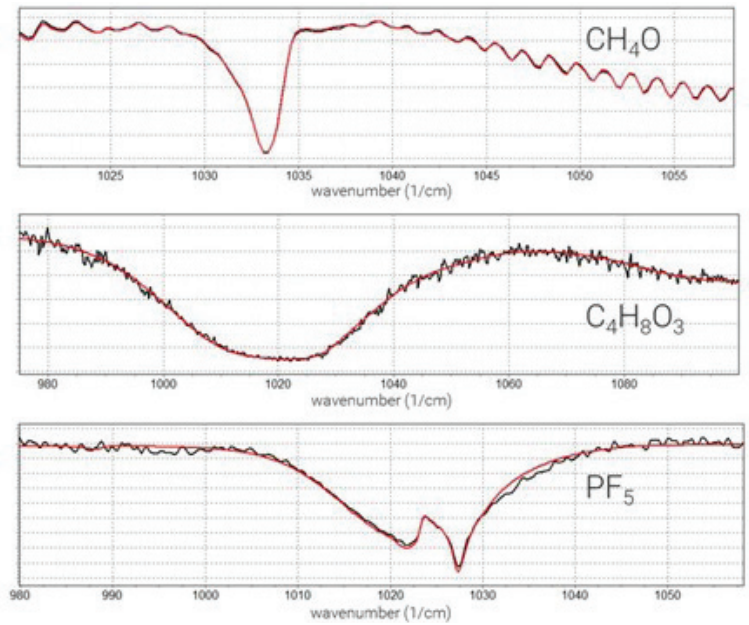
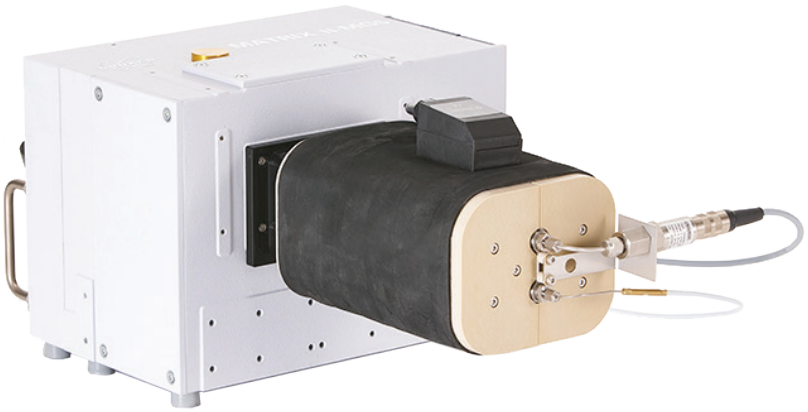


Fig. 2
Definite identification and quantification of CH_4O, $C_4H_8O_3$ and PF_5 in the narrow spectral region from 980 – 1100 cm^{-1}. Black: Measured IR spectrum corrected by the contribution of interfering compounds in the selected spectral range. Red: Pure reference spectrum of respective analyte in the selected frequency range.

Summary and Conclusion

The Bruker Gas Analyzer MATRIX II-MG and the software OPUS GA enable the quantification of battery gases in real-time. The quantification methods can be readily adapted to new fields of applications without any calibration measurements. Even in the case of severe spectral interference, the optical performance and sophisticated quantification algorithm lead to clear identification and accurate quantification of the compounds of interest.



Gas Analyzer MATRIX II-MG5

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